

TITLE OF THE INVENTION

VOLTAGE-DEPENDENT NONLINEAR RESISTOR CERAMIC, VOLTAGE-DEPENDENT NONLINEAR RESISTOR WITH THE CERAMIC, AND METHOD OF MANUFACTURING VOLTAGE-DEPENDENT NONLINEAR RESISTOR CERAMIC

FIELD OF THE INVENTION

The present invention relates to a ceramic used for a voltage-dependent nonlinear resistor (varistor), and in particular, to composite perovskite-based ceramic having a (Sr, Ba, Ca) TiO_3 content, to a varistor provided with this ceramic, and to a method of manufacturing the ceramic.

DESCRIPTION OF THE RELATED ART

A varistor is a resistive element whose resistance nonlinearly changes according to the change of an applied voltage, and specifically, is a resistor whose resistance rapidly drops when a voltage beyond a certain voltage value is applied.

There are various compositions of ceramics that mainly constitute varistors. Since having both functions of the nonlinearity of a resistance and the electrostatic capacitance characteristics, composite perovskite-based ceramic having contents of (Sr, Ba, Ca) TiO_3 is very suitable for absorbing a surge voltage, generated in electronic equipment, or for removing noise. For example, the ceramic is applied to a ring varistor for DC micro motors etc.

In a varistor made of this composite perovskite-based ceramic, it is possible to control the temperature dependency of a varistor voltage (voltage at which varistor's resistance rapidly drops) by selecting mole ratios of Sr, Ba and Ca. Namely, in order to prevent excessive current from flowing into a varistor or thermal runaway from arising due to the varistor voltage dropping in connection with the increase of operating temperature, it is possible to adjust the temperature dependency. Varistors where the temperature dependency of the varistor voltage is adjusted in this way are disclosed in Japanese Patent Publication No. 0828287B (Japanese Patent Publication No. 02146702A), Japanese Patent Publication No. 03045559A, and Japanese Patent No. 2944697C (Japanese Patent Publication No. 03237057A).

In recent years, since acceleration in soldering work speed has been requested and high temperature solder and lead-free solder have been used at the time of mounting electronic parts such as varistors, soldering temperature has been promoted. For this reason, since varistors are exposed to severe soldering conditions, it becomes frequent that thermal cracks caused by local thermal shocks arise. As for electrodes of the varistor, an Ag (silver) electrode is generally used. Nevertheless, since the Ag content of this electrode dissolves into the solder due to the increase of soldering temperature, there is a possibility that a function as the varistor may be spoiled because of disappearance of all or a part of the

electrode.

In order to provide a varistor strong against such a thermal shock, a ring varistor with a TiO_2 -based ceramic is disclosed in Japanese Patent Publication No. 63276201A. However, in the publication, no specific data is mentioned at all. In addition, such TiO_2 -based varistor ceramic is considerably inferior to composite perovskite-based varistor ceramic in respect of the electrical characteristics about electrostatic capacity, and the varistor voltage controllability, and hence, such ceramic cannot be adopted.

Therefore, demands of composite perovskite-based varistor ceramics is increasing because of the superiority of electrical characteristics and a feature that its functions are not spoiled even if hot soldering is performed. Furthermore, so as to increase operation efficiency, varistor ceramics more excellent in hardness to for example bending stress are desired.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide composite perovskite-based varistor ceramic and a varistor that have excellent electrical characteristics and a feature that its functions are not spoiled even if hot soldering is performed.

Another object of the present invention is to provide varistor ceramic which is excellent in electrical characteristics, bending strength and thermal shock-proof

property, and to provide a manufacturing method of the varistor ceramic.

According to the present invention, a composite perovskite-based semiconductor varistor ceramic and a varistor contain a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si. The ceramic substantially containing no Mg. A composition of the ceramic is $0.10 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.50$, $0.20 < c/(a + b + c) \leq 0.50$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $1.0 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of the first component as SrO, b is the number of moles calculated for Ba of the first component as BaO, c is the number of moles calculated for Ca of the first component as CaO, d is the number of moles calculated for Ti of the first component as TiO₂, e is the number of moles calculated for R of the second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4} and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of the fourth component as SiO₂.

The present invention not only enhances the thermal shock-proof property of a varistor and suppresses the

generating of a thermal crack on the basis of a local thermal shock due to severe soldering conditions by decreasing an amount of SiO_2 used as a sintering additive as small as possible, but also compensates the deterioration of a degree of sintering caused by the decreased amount of SiO_2 by adjusting a total A/B (a ratio of a total number of moles of an A site component containing other elements which can enter in lattices of the A site component in relation to an ion radius, to a total number of moles of a B site component containing other elements which can enter in lattices of the B site component), expressed in $(a + b + c + e)/(d + f)$. In addition, the present invention further enhances the thermal shock-proof property of a varistor by not containing Mg substantially to further suppress local thermal shock generating. Moreover, it is possible to enhance the electrical characteristics of the varistor by appropriately selecting A site mole ratios, and an amount and a kind of semiconductorizing agent.

In addition, a parameter adopted in the present invention is not a simple A/B ratio which is a ratio of the number of moles of the A site component consisting of only Sr, Ba and Ca, and the number of moles of the B site component consisting of only Ti, but the total A/B that is a mole ratio of ions that constitute the perovskite structure and also contain additives. Namely, it is because what truly contributes to a degree of sintering is not the simple A/B but such total A/B. In particular, since the semiconductorizing agent is important

solid solution ions among additives, in the case of the present invention where a dosage of the semiconductorizing agent is much, an error becomes large if the simple A/B ratio is used. Nevertheless, it becomes possible to provide a varistor hardly having the dispersion of characteristics since exact control is attained for the first time by using the total A/B.

It is preferable that a composition of the first component is $0.30 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.40$, and $0.25 \leq c/(a + b + c) \leq 0.35$. Also it is preferable that a composition of the first component and at least one component of the second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$. It is still more preferable that a composition of at least one component of the second and third components is $1.0 \leq (e + f)/d \times 100 \leq 4.0$. Furthermore, it is also preferable that the composition of the fourth component is $g/d \times 100 \leq 0.3$.

It is preferable that the ceramic further contains a fifth component consisting of at least one kind of oxide selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W. It is also preferable that $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of the fifth component, as $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 .

This fifth component is effective in enhancing electrical characteristics, such as enhancement of a nonlinear coefficient

α .

Preferably, the varistor has electrodes formed on at least one surface of the ceramic, and the electrodes consist of Cu or material mainly made of Cu. In the case of the latter, it is more preferable that the electrodes are made of a Cu alloy or Cu containing glass frit.

Furthermore, according to the present invention, a varistor ceramic contains oxides consisting of at least one kind of element among Sr, Ba, and Ca and Ti, and on a surface of which compressive stress exists.

Since the large compressive stress exists on the ceramic surface, it is also possible not only to improve bending strength at the time of soldering, but also to obtain high thermal shock-proof property preventing a crack from arising even when temperature locally rises at the time of soldering. That is, at the time of soldering, local expansion arises by local heating and becomes tensile stress that makes a crack arise on a surface of the ceramic. It is possible to obtain the varistor ceramic strong against a local thermal shock so long as the compressive stress that can balance this tensile stress is introduced beforehand on the surface of the varistor ceramic. In addition, if residual compressive stress exists in a surface of the varistor ceramic, bending strength increases. This is the same principle as that of tempered glass.

Assuming that X-ray stress constant is -100 MPa/degree, it is preferable that the compressive stress is 15 MPa or more,

it is more preferable to be 25 MPa or more, and it is still more preferable to be 40 MPa or more.

In this case, it is preferable that the ceramic contains a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, that values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in trilinear coordinates exist on a line segment connecting a point (0.2, 0.0, 0.8) and a point (0.0, 0.4, 0.6), or in a range where $a/(a + b + c)$ and $b/(a + b + c)$ are larger than this line segment, and that its composition is $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of the first component as SrO, b is the number of moles calculated for Ba of the first component as BaO, c is the number of moles calculated for Ca of the first component as CaO, d is the number of moles calculated for Ti of the first component as TiO₂, e is the number of moles calculated for R of the second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4}, and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of the fourth component as SiO₂.

In this way, the present invention not only enhances the

thermal shock-proof property of a varistor and suppresses the generating of a thermal crack on the basis of a local thermal shock due to severe soldering conditions by decreasing an amount of SiO_2 used as a sintering additive as small as possible, but also compensates the deterioration of a degree of sintering caused by the decreased amount of SiO_2 by adjusting a total A/B (a ratio of a total number of moles of an A site component containing other elements which can enter in lattices of the A site component in relation to an ion radius, to a total number of moles of a B site component containing other elements which can enter in lattices of the B site component), expressed in $(a + b + c + e)/(d + f)$. Moreover, it is possible to enhance the strength and electrical characteristics of the varistor by appropriately selecting A site mole ratios, and an amount and a kind of semiconductorizing agent.

In addition, a parameter adopted in the present invention is not a simple A/B ratio which is a ratio of the number of moles of the A site component consisting of only Sr, Ba and Ca, and the number of moles of the B site component consisting of only Ti, but the total A/B that is a mole ratio of ions that constitute the perovskite structure and also contain additives. That is, it is because it is thought that what truly contributes to a degree of sintering is not the simple A/B but such total A/B. In particular, since the semiconductorizing agent is important solid solution ions among additives, in the case of the present invention where a dosage of the

semiconductorizing agent is much, an error becomes large if the simple A/B ratio is used. Nevertheless, it becomes possible to provide a varistor hardly having the dispersion of characteristics since exact control is attained for the first time by using the total A/B.

It is more preferable that values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in the trilinear coordinates exist on a first line segment connecting a point (0.5, 0.0, 0.5) and a point (0.2, 0.2, 0.6), a second line segment connecting a point (0.2, 0.2, 0.6) and a point (0.1, 0.4, 0.5), a third line segment connecting a point (0.1, 0.4, 0.5) and a point (0.1, 0.5, 0.4), or a fourth line segment connecting a point (0.1, 0.5, 0.4) and a point (0.2, 0.8, 0.0), or $a/(a + b + c)$ exists in a range larger than these first to fourth line segments.

It is still more preferable that values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in the trilinear coordinates exist on a fifth line segment connecting a point (0.4, 0.2, 0.4) and a point (0.2, 0.4, 0.4), a sixth line segment connecting a point (0.2, 0.4, 0.4) and a point (0.2, 0.5, 0.3), a seventh line segment connecting a point (0.2, 0.5, 0.3) and a point (0.3, 0.5, 0.2), an eighth line segment connecting a point (0.3, 0.5, 0.2) and a point (0.6, 0.2, 0.2), or a ninth line segment connecting a point (0.6, 0.2, 0.2) and a point (0.4, 0.2, 0.4), or in a range surrounded by these fifth to ninth line segments.

It is more preferable that a composition of the first

component and at least one component of the second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$.

It is also more preferable that a composition of at least one component of the second and third components is $0.75 \leq (e + f)/d \times 100 \leq 4.0$.

It is also more preferable that a composition of the fourth component is $g/d \times 100 \leq 0.3$.

It is preferable that the ceramic further contains a fifth component consisting of at least one kind of oxide selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W. It is also preferable that $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of the fifth component, as $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 .

Furthermore, according to the present invention, a manufacturing method of a varistor ceramic includes a step of performing reduction sintering to obtain a ceramic containing oxides of at least one kind of Sr, Ba and Ca, and Ti, and a step of performing reoxidation of the obtained ceramic to generate a compressive stress in a surface of the ceramic.

Since the large compressive stress is generated by the reduction sintering and reoxidation processing to exist on the ceramic surface, it is also possible not only to improve bending strength at the time of soldering, but also to obtain high thermal shock-proof property preventing a crack from

arising even when temperature locally rises at the time of soldering. It can be analogized from the relation between an amount of oxygen defects in reduction sintering and supplementation of the oxygen defects by oxygen in reoxidation processing that the thermal shock-proof property and residual compressive stress are generated by the combination of the reduction sintering and reoxidation processing.

At the time of soldering, local expansion arises by local heating and becomes tensile stress that makes a crack arise on a surface of the ceramic. It is possible to obtain the varistor ceramic strong against a local thermal shock so long as the compressive stress that can balance this tensile stress is introduced beforehand on the surface of the varistor ceramic. In addition, if residual compressive stress exists on a surface of the varistor ceramic, bending strength increases. This is the same principle as that of tempered glass.

It is preferable to weigh and mix raw material powder so that the powder may have predetermined composition, to grind and form the powder after performing calcining, and to performing the reduction sintering of this formed object, and the reoxidation.

Assuming that X-ray stress constant is $-100 \text{ MPa}/^\circ\text{C}$, it is preferable that the compressive stress is 15 MPa or more, it is more preferable to be 25 MPa or more, and it is still more preferable to be 40 MPa or more.

It is preferable that the temperature of reoxidation

processing is between 850°C and 1050°C inclusive. It is more preferable that the temperature is between 900°C and 1000°C inclusive. Thus, it is possible to secure a wide range of varistor voltage values and sufficient nonlinear coefficient α with keeping large surface residual compressive stress by controlling a varistor voltage value through changing the temperature in the reoxidation processing without changing the composition.

Consequently, since wide range of varistor voltages and practical α are obtained in the same composition with maintaining the high strength and the high heat-resisting property owing to the large surface residual compressive stress, it becomes unnecessary to prepare various materials and it becomes easy to control materials.

It is preferable that a time of the reoxidation processing is 32 hours or less, more preferable that the time is between 0.25 hour and 16 hours inclusive, and still more preferable that the time is between 0.5 hour and 8 hours inclusive.

It is also preferable that a partial pressure of oxygen in the reoxidation processing is 0.1 atmospheric pressure or more.

It is preferable that the ceramic contains a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and

a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, that values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in trilinear coordinates exist on a line segment connecting a point (0.2, 0.0, 0.8), and a point (0.0, 0.4, 0.6), or in a range where $a/(a + b + c)$ and $b/(a + b + c)$ are larger than this line segment, and that its composition is $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of the first component as SrO, b is the number of moles calculated for Ba of the first component as BaO, c is the number of moles calculated for Ca of the first component as CaO, d is the number of moles calculated for Ti of the first component as TiO₂, e is the number of moles calculated for R of the second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4} and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of the fourth component as SiO₂.

It is more preferable that values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in the trilinear coordinates exist on a first line segment connecting a point (0.5, 0.0, 0.5) and a point (0.2, 0.2, 0.6), a second line segment connecting a point (0.2, 0.2, 0.6) and a point (0.1, 0.4, 0.5), a third line segment connecting a point (0.1, 0.4, 0.5) and a point (0.1, 0.5, 0.4), or a fourth line segment connecting a point (0.1,

0.5, 0.4) and a point (0.2, 0.8, 0.0), or $a/(a + b + c)$ exists in a range larger than these first to fourth line segments.

It is still more preferable that values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in the trilinear coordinates exist on a fifth line segment connecting a point (0.4, 0.2, 0.4) and a point (0.2, 0.4, 0.4), a sixth line segment connecting a point (0.2, 0.4, 0.4) and a point (0.2, 0.5, 0.3), a seventh line segment connecting a point (0.2, 0.5, 0.3) and a point (0.3, 0.5, 0.2), an eighth line segment connecting a point (0.3, 0.5, 0.2) and a point (0.6, 0.2, 0.2), or a ninth line segment connecting a point (0.6, 0.2, 0.2) and a point (0.4, 0.2, 0.4), or in a range surrounded by these fifth to ninth line segments.

It is more preferable that a composition of the first component and at least one component of the second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$.

It is also more preferable that a composition of at least one component of the second and third components is $0.75 \leq (e + f)/d \times 100 \leq 4.0$.

It is also preferable that a composition of the fourth component is $g/d \times 100 \leq 0.3$.

It is preferable that the ceramic further contains a fifth component consisting of at least one kind of oxide selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W. It is also preferable that $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co,

Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of the fifth component, as $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 .

Furthermore, according to the present invention, a manufacturing method of a varistor ceramic has a step of performing reduction sintering to obtain a ceramic containing oxides of at least one kind of Sr, Ba and Ca, and Ti, and a step of performing reoxidation of the obtained ceramic. A temperature in the reoxidation performing step is between 850°C and 900°C inclusive and a time of the reoxidation performing step is between 0.25 hour and 32 hours inclusive, or a temperature in the reoxidation performing step is between 900°C and 1050°C inclusive and a time of the reoxidation performing step is between 0.1 hour and 32 hours inclusive.

Also, according to the present invention, a manufacturing method of a varistor ceramic has a step of performing reduction sintering to obtain a ceramic containing oxides of at least one kind of Sr, Ba and Ca, and Ti, and a step of performing reoxidation of the obtained ceramic. A temperature in the reoxidation performing step is between 900°C and 950°C inclusive and a time of the reoxidation performing step is between 0.5 hour and 16 hours inclusive, or a temperature in the reoxidation performing step is between 950°C and 1000°C inclusive and a time of the reoxidation performing step is between 0.25 hour and 16 hours inclusive.

It is possible to maintain the strength of the ceramic

itself in a high level, and to obtain sufficient bending strength to the bending stress and sufficient resistance over a local thermal shock at the time of soldering without changing the composition by adjusting the temperature and time in reoxidation processing for controlling a varistor voltage. Of course, it is possible to secure a sufficient nonlinear coefficient α in a wide range of varistor voltages, and to lessen the dependency of the varistor voltage to the change of heat treatment temperature. Thus, since practical nonlinear coefficient α and sufficient strength in a wide range of varistor voltages are obtained in the single composition, it becomes unnecessary to prepare various materials and it becomes easy to control materials.

It is preferable to adjust the time of the reoxidation processing to control a varistor voltage value. With considering the influence of changes of the reoxidation processing conditions over a varistor voltage, time of the reoxidation processing has less impact than temperature in the reoxidation processing. Hence, by controlling a varistor voltage value through finally adjusting the time of the reoxidation processing, the shift of the varistor voltage due to the fluctuation of reoxidation processing conditions becomes small, and hence a yield improves and the control of reoxidation processing conditions becomes easy.

It is preferable to weigh and mix raw material powder so that the powder may have predetermined composition, to grind

and form the powder after performing calcining, and to perform the reduction sintering of this formed object, and the reoxidation.

It is also preferable to weigh and mix raw material powder, to add a part of contents after performing calcining, to adjust the contents so that the powder may have predetermined composition, to grind and form the powder, and to perform the reduction sintering of this formed object, and the reoxidation.

It is preferable that the reoxidation processing is performed at a single heat treatment process accompanied by one cycle of temperature rise and fall, as shown in Fig. 5. Alternatively, it is preferable that the reoxidation processing is performed at a heat treatment processes accompanied by a plurality of independent temperature rises and falls, as shown in Fig. 6.

In this case, it is preferable that the ceramic contains a first component consisting oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si and that a composition of the ceramic is $0.30 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.40$, $0.25 \leq c/(a + b + c) \leq 0.35$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$,

and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of the first component as SrO, b is the number of moles calculated for Ba of the first component as BaO, c is the number of moles calculated for Ca of the first component as CaO, d is the number of moles calculated for Ti of the first component as TiO_2 , e is the number of moles calculated for R of the second component as $YO_{3/2}$, CeO_2 , $PrO_{11/6}$, $TbO_{7/4}$ and $RO_{3/2}$ (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as $NbO_{5/2}$ and $TaO_{5/2}$ respectively, and g is the number of moles calculated for Si of the fourth component as SiO_2 .

The present invention not only enhances the thermal shock-proof property of a varistor and suppresses the generating of a thermal crack on the basis of a local thermal shock due to severe soldering conditions by decreasing an amount of SiO_2 used as a sintering additive as small as possible, but also compensates the deterioration of a degree of sintering caused by the decrease amount of SiO_2 by adjusting a total A/B (a ratio of a total number of moles of an A site component containing other elements, which can enter in lattices of the A site component in relation to an ion radius, to a total number of moles of a B site component containing other elements which can enter in lattices of the B site component), expressed in $(a + b + c + e)/(d + f)$. Moreover, it is possible to enhance the strength and electrical characteristics of the varistor by appropriately selecting A site mole ratios, and an amount and a

kind of semiconductorizing agent.

In addition, a parameter adopted in the present invention is not a simple A/B ratio which is a ratio of the number of moles of the A site component consisting of only Sr, Ba and Ca, and the number of moles of the B site component consisting of only Ti, but the total A/B that is a mole ratio of ions that constitute the perovskite structure and also contain additives. That is, it is because it is thought that what truly contributes to a degree of sintering is not the simple A/B but such total A/B. In particular, since the semiconductorizing agent is important solid solution ions among additives, in the case of the present invention where a dosage of the semiconductorizing agent is much, an error becomes large if the simple A/B ratio is used. Nevertheless, it becomes possible to provide a varistor hardly having the dispersion of characteristics since exact control is attained for the first time by using the total A/B.

It is preferable that a composition of the first component and at least one component of the second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$. It is still more preferable that a composition of at least one component of the second and third components is $0.75 \leq (e + f)/d \times 100 \leq 4.0$. Furthermore, it is also preferable that the composition of the fourth component is $g/d \times 100 \leq 0.3$.

It is also preferable that the ceramic further contains a fifth component consisting of at least one kind of oxide

selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W. It is also preferable that $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of the fifth component, as $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 . This fifth component is effective in enhancing electrical characteristics, such as enhancement of a nonlinear coefficient α .

In addition, according to the present invention, a manufacturing method of a varistor ceramic has a step of weighing raw material powder containing oxides of at least one kind of Sr, Ba and Ca, and Ti so that a weighed powder has a predetermined composition, a step of mixing the weighed powder, a step of performing calcining of the mixed powder, a step of grinding a calcined object, a step of forming the ground object, a step of performing reduction sintering of the formed object, and a step of performing reoxidation of the reduction sintered object. The grinding step is performed so that a specific surface area of each grain after the grinding becomes between 0.5 and 5.0 m^2/g inclusive, and the forming step is performed so that a density of the formed object becomes between 2.80 and 3.40 g/cm^3 inclusive.

Furthermore, according to the present invention, a manufacturing method of a varistor ceramic has a step of weighing raw material powder containing oxides of at least one kind of Sr, Ba and Ca, and Ti so that a weighed powder has a

predetermined composition, a step of mixing the weighed powder, a step of performing calcining of the mixed powder, a step of adding a part of contents so as to adjust a composition of a calcined object to a predetermined component, a step of grinding the adjusted object, a step of forming the ground object, a step of performing reduction sintering of the formed object, and a step of performing reoxidation of the reduction sintered object. The grinding step is performed so that a specific surface area of each grain after the grinding becomes between 0.5 and 5.0 m²/g inclusive, and the forming step is performed so that a density of the formed object becomes between 2.80 and 3.40 g/cm³ inclusive.

Up to now, various investigations have been made about composition and regular sintering of varistor ceramic. However, the grain size which varies depending upon a grinding degree in a manufacture process, the change of the density of a sintered object due to change in forming conditions, the bending strength and the resistance over a thermal shock that accompany them have been not investigated. The processing conditions in the grinding process that is one of manufacturing processes is an important factor of influencing the characteristics of the sintered ceramic obtained by subsequent regular sintering. Thus, the processing conditions in the grinding process is very important also to prevent the compositional heterogeneity and the compositional concentration gradient of material when determining materials such as strontium titanate-based material.

In addition, it was found that the processing conditions in the forming process strongly influence the bending strength and thermal shock-proof property of sintered ceramic.

That is, if a specific surface area of each grain after grinding in a grinding process is more than $0.5 \text{ m}^2/\text{g}$, the compositional heterogeneity or composition concentration gradient of material do not arise. Hence it is possible to obtain the sufficient bending strength and thermal shock-proof property of sintered ceramic. If the specific surface area exceeds $5.0 \text{ m}^2/\text{g}$, grinding time becomes too much long. Hence not only this is inefficient in manufacturing, but also compositional heterogeneity easily arises since a Ti-rich liquid phase is easily generated due to its activity. Therefore, it is desirable that the specific surface area is $5.0 \text{ m}^2/\text{g}$ or less.

If the density of a formed object is 2.80 g/cm^3 or more, a fault seems never arises in manufacturing processes since the strength of a formed object becomes enough. On the other hand, since the life time of forming equipment and forming dies are shortened when the density of a formed object exceeds 3.40 g/cm^3 , maintenance cost therefor increases, and hence this is inefficient in manufacturing. Therefore, it is desirable that the density of a formed object is 3.40 g/cm^3 or less.

It is possible to maintain the strength of the ceramic itself in a high level, and to obtain sufficient bending strength to the bending stress and sufficient resistance over a

local thermal shock at the time of soldering by grinding raw material so that the specific surface area of a grain after grinding become between 0.5 and 5.0 m²/g inclusive, and forming the grains so that the density of a formed object become between 2.80 and 3.40 g/cm³ inclusive.

In this case, it is preferable that the ceramic contains a first component consisting oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, and that a composition of the ceramic is $0.10 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.50$, $0.20 < c/(a + b + c) \leq 0.50$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of the first component as SrO, b is the number of moles calculated for Ba of the first component as BaO, c is the number of moles calculated for Ca of the first component as CaO, d is the number of moles calculated for Ti of the first component as TiO₂, e is the number of moles calculated for R of the second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4} and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of the fourth component as SiO₂.

The present invention not only enhances the thermal shock-proof property of a varistor and suppresses the generating of a thermal crack on the basis of a local thermal shock due to severe soldering conditions by decreasing an amount of SiO_2 used as a sintering additive as small as possible, but also compensates the deterioration of a degree of sintering caused by the decreased amount of SiO_2 by adjusting a total A/B (a ratio of a total number of moles of an A site component containing other elements which can enter in lattices of the A site component in relation to an ion radius, to a total number of moles of a B site component containing other elements which can enter in lattices of the B site component), expressed in $(a + b + c + e)/(d + f)$. Moreover, it is possible to enhance the strength and electrical characteristics of the varistor by appropriately selecting A site mole ratios, and an amount and a kind of semiconductorizing agent.

In addition, a parameter adopted in the present invention is not a simple A/B ratio which is a ratio of the number of moles of the A site component consisting of only Sr, Ba and Ca, and the number of moles of the B site component consisting of only Ti, but the total A/B that is a mole ratio of ions that constitute the perovskite structure and also contain additives. That is, it is because it is thought that what truly contributes to a degree of sintering is not the simple A/B but such a total A/B. In particular, since the semiconductorizing agent is important solid solution ions among additives, in the

case of the present invention where a dosage of the semiconductorizing agent is much, an error becomes large if the simple A/B ratio is used. Nevertheless, it becomes possible to provide a varistor hardly having the dispersion of characteristics since exact control is attained for the first time by using the total A/B.

It is preferable that a composition of the first component is $0.30 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.40$, and $0.25 \leq c/(a + b + c) \leq 0.35$. It is preferable that a composition of the first component and at least one component of the second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$. It is still more preferable that a composition of at least one component of the second and third components is $0.75 \leq (e + f)/d \times 100 \leq 4.0$. Furthermore, it is also preferable that the composition of the fourth component is $g/d \times 100 \leq 0.3$.

It is preferable that the ceramic further contains a fifth component consisting of at least one kind of oxide selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W. It is also preferable that $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of the fifth component, as $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 . This fifth component is effective in enhancing electrical characteristics, such as enhancement of a nonlinear coefficient α .

Other objects and advantages of the present invention will become clear from the following description relating to preferred embodiments of the present invention described by the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1a is a plane view illustrating the structure of a ring varistor as an embodiment of the present invention;

Fig. 1b is a sectional view taken on a line A-A shown in Fig. 1a;

Fig. 2 is a characteristic graph illustrating a rate of the residual electrode area to the solder temperature at the time of using Cu and Ag as electrode material, respectively;

Fig. 3 is a circuit diagram illustrating an E_1 and E_{10} measuring circuit;

Fig. 4 is a characteristic diagram illustrating preferable ranges of A site mole ratios;

Fig. 5 is a schematic diagram for explaining an example of a heat treatment step in reoxidation processing; and

Fig. 6 is a schematic diagram for explaining another example of a heat treatment step in reoxidation processing.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

First Embodiment

In Fig. 1a, 10 denotes a varistor ceramic 10 formed in ring geometry, and 11 denotes electrodes formed on one face of

the varistor ceramic 10. In this embodiment, five electrodes 11 are provided in equal angular intervals. As shown in Fig. 1b, the varistor ceramic 10 consists of internal semiconductor sections 10a and an insulating layer 10b formed near the entire surface thereof.

Hereinafter, the composition of the varistor ceramic 10 in this first embodiment will be described.

The varistor ceramic 10 contains a first component of the composite perovskite which consists oxides of Sr, Ba, Ca and Ti, at least one component of a second component which consists of at least one kind of oxide selected from oxides of R (Y and lanthanoids (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu)) and a third component which consists of at least one kind of oxide selected from oxide of M (Nb and Ta), and a fourth component which consists of an oxide of Si. In this embodiment, the varistor ceramic does not contain Mg substantially. It is assumed that a is the number of moles calculated for Sr of the first component as SrO, b is the number of moles calculated for Ba of the first component as BaO, c is the number of moles calculated for Ca of the first component as CaO, d is the number of moles calculated for Ti of the first component as TiO_2 , e is the number of moles calculated for R of the second component as $\text{YO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{TbO}_{7/4}$ and $\text{RO}_{3/2}$ (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as $\text{NbO}_{5/2}$ and $\text{TaO}_{5/2}$ respectively, and g is the number of moles calculated for Si of

the fourth component as SiO_2 . Then, the composition of this varistor ceramic is $0.10 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.50$, $0.20 < c/(a + b + c) \leq 0.50$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $1.0 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$. It is more preferable that this composition is $0.30 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.40$, $0.25 \leq c/(a + b + c) \leq 0.35$, and $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$, $1.0 \leq (e + f)/d \times 100 \leq 4.0$, and $g/d \times 100 \leq 0.3$.

The first component is a main component of the varistor ceramic 10. This first component consists of, in composite perovskite, an A site component of Sr, Ba and Ca, and a B site component of Ti. The second and third components are metallic oxides that contribute to semiconductorization, and the fourth component is mainly added for the improvement of a degree of sintering.

Electrical characteristics as a varistor are mainly expressed with a temperature characteristic of a varistor voltage E_{10} and nonlinear coefficient α . The varistor voltage E_{10} expresses an applied voltage value at the time of 10-mA electric current flowing in the varistor, and the nonlinear coefficient α is generally expressed in $\alpha = 1/\log(E_{10}/E_1)$. Where, E_1 is an applied voltage value at the time of 1-mA electric current flowing in the varistor.

As for mole ratios of Sr, Ba and Ca which are contents of the A site component, it is preferable that Sr is set 0.10 or more but 0.40 or less, Ba is 0.30 or more but 0.50 or less, and

Ca is more than 0.20 but 0.50 or less. It is more preferable that Sr is set 0.30 or more but 0.40 or less, Ba is 0.30 or more but 0.40 or less, and Ca is 0.25 or more but 0.30 or less. Then, it becomes possible to enhance electrical characteristics such as the controllability of the varistor voltage E_{10} , temperature characteristics of the varistor voltage E_{10} and nonlinear coefficient α , and to enhance the thermal shock-proof property of the varistor. That is, if there is too much Sr, the temperature characteristic of E_{10} will become negative, and if too few, strength will drop. In addition, if there is too much Ba, the positive trend of temperature characteristic of E_{10} becomes strong too much, and if too few, the temperature characteristic of E_{10} becomes negative. Furthermore, even if there is too much Ca or too few Ca, the nonlinear coefficient α to the varistor voltage E_{10} becomes small. In addition, if there is too much Ca, the varistor voltage E_{10} becomes extremely large to become difficult of control, and a base is made an insulator by reoxidation.

It is preferable that the mole percent (this is calculated by the number of moles of metal ions) of a semiconductorizing agent (the second and/or third components) to a principal component (TiO_2) is between 1.0 and 10.0 inclusive. Alternatively, it is more preferable that the mole percent is between 1.0 and 4.0 inclusive. Then, it is possible to enhance the thermal shock-proof property of the varistor. That is, even if there are too much semiconductorizing agent or

too few, it becomes easy that a thermal crack arises.

In addition, it is preferable that the total A/B is between 0.84 and 1.16 inclusive. Furthermore, it is more preferable that the total A/B is between 0.96 and 1.01 inclusive. Then, even if an amount of the fourth component (SiO_2) is reduced, as described later, a degree of sintering can be improved. That is, this is because sintering is blocked even if the total A/B is too large or too small, and hence the base is made an insulator owing to reoxidation. In addition, this is also because a thermal crack easily arises if total A/B is too large or too small. In a range where an amount of SiO_2 is few and a lot of semiconductorizing agent is added as described above, in order to maintain the thermal crack-proof property, it becomes indispensable to restrict an upper limit of the total A/B to be 1.16 or less, or more preferably, to be 1.01 or less.

The thermal shock-proof property of a varistor can be sharply enhanced by setting the mole percent of the fourth component (SiO_2) to the principal component (TiO_2) to be 0.6 or less, or more preferably, to be 0.3 or less. That is, SiO_2 is added as a sintering additive and it is possible to stably perform sintering even if the composition fluctuates, but however, if the amount of SiO_2 increases, it becomes easy for a thermal crack to arise. It should be noted that the content (mole percent) of SiO_2 of 0.6 or less or of 0.3 or less also includes the case where its dosage is zero.

The thermal shock-proof property of a varistor can be enhanced by not including Mg substantially. Namely, this is because, if Mg is included in ceramic, it becomes easy for a thermal crack to arise. That material is not contained substantially means that the content of the material is in general less than about 0.001 mole percents.

The varistor ceramic 10 may also contain the fifth component (additive) that consists of at least one kind of oxide selected from among oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W. Supposing the content is the number of moles obtained by converting Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W into $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 , it is preferable that the composition is $0 < h/d \times 100 \leq 1.000$. Thereby, there is an effect of improving the nonlinear coefficient α .

In addition, the varistor ceramic 10 may also contain other elements such as P, S, K, Al and Zr as unavoidable impurities besides such additives. Such elements usually exist as oxides.

As described above, the varistor ceramic 10 is a polycrystal consisting of perovskite type crystals. A part of each component is contained in the perovskite type crystals with being solidly solved in grains, and another part exists in crystal grain boundaries as oxides or complex oxides. For example, Ba, Ca, Sr, Ti, Nb, Ta, Y, lanthanoids and the like exist mostly in grains, and Mo, W, Mn, Si, Co and the like

exist mostly in crystal grain boundaries.

A mean grain diameter of the varistor ceramic 10 usually is about 0.5 to 10 μm , and in particular, 1 to 6 μm .

The electrodes 11 are formed with Cu or material mainly made of Cu. If the electrodes are made of Ag, the Ag content of these electrodes dissolves into the solder due to the increase of soldering temperature, and hence, at least a part of the electrodes disappears. Nevertheless, the electrodes 11 made of the material made of Cu or mainly made Cu are hard to be etched even under elevated temperature, and are endurable in hot soldering work.

The material mainly made of Cu means each Cu alloy of Cr, Zr, Ag, Ti, Be, Zn, Sn, Ni, Al, Si or the like, or Cu containing glass frit made of oxides of Li, Na, K, Sr, Ba, Mn, Cu, Zn, B, Si, Al, Bi, Pb or the like.

Fig. 2 illustrates a rate of the residual electrode area to the solder temperature at the time of using Cu and Ag as electrode material, respectively.

After coating flux and preheating a ring varistor which is a sample, it is performed to dip the ring varistor in a solder bath, containing eutectic solder at each temperature, for 5 seconds.

As apparent from the figure, when the solder temperature becomes 400°C, etching progresses in the Ag electrode for a residual electrode area to become about 55.5% of the original, but on the other hand, Cu electrode is never etched for the

residual electrode area to be 100% of the original.

Next, a manufacturing method of this varistor ceramic 10 will be described simply.

The varistor ceramic 10 is obtained by processing raw material powder in order of mixing, calcining, grinding, forming, binder removal, reduction sintering, and reoxidation.

The powder of a compound of each structural element of ceramic is usually used for the raw material powder. An oxide or a compound which becomes an oxide by sintering, such as carbonate and a hydroxide can be used for the raw material powder. For example, if an example is given about Ba, at least one kind of barium compound such as BaCO_3 , BaSiO_3 , BaO , BaCl_2 , Ba(OH)_2 and $\text{Ba(NO}_3)_2$, and alkoxide (for example, $(\text{CH}_3\text{O})_2\text{Ba}$), can be used as the raw material. The mean particle diameter of the raw material powder may be usually about 0.2 to 5 μm .

First, the weighing of the raw material powder is performed so that the final composition may become the above-described composition, and usually, wet blending is performed. Subsequently, after performing dehydration processing, the raw material powder is dried and calcining is performed at about 1080 to 1250°C for about 2 to 4 hours. Next, after grinding a calcining object, an organic binder is added, and further, water, a pH regulator, a moisturizer and etc. are added and mixed. Subsequently, a mixture is molded, and is sintered at about 1250-1400°C in a reducing atmosphere for about 2 to 4 hours, after performing binder removal processing, for

obtaining semiconductor ceramic.

Each raw material powder such as Nb, Ta, Y, lanthanoids, Mo, W, Mn, Si, Co and the like may be added at the time of mixing after the calcining.

The semiconductor ceramic obtained in this manner is given heat treatment (reoxidation processing), for example, at the temperature of about 800 to 1000°C in an oxidizing atmosphere such as air, so that a suitable varistor voltage according to an object may be obtained. The insulating layer 10b is formed in a surface portion by this heat treatment. Varistor characteristics appear owing to the presence of this insulating layer. Since the nonlinear coefficient α and varistor voltage become large if this insulating layer is thick, and they become small if thin, what is necessary is just to select heat treatment conditions so that the insulating layer may become suitable thickness according to the characteristics demanded as a product.

Electrodes are formed on one surface of the varistor ceramic after the reoxidation processing with Cu or the material mainly made of Cu, and a varistor is obtained.

Hereinafter, the present invention will be described further in detail with reference to examples according to the first embodiment.

Example 1-1

What is performed in this example 1-1 is comparison of samples obtained by fixing other parameters such as a mole

percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and changing mole ratios of an A site component.

First, after respectively weighing by conversion and blending SrCO_3 , BaCO_3 , CaCO_3 , TiO_2 , $\text{NbO}_{5/2}$ and SiO_2 as raw material so that they might have the composition shown in Table 1-1, they were mixed for 10 to 20 hours with using an wet media mill, dehydrated and dried.

After calcining a mixture obtained, at 1150°C with using a tunnel kiln, the mixture was rough-ground, and again, dehydrated and dried after being mixed with a wet media mill for 10 to 20 hours. Subsequently, 1.0 to 1.5 wt% of polyvinyl alcohol was mixed to the mixture as an organic binder to be granulated, and the granulated mixture was formed at forming pressure of 2 t/cm^2 to become a formed object having an outer diameter of 12 mm, an inside diameter of 9 mm and a thickness of 1.0 mm.

After performing the binder removal processing of this forming object at about 1000°C in an air atmosphere, sintering was performed for 2 hours at about 1350°C in a reducing atmosphere of N_2 (95 volume percent) + H_2 (5 volume percent) for the semiconductor ceramic to be obtained. Subsequently, two-hours reoxidation processing of the semiconductor ceramic was performed at 950°C in the air for the varistor ceramic to be obtained.

Next, Cu paste was applied to one surface of the varistor

ceramic 10 as shown in Figs. 1a and 1b, in a neutral atmosphere, the five Cu electrodes 11 shown in these figures were formed by baking the Cu paste at 750°C to obtain test samples of the varistors for measuring.

Then, after measuring the voltages E_1 and E_{10} of each sample at 20°C, the nonlinear coefficient α was obtained from $\alpha = 1/\log(E_{10}/E_1)$ with using the measured voltages E_1 and E_{10} . Furthermore, the temperature characteristic (temperature coefficient) of the varistor voltage E_{10} was obtained. Moreover, a thermal crack test of each sample was performed.

The voltages E_1 and E_{10} were measured with using a measuring circuit shown in Fig. 3. In this measuring circuit, an ammeter 30 is connected in series between a varistor 31 and a DC constant current source 32, and a voltmeter 33 is connected in parallel with the varistor 31. The voltages E_1 and E_{10} were measured by measuring the voltage values between both terminals of the varistor 31 when electric current of 1 mA and 10 mA flow in the varistor 31 respectively with using the ammeter 30 and the voltmeter 33.

Temperature characteristics (temperature coefficient) ΔE_{10T} of the varistor voltage E_{10} were obtained with $\Delta E_{10T} = \{(E_{10}(85) - E_{10}(20)) / \{E_{10}(20) \times (85 - 20)\} \times 100$ [%/°C] about each sample. The voltages $E_{10}(20)$ and $E_{10}(85)$ are the varistor voltages E_{10} at the temperature of 20°C and 85°C, respectively. These were measured with using a thermostat oven.

The thermal crack test was performed by contacting a

soldering iron, where temperature was set beforehand, to the electrode side of the sample left at the room temperature, for 3 seconds with supplying eutectic solder. As temperature of the soldering iron, two kinds of temperature, that is, 360°C and 400°C were used. Hundred samples were visually inspected for cracks with using alcohol. The result is shown in Table 1-1.

Table 1-1

Sample No.	Composition					Electrical Characteristics			Thermal Crack Test (Soldering Iron Temperature °C)				
	Sr mole ratio a/(a+b+c)	Ba mole ratio b/(a+b+c)	Ca mole ratio c/(a+b+c)	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	E ₁₀ Temperature Characteristics ΔE _{10T} (°/°C)	360 °C	400 °C
1-1	0.30	0.35	0.35	NbO _{5/2}	3.00	0.98	0.20	None	15.8	3.7	0.01	Good	Good
1-2	0.30	0.40	0.30	NbO _{5/2}	3.00	0.98	0.20	None	12.9	3.5	0.02	Good	Good
1-3	0.35	0.30	0.35	NbO _{5/2}	3.00	0.98	0.20	None	16.1	4.0	0.00	Good	Good
1-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	0.01	Good	Good
1-5	0.35	0.40	0.25	NbO _{5/2}	3.00	0.98	0.20	None	11.6	3.5	0.02	Good	Good
1-6	0.40	0.30	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.8	3.7	0.00	Good	Good
1-7	0.40	0.35	0.25	NbO _{5/2}	3.00	0.98	0.20	None	10.9	3.5	0.01	Good	Good
1-8	0.10	0.40	0.50	NbO _{5/2}	3.00	0.98	0.20	None	39.9	3.9	0.03	Good	Good
1-9	0.10	0.50	0.40	NbO _{5/2}	3.00	0.98	0.20	None	20.1	3.5	0.04	Good	Good
1-10	0.20	0.30	0.50	NbO _{5/2}	3.00	0.98	0.20	None	33.5	4.2	0.01	Good	Good
1-11	0.20	0.40	0.40	NbO _{5/2}	3.00	0.98	0.20	None	20.6	3.8	0.03	Good	Good
1-12	0.20	0.50	0.30	NbO _{5/2}	3.00	0.98	0.20	None	15.7	3.4	0.04	Good	Good
1-13	0.30	0.50	0.20	NbO _{5/2}	3.00	0.98	0.20	None	11.0	2.8	0.04	Good	Good
1-14	0.40	0.40	0.20	NbO _{5/2}	3.00	0.98	0.20	None	10.6	2.8	0.02	Good	Good
1-15	0.50	0.30	0.20	NbO _{5/2}	3.00	0.98	0.20	None	10.0	2.7	-0.01	Good	Good
1-16	1.00	0.00	0.00	NbO _{5/2}	3.00	0.98	0.20	None	4.3	2.9	-0.50	Good	Good
1-17	0.80	0.20	0.00	NbO _{5/2}	3.00	0.98	0.20	None	4.8	3.0	-0.08	Good	Good
1-18	0.50	0.50	0.00	NbO _{5/2}	3.00	0.98	0.20	None	8.0	3.1	0.15	Good	Good
1-19	0.20	0.80	0.00	NbO _{5/2}	3.00	0.98	0.20	None	2.2	2.3	0.71	Good	Good
1-20	0.00	1.00	0.00	NbO _{5/2}	3.00	0.98	0.20	None	0.4	1.6	1.20	Good	No Good
1-21	0.00	0.80	0.20	NbO _{5/2}	3.00	0.98	0.20	None	4.6	2.5	0.23	Good	No Good
1-22	0.00	0.60	0.40	NbO _{5/2}	3.00	0.98	0.20	None	18.4	3.4	0.10	Good	No Good
1-23	0.00	0.40	0.60	NbO _{5/2}	3.00	0.98	0.20	None	74.0	3.1	0.06	Good	No Good
1-24	0.00	0.20	0.80	NbO _{5/2}	3.00	0.98	0.20	None	187.0	2.7	0.01	No Good	No Good
1-25	0.00	0.00	1.00	NbO _{5/2}	3.00	0.98	0.20	None	Isolated	—	—	No Good	No Good
1-26	0.80	0.00	0.20	NbO _{5/2}	3.00	0.98	0.20	None	138.0	2.4	-0.15	Good	Good
1-27	0.50	0.00	0.50	NbO _{5/2}	3.00	0.98	0.20	None	39.5	4.4	-0.08	Good	No Good
1-28	0.20	0.00	0.80	NbO _{5/2}	3.00	0.98	0.20	None	9.1	3.5	-0.01	Good	No Good
1-29	0.60	0.20	0.20	NbO _{5/2}	3.00	0.98	0.20	None	9.2	3.3	-0.07	Good	Good
1-30	0.20	0.60	0.20	NbO _{5/2}	3.00	0.98	0.20	None	9.9	3.2	0.11	Good	Good
1-31	0.40	0.20	0.40	NbO _{5/2}	3.00	0.98	0.20	None	22.0	4.1	-0.03	Good	Good
1-32	0.20	0.20	0.60	NbO _{5/2}	3.00	0.98	0.20	None	47.1	2.8	0.00	Good	Good

Mole ratios of the A site component have large influence on the electrical characteristic of a varistor, and in particular, to the temperature characteristic of the varistor voltage E_{10} . When the temperature characteristic of the voltage E_{10} is negative, the varistor voltage drops in connection with the rise of operating temperature, and hence, excessive electric current flows to the varistor or a possibility of causing a thermal runaway exists. Therefore, this is not adoptable. Therefore, the samples 1-15 to 1-17, 1-26 to 1-29 and 1-31 are in ranges where samples cannot be used as varistors.

Even if the temperature characteristic of the voltage E_{10} is zero or positive, it is not desirable to exceed 0.06, and hence, the samples 1-18 to 1-23 and 1-30 are not preferable as varistors.

Since being insulated as a whole by reoxidation processing, the sample 1-25 does not operate as a varistor. In addition, since the samples 1-24 and 1-26 contain too much Ca, their varistor voltage E_{10} is extremely high, and hence, control is difficult.

Since Ca contained is too much or too little although the E_{10} characteristics of the samples 1-13, 1-14 and 1-32 are 0.06 or less, their nonlinear coefficients α to the varistor voltage E_{10} are low, and hence they are not preferable.

Therefore, it can be said that the samples 1-1 to 1-12 are preferable because the temperature characteristic of the

varistor voltages E_{10} are 0.06 or less and the coefficients α to the varistor voltages E_{10} are not so low. This corresponds to A site mole ratios specified in claim 1. In this range, no crack arose at the thermal crack test where the temperature of the soldering iron was 360°C, and furthermore, no crack also arose at the thermal crack test where the temperature of the soldering iron was 400°C.

Furthermore, the samples 1-1 to 1-7 whose temperature characteristics of the voltages E_{10} are 0.02 or less are more preferable in the present invention. This corresponds to the A site mole ratios specified in claim 2. In particular, the sample 1-4 has the best balance of the temperature characteristic of the voltage E_{10} and the nonlinear coefficient α , and the mole ratios of the A site component near that of this sample are most preferable in the present invention.

Example 1-2

What is performed in this example 1-2 is comparison of samples obtained by changing an amount of a semiconductorizing agent.

With fixing other parameters such as A site mole ratios, a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 1-1 except for setting the mole percent of a semiconductorizing agent as shown in Table 1-2, samples were produced, which were measured similarly to those in the example 1-1. The result is shown in Table 1-2.

Table 1-2

Sample No.	Composition								Electrical Characteristics		Thermal Crack Test (Soldering Iron Temperature °C)		
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α			
1-33	0.35	0.35	0.30	NbO _{5/2}	0.10	0.98	0.20	None	30.2	3.1	No Good	360 °C	400 °C
1-34	0.35	0.35	0.30	NbO _{5/2}	1.00	0.98	0.20	None	15.5	3.4	Good		
1-35	0.35	0.35	0.30	NbO _{5/2}	2.00	0.98	0.20	None	12.4	3.4	Good	Good	Good
1-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	Good	Good	Good
1-36	0.35	0.35	0.30	NbO _{5/2}	4.00	0.98	0.20	None	12.1	3.5	Good	Good	Good
1-37	0.35	0.35	0.30	NbO _{5/2}	10.00	0.98	0.20	None	11.5	3.5	Good	Good	No Good
1-38	0.35	0.35	0.30	NbO _{5/2}	15.00	0.98	0.20	None	14.3	3.3	No Good	No Good	No Good

The amount of semiconductorizing agent affects the thermal crack-proof property of varistor ceramic. Since the samples 1-33 and 1-38 have too few and too much semiconductorizing agent respectively, thermal cracks arose in the test where the temperature of the soldering iron was 360°C, and hence, these are not preferable. Therefore, the samples 1-4 and 1-34 to 1-37 where thermal cracks did not arise in the test where the temperature of the soldering iron was 360°C are preferable in the present invention. This corresponds to the mole percent of a semiconductorizing agent specified in claim 1.

Furthermore, since a thermal crack arose in the test where the temperature of the soldering iron was 400°C in the sample 1-37, the samples 1-4 and 1-34 to 1-36 where cracks did not arise in this 400°C thermal crack test are more preferable in the present invention. This corresponds to the mole percent of a semiconductorizing agent specified in claim 4. In addition, mole percents near the mole percent of the semiconductorizing agent of the sample 1-4 are most preferable in the present invention.

Example 1-3

What is performed in this example 1-3 is comparison of samples where a kind of semiconductorizing agent was changed.

With fixing other parameters such as A site mole ratios, mole percents of semiconductorizing agents, a total A/B, and mole percent of SiO₂, and performing the same setup as that in the example 1-1 except for changing the kind of

semiconductorizing agents as shown in Table 1-3, samples were produced, which were measured similarly to those in the example 1-1. The result is shown in Table 1-3.

Table 1-3

Sample No.	Composition								Electrical Characteristics		Thermal Crack Test (Soldering Iron Temperature °C)	
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α		
1-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5		360 °C	400 °C
1-39	0.35	0.35	0.30	TaO _{5/2}	3.00	0.98	0.20	None	15.4		Good	Good
1-40	0.35	0.35	0.30	YO _{3/2}	3.00	0.98	0.20	None	26.6		Good	Good
1-41	0.35	0.35	0.30	LiO _{3/2}	3.00	0.98	0.20	None	15.1		Good	Good
1-42	0.35	0.35	0.30	CeO ₂	3.00	0.98	0.20	None	14.9		Good	Good
1-43	0.35	0.35	0.30	PrO _{11/4}	3.00	0.98	0.20	None	16.2		Good	Good
1-44	0.35	0.35	0.30	NdO _{3/2}	3.00	0.98	0.20	None	16.8		Good	Good
1-45	0.35	0.35	0.30	SmO _{3/2}	3.00	0.98	0.20	None	14.8		Good	Good
1-46	0.35	0.35	0.30	EuO _{3/2}	3.00	0.98	0.20	None	19.0		Good	Good
1-47	0.35	0.35	0.30	GdO _{3/2}	3.00	0.98	0.20	None	16.2		Good	Good
1-48	0.35	0.35	0.30	TbO _{7/4}	3.00	0.98	0.20	None	21.3		Good	Good
1-49	0.35	0.35	0.30	DyO _{3/2}	3.00	0.98	0.20	None	18.3		Good	Good
1-50	0.35	0.35	0.30	HoO _{3/2}	3.00	0.98	0.20	None	25.4		Good	Good
1-51	0.35	0.35	0.30	ErO _{3/2}	3.00	0.98	0.20	None	27.9		Good	Good
1-52	0.35	0.35	0.30	TmO _{3/2}	3.00	0.98	0.20	None	24.1		Good	Good
1-53	0.35	0.35	0.30	YbO _{3/2}	3.00	0.98	0.20	None	29.2		Good	Good
1-54	0.35	0.35	0.30	LuO _{3/2}	3.00	0.98	0.20	None	28.2		Good	Good
1-55	0.35	0.35	0.30	NbO _{5/2} +YO _{3/2} Equal numbers of moles	3.00	0.98	0.20	None	22.0		Good	Good

Since thermal cracks did not arise in all the samples 1-4 and 1-39 to 1-55 in the tests where the temperature of the soldering iron was 360°C and 400°C, it is preferable in the present invention to use $\text{NbO}_{5/2}$, $\text{TaO}_{5/2}$, $\text{YO}_{3/2}$, $\text{LaO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{NdO}_{3/2}$, $\text{SmO}_{3/2}$, $\text{EuO}_{3/2}$, $\text{GdO}_{3/2}$, $\text{TbO}_{7/4}$, $\text{DyO}_{3/2}$, $\text{HoO}_{3/2}$, $\text{ErO}_{3/2}$, $\text{TmO}_{3/2}$, $\text{YbO}_{3/2}$, $\text{LuO}_{3/2}$ or $\text{NbO}_{5/2} + \text{YO}_{3/2}$ (equal numbers of moles) as a semiconductorizing agent.

Example 1-4

What is performed in this example 1-4 is comparison of samples obtained by changing a total A/B.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of semiconductorizing agent, and a mole percent of SiO_2 , and performing the same setup as that in the example 1-1 except for changing the total A/B as shown in Table 1-4, samples were produced, which were measured similarly to those in the example 1-1. The result is shown in Table 1-4.

Table 1-4

Sample No.	Composition							Electrical Characteristics		Thermal Crack Test (Soldering Iron Temperature °C)	
	Sr mole ratio a/(a+b+c)	Ba mole ratio b/(a+b+c)	Ca mole ratio c/(a+b+c)	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)		
1-56	0.35	0.35	0.30	NbO _{5/2}	3.00	0.80	0.20	None	Isolated	360 °C	No Good
1-57	0.35	0.35	0.30	NbO _{5/2}	3.00	0.84	0.20	None	4.4	360 °C	No Good
1-58	0.35	0.35	0.30	NbO _{5/2}	3.00	0.96	0.20	None	7.0	360 °C	Good
1-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	360 °C	Good
1-59	0.35	0.35	0.30	NbO _{5/2}	3.00	1.00	0.20	None	9.5	360 °C	Good
1-60	0.35	0.35	0.30	NbO _{5/2}	3.00	1.01	0.20	None	6.3	360 °C	Good
1-61	0.35	0.35	0.30	NbO _{5/2}	3.00	1.16	0.20	None	51.5	360 °C	No Good
1-62	0.35	0.35	0.30	NbO _{5/2}	3.00	1.20	0.20	None	Isolated	360 °C	No Good

The value of the total A/B affects the degree of sintering of ceramic. The samples 1-56 and 1-62 have too small and too large total A/B respectively, these could not operate as varistors because it was impossible to sinter precise ceramic, and they were insulated as a whole by reoxidation processing. Furthermore, a thermal crack arose when the temperature of the soldering iron was 360°C.

As shown in Table 1-4, in a range where an amount of SiO_2 is few and a lot of semiconductorizing agent is added, in order to maintain the thermal crack-proof property, it is indispensable to especially control an upper limit of the total A/B. If the total A/B exceeds 1.16, a thermal crack arises at 360°C, and if the total A/B exceeds 1.01, a thermal crack arises at 400°C.

That is, since a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C, the samples 1-4 and 1-57 to 1-61 are preferable in the present invention. This corresponds to a total A/B specified in claim 1.

Furthermore, since a thermal crack did not arise in the test where the temperature of the soldering iron was 400°C, the samples 1-4 and 1-58 to 1-60 are preferable in the present invention. This corresponds to a total A/B specified in claim 3. The vicinity of the total A/B where the B site component is a little rich like the sample 1-4 is a most preferable range of the present invention.

Example 1-5

What is performed in this example 1-5 is comparison of samples obtained by changing a mole percent of SiO_2 .

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, and a total A/B, and performing the same setup as that in the example 1-1 except for changing the mole percent of SiO_2 as shown in Table 1-5, samples were produced, which were measured similarly to those in the example 1-1. The temperature of a soldering iron in a thermal crack test was three kinds of temperature, that is, 360°C , 400°C and 450°C . The result was shown in Table 1-5.

Table 1-5

Sample No.	Composition								Electrical Characteristics		Thermal Crack Test (Soldering Iron Temperature °C)		
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	360 °C	400 °C	450 °C
1-63	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.00	None	7.7	3.3			
1-64	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.10	None	8.5	3.4	Good	Good	Good
1-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	Good	Good	Good
1-65	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.30	None	13.7	3.6	Good	Good	Good
1-66	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.60	None	10.4	3.4	Good	Good	No Good
1-67	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	1.00	None	337.0	2.9	No Good	No Good	No Good
1-68	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	1.50	None	Isolated	—	No Good	No Good	No Good

SiO_2 is added as a sintering additive. If SiO_2 is contained, it becomes possible to perform stable sintering even if composition fluctuates. However, if its amount increases, it becomes easy for a thermal crack to arise.

Since there was too much SiO_2 and thus a thermal crack arose in the test, where the temperature of the soldering iron was 360°C , the samples 1-67 and 1-68 are not preferable. Therefore, the samples 1-4 and 1-63 to 1-66, where a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C and 400°C , are preferable in the present invention. This corresponds to the mole percent of SiO_2 specified in claim 1. Although a dosage of SiO_2 in the sample 1-63 is zero nominally, in fact, SiO_2 is contained in each raw material as an impurity, and hence actual SiO_2 content of the sample 1-63 does not become zero.

A thermal crack arose in the sample 1-66 in the test where the temperature of the soldering iron was 450°C . Thus, the sample 1-4 and 1-63 to 1-65 become more preferable in the present invention where a thermal crack did not arise in the test at the temperature of the soldering iron of 450°C . This corresponds to the mole percent of SiO_2 specified in claim 5. In addition, the mole percent of SiO_2 near that of the sample 1-4 is most preferable in the present invention.

Example 1-6

What is performed in this example 1-6 is comparison of samples where a kind and an amount of an additive were changed.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 1-1 except for changing the kind and amount of an additive as shown in Table 1-6, samples were produced, which were measured similarly to those in the example 1-1. The result is shown in Table 1-6.

Table 1-6

Sample No.	Composition										Electrical Characteristics		Thermal Crack Test (Soldering Iron Temperature °C)	
	Sr mole ratio a/(a+b+c)	Ba mole ratio b/(a+b+c)	Ca mole ratio c/(a+b+c)	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	Mole % of additive	E ₁₀ (V)	α			
												360 °C	400 °C	
1-69	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.01	15.6	4.0	Good	Good	
1-70	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.03	15.0	4.1	Good	Good	
1-71	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.60	19.6	4.2	Good	Good	
1-72	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	1.00	26.3	4.4	Good	Good	
1-73	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	2.00	Isolated	—	No Good	No Good	
1-74	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	CoO _{4/3}	0.01	13.1	3.4	Good	Good	
1-75	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	CoO _{4/3}	0.50	22.1	3.7	Good	Good	
1-76	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	CoO _{4/3}	1.00	28.8	3.7	Good	Good	
1-77	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	CoO _{4/3}	2.00	Isolated	—	No Good	No Good	
1-78	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MoO ₃	0.20	12.0	3.6	Good	Good	
1-79	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	WO ₃	0.20	11.8	3.6	Good	Good	

An additive has the action of adjusting electrical characteristics such as the varistor voltage E_{10} and the nonlinear coefficient α . Mn enlarges the varistor voltage E_{10} and the nonlinear coefficient α , and Co enlarges varistor voltage E_{10} . In addition, it is found that Mo and W have the action of enlarging the nonlinear coefficient α . Although not shown in Table 1-6, it is found that other elements such as Li, Na, Ni, Cu, Zn, Sc, Fe, Ga and In also have the same action.

Since the samples 1-73 and 1-77 had a too large amount of dosage, the degree of sintering was blocked and the ceramic was insulated by the reoxidation processing. Therefore, the samples 1-69 to 1-72, 1-74 to 1-76 and 1-78 to 1-79 each having the mole percent to a principal component that is 1.00 or less are preferable in the present invention. This is included in the kind and mole percent of an additive specified in claim 6.

Example 1-7

What is performed in this example 1-7 is comparison of a sample, where Mg is not added substantially, and samples obtained by changing a dosage of Mg.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 1-1 except for changing the dosage of Mg as shown in Table 1-7, samples were produced, which were measured similarly to those in the example 1-1. The result is shown in Table 1-7.

Table 1-7

Sample No.	Composition										Electrical Characteristics		Thermal Crack Test (Soldering Iron Temperature °C)	
	Sr mole ratio a/(a+b+c)	Ba mole ratio b/(a+b+c)	Ca mole ratio c/(a+b+c)	Component of semiconductorizing agent	Mole % of semiconductorizing agent	Total A/B	SiO ₂ mole %	Component of additive	Mole % of additive	E ₁₀ (V)	α			
													360 °C	400 °C
1-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	—	11.5	3.4	Good	Good	
1-80	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MgO	0.001	12.0	3.5	No Good	No Good	
1-81	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MgO	0.01	14.4	3.8	No Good	No Good	
1-82	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MgO	0.50	16.5	4.2	No Good	No Good	

If Mg is contained, it becomes very easy for a thermal crack to arise. Since a thermal crack arose even in the test where the temperature of the soldering iron was 360°C, samples 1-80 to 1-82 each having the content to a principal component that is 0.001 or more mole percent are not preferable.

Therefore, it is preferable in the present invention that Mg is not contained at all like the sample 1-4, or the content of Mg is less than about 0.001 mole percent in general (Mg should not be contained substantially). This corresponds to contents specified in claim 1.

Second Embodiment

Hereinafter, the composition of the varistor ceramic 10 in this second embodiment will be described.

The varistor ceramic 10 contains a first component of the composite perovskite which consists of oxides of Sr, Ba, Ca and Ti, at least one component of a second component which consists of at least one kind of oxide selected from oxides of R (Y and lanthanoids (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu)) and a third component which consists of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component which consists of an oxide of Si. It is assumed that a is the number of moles calculated for Sr of the first component as SrO, b is the number of moles calculated for Ba of the first component as BaO, c is the number of moles calculated for Ca of the first component as CaO, d is the

number of moles calculated for Ti of the first component as TiO_2 , e is the number of moles calculated for R of the second component as $\text{YO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{TbO}_{7/4}$ and $\text{RO}_{3/2}$ (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as $\text{NbO}_{5/2}$ and $\text{TaO}_{5/2}$ respectively, and g is the number of moles calculated for Si of the fourth component as SiO_2 . As for the component of this varistor ceramic in the trilinear coordinates of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$, shown in Fig. 4, values of Sr, Ba and Ca, that is, $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ exist on a line segment connecting a point (0.2, 0.0, 0.8) and a point (0.0, 0.4, 0.6), or in a range where $a/(a + b + c)$ and $b/(a + b + c)$ are larger than this line segment (hereinafter, a first range). And the component is $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$.

As for mole ratios of this A site component, it is more preferable that values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in the trilinear coordinates exist on a first line segment connecting a point (0.5, 0.0, 0.5) and a point (0.2, 0.2, 0.6), on a second line segment connecting a point (0.2, 0.2, 0.6) and a point (0.1, 0.4, 0.5), on a third line segment connecting a point (0.1, 0.4, 0.5) and a point (0.1, 0.5, 0.4), or on a fourth line segment connecting a point (0.1, 0.5, 0.4) and a point (0.2, 0.8, 0.0), or $a/(a + b + c)$ exists in a range larger than these first to fourth line segments (hereinafter, a second range).

Furthermore, as for a mole ratio of this A site component, it is still more preferable that values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in the trilinear coordinates exist on a fifth line segment connecting a point (0.4, 0.2, 0.4) and a point (0.2, 0.4, 0.4), on a sixth line segment connecting a point (0.2, 0.4, 0.4) and a point (0.2, 0.5, 0.3), on a seventh line segment connecting a point (0.2, 0.5, 0.3) and a point (0.3, 0.5, 0.2), on an eighth line segment connecting a point (0.3, 0.5, 0.2) and a point (0.6, 0.2, 0.2), or a ninth line segment connecting a point (0.6, 0.2, 0.2) and a point (0.4, 0.2, 0.4), or in a range surrounded by these fifth to ninth line segments (hereinafter, a third range).

It is more preferable that the total A/B is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$.

It is more preferable that, as the amount of a semiconductorizing agent is $0.75 \leq (e + f)/d \times 100 \leq 4.0$.

It is more preferable that, the amount of SiO_2 is $g/d \times 100 \leq 0.3$.

The first component is a main component of the varistor ceramic 10. This first component consists of, in composite perovskite, an A site component of Sr, Ba and Ca, and a B site component of Ti. The second and third components are metallic oxides that contribute to semiconductorization, and the fourth component is mainly added for the improvement of a degree of sintering.

Electrical characteristics as a varistor are mainly

expressed with a temperature characteristic of a varistor voltage E_{10} and a nonlinear coefficient α . The varistor voltage E_{10} expresses an applied voltage value at the time of 10-mA electric current flowing in the varistor, and the nonlinear coefficient α is generally expressed in $\alpha = 1/\log(E_{10}/E_1)$. Where, E_1 is an applied voltage value at the time of 1-mA electric current flowing in the varistor.

It is preferable that mole ratios of Sr, Ba and Ca which are contained in the A site component exist in the first range. It is more preferable to exist in the second range, and still more preferable to exist in the third range. Then, it becomes possible to enhance electrical characteristics such as the controllability of the varistor voltage E_{10} , temperature characteristics of the varistor voltage E_{10} and nonlinear coefficient α , and to enhance the thermal shock-proof property of the varistor. That is, if there is too much Sr, the temperature characteristic of E_{10} will become negative, and if too few, strength will drop. In addition, if there is too much Ba, the positive trend of temperature characteristic of E_{10} becomes strong too much, and if too few, the temperature characteristic of E_{10} becomes negative. Furthermore, even if there is too much Ca or too few Ca, the nonlinear coefficient α to the varistor voltage E_{10} becomes small. In addition, if there is too much Ca, the varistor voltage E_{10} becomes extremely large to become difficult of control, and a base is made an insulator by reoxidation.

It is preferable that the mole percent (this is calculated by the number of moles of metal ions) of a semiconductorizing agent (the second and/or third components) to a principal component (TiO_2) is between 0.75 and 10.0 inclusive. Alternatively, it is more preferable that the mole percent is between 0.75 and 4.0 inclusive. Then, it is possible to enhance the strength and the thermal shock-proof property of the varistor. That is, even if there are too much semiconductorizing agent or too few, it becomes easy that a thermal crack arises.

In addition, it is preferable that the total A/B is between 0.84 and 1.16 inclusive. Furthermore, it is more preferable that the total A/B is between 0.96 and 1.01 inclusive. Then, even if an amount of the fourth component (SiO_2) is reduced, as described later, a degree of sintering can be improved. That is, this is because sintering is blocked even if the total A/B is too large or too small, and hence the base is made an insulator owing to reoxidation. In addition, this is also because a thermal crack easily arises if total A/B is too large or too small. In a range where an amount of SiO_2 is few and a lot of semiconductorizing agent is added as described above, in order to maintain the thermal crack-proof property, it becomes indispensable to restrict an upper limit of the total A/B to be 1.16 or less, or more preferably, to be 1.01 or less.

The strength and the thermal shock-proof property of a

varistor can be sharply enhanced by setting the mole percent of the fourth component (SiO_2) to the principal component (TiO_2) to be 0.6 or less, or more preferably, to be 0.3 or less. That is, SiO_2 is added as a sintering additive and it is possible to stably perform sintering even if the composition fluctuates, but however, if the amount of SiO_2 increases, it becomes easy for a thermal crack to arise. It should be noted that the content (mole percent) of SiO_2 of 0.6 or less or of 0.3 or less also includes the case where its dosage is zero.

The varistor ceramic 10 may also contain an additive that consists of at least one kind of oxide selected from among oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W. Supposing the content is the number of moles obtained by converting Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W into $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 , it is preferable that the composition is $0 < h/d \times 100 \leq 1.000$. Thereby, there is an effect of improving the nonlinear coefficient α .

In addition, the varistor ceramic 10 may also contain other elements such as P, S, K, Al and Zr as unavoidable impurities besides such additives. Such elements usually exist as oxides.

As described above, the varistor ceramic 10 is a polycrystal consisting of perovskite type crystals. A part of each component is contained in the perovskite type crystals with being solidly solved in grains, and another part exists in

crystal grain boundaries as oxides or complex oxides. For example, Ba, Ca, Sr, Ti, Nb, Ta, Y, lanthanoids and the like exist mostly in grains, and Mo, W, Mn, Si, Co and the like exist mostly in crystal grain boundaries.

A mean grain diameter of the varistor ceramic 10 usually is about 0.5 to 10 μm , and in particular, 1 to 6 μm .

Next, a manufacturing method of this varistor ceramic 10 will be described simply.

The varistor ceramic 10 is obtained by processing raw material powder in order of mixing, calcining, grinding, forming, binder removal, reduction sintering, and reoxidation.

The powder of a compound of each structural element of ceramic is usually used for the raw material powder. An oxide or a compound which becomes an oxide by sintering, such as carbonate and a hydroxide can be used for the raw material powder. For example, if an example is given about Ba, at least one kind of barium compound such as BaCO_3 , BaSiO_3 , BaO , BaCl_2 , Ba(OH)_2 and $\text{Ba(NO}_3)_2$, and alkoxide (for example, $(\text{CH}_3\text{O})_2\text{Ba}$), can be used as the raw material. The mean particle diameter of the raw material powder may be usually about 0.2 to 5 μm .

First, the weighing of the raw material powder is performed so that the final composition may become the above-described composition, and usually, wet blending is performed. Subsequently, after performing dehydration processing, the raw material powder is dried and calcining is performed at about 1080 to 1250°C for about 2 to 4 hours. Next, after grinding a

calcining object, an organic binder is added, and further, water, a pH regulator, a moisturizer and etc. are added and mixed. Subsequently, a mixture is molded, and is sintered at about 1250-1400°C in a reducing atmosphere for about 2 to 4 hours, after performing binder removal processing, for obtaining semiconductor ceramic.

Each raw material powder such as Nb, Ta, Y, lanthanoids, Mo, W, Mn, Si, Co and the like may be added at the time of mixing after the calcining.

The semiconductor ceramic obtained in this manner is given heat treatment (reoxidation processing) in an oxidizing atmosphere such as air, so that a suitable varistor voltage according to an object may be obtained. The temperature rise and fall speed in this reoxidation processing is usually at about 100°C/h to 600°C/h. In addition, the preferable temperature of this reoxidation processing is between 850°C and 1050°C inclusive, or the more preferable temperature is between 900°C and 1000°C inclusive. In addition, its preferable time is 32 hours or less, and more preferable time is between 0.25 and 16 hours inclusive. Furthermore, it is preferable that its partial pressure of an oxygen gas is 0.1 atmospheric pressure or more.

The insulating layer 10b is formed on a surface portion by this reoxidation processing. Varistor characteristics appear owing to the presence of this insulating layer. Since the nonlinear coefficient α and varistor voltage become large if

this insulating layer is thick, and they become small if thin, what is necessary is just to select processing conditions so that the insulating layer may become suitable thickness according to the characteristics demanded as a product.

Assuming that X-ray stress constant is -100 MPa/degree, it is preferable in this reoxidation processing according to this embodiment that the compressive stress on a surface of the varistor ceramic is 15 MPa or more, it is more preferable to be 25 MPa or more, and it is still more preferable to be 40 MPa or more.

Since the compressive stress exists on the ceramic surface, it is also possible not only to improve bending strength at the time of soldering, but also to obtain high thermal shock-proof property preventing a crack from arising even when temperature locally rises at the time of soldering.

Electrodes 11 are formed on one surface of the varistor ceramic after reoxidation processing with Cu or material mainly made of Cu, and a varistor is obtained. The material mainly made of CU is the same as that in the first embodiment.

In the second embodiment described above, although the electrodes are provided in one surface of varistor ceramic, an electrode(s) may be provided in top and back faces or sides of the varistor ceramic.

Hereafter, the present invention is described still in detail according to examples according to the second embodiment.

Example 2-1

What is performed in this example 2-1 is comparison of samples obtained by fixing other parameters such as a mole percent and a kind of a semiconductorizing agent, a total A/B ratio, and a mole percent of SiO_2 , and changing mole ratios of an A site component.

First, after respectively weighing by conversion and blending SrCO_3 , BaCO_3 , CaCO_3 , TiO_2 , $\text{NbO}_{5/2}$ and SiO_2 as raw material so that they might have the composition shown in Table 2-1, they were mixed for 10 to 20 hours with using a wet media mill, dehydrated and dried.

After calcining a mixture obtained, at 1150°C , the mixture was rough-ground, and again, dehydrated and dried after being mixed with a wet media mill for 10 to 20 hours. Subsequently, 1.0 to 1.5 wt% of polyvinyl alcohol was mixed to the mixture as an organic binder to be granulated, and the granulated mixture was formed at forming pressure of 2 t/cm^2 to become a formed object having an outer diameter of 12 mm, an inside diameter of 9 mm and thickness of 1.0 mm.

After performing the binder removal processing of this forming object at about 600°C in an air atmosphere, sintering was performed for 2 hours at about 1350°C in a reducing atmosphere of N_2 (95 volume percent) + H_2 (5 volume percent) for the semiconductor ceramic to be obtained. Subsequently, two-hours reoxidation processing of the semiconductor ceramic was performed at 950°C in the air for the varistor ceramic to be obtained.

Next, Cu paste was applied to one surface of the varistor ceramic 10 as shown in Figs. 1a and 1b, in a neutral atmosphere, and the five Cu electrodes 11 shown in these figures were formed by baking the Cu paste at 750°C to obtain test samples of the varistors for measuring.

Then, after measuring the voltages E_1 and E_{10} of each sample at 20°C, the nonlinear coefficient α was obtained from $\alpha = 1/\log(E_{10}/E_1)$ with using the measured voltages E_1 and E_{10} . Furthermore, the temperature characteristic (temperature coefficient) of the varistor voltage E_{10} was obtained. Furthermore, while performing the thermal crack test of each sample, the residual compressive stress on a surface of each sample was measured.

The voltages E_1 and E_{10} were measured with using a measuring circuit shown in Fig. 3. In this measuring circuit, an ammeter 30 is connected in series between a varistor 31 and a DC constant current source 32, and a voltmeter 33 is connected in parallel with the varistor 31. The voltages E_1 and E_{10} were measured by measuring the voltage values between both terminals of the varistor 31 when electric current of 1 mA and 10 mA flows in the varistor 31 respectively with using the ammeter 30 and the voltmeter 33.

Temperature characteristics (temperature coefficient) ΔE_{10T} of the varistor voltage E_{10} were obtained with $\Delta E_{10T} = \{E_{10}(85) - E_{10}(20)\} / \{E_{10}(20) \times (85 - 20) \times 100\}$ [%/°C] about each sample. The voltages $E_{10}(20)$ and $E_{10}(85)$ are the varistor

voltages E_{10} at the temperature of 20°C and 85°C, respectively. These were measured with using a thermostat oven.

The thermal crack test was performed by contacting a soldering iron, where temperature was set beforehand, to the electrode side of the sample left at the room temperature, for 3 seconds with supplying eutectic solder. As temperature of the soldering iron, three kinds of temperature, that is, 360°C, 400°C and 450°C were used. Hundred samples were visually inspected for cracks with using alcohol.

The residual compressive stress on the surface of each sample was measured with using a stress measuring method by X-ray diffraction. Since the perovskite structure which is a main phase of each sample belongs to a cubic system, the surface stress generated in the plane direction can be estimated, by X-ray diffraction on the surface of the ceramic, from the ratio of a face gap of the perovskite in a direction perpendicular to the face and a face gap of the perovskite in a direction parallel to the face. Here, stress measurement was performed by a side gradient method with using a collimated beam generated by a Cr bulb. In addition, two times of rocking was added at the time of measurement. The diffraction line used for measurement was (310) that was near 134 degrees.

The stress measuring method by such X-ray diffraction is known. For example, it is described in detail in B.D. Cullity (translated by Gentaro Matsumura), "Newly-edited summary of X-ray diffraction", Agune Co., Ltd., pp. 412-442, June, 1980, and

"X-ray diffraction handbook", Rigaku Denki Co., Ltd., pp. 103-105, February, 2000.

A formula used when estimating the surface residual stress in this example was as follows:

$$\sigma = -\frac{E}{2(1+\nu)} \cdot \cot \theta_0 \cdot \frac{\pi}{180} \cdot \frac{\Delta(2\theta)}{\Delta(\sin^2 \psi)} = K \cdot \frac{\Delta(2\theta)}{\Delta(\sin^2 \psi)}$$

where, σ is a residual stress (MPa), E is a Young's modulus (MPa), ν is a Poisson ratio, and θ_0 is a standard Bragg angle (degree) (here, $\theta_0 = 134$ (degrees)/2). Further, ψ is an angle (degree) between a normal to a surface of the sample and a measuring normal, 2θ is an angle of diffraction (degree), and K is a stress constant (MPa/degree) determined by material and the angle of diffraction.

The estimation of the residual stress can be obtained by finding its gradient with the method of least squares from the relation of the angle of diffraction 2θ , which is measured, to $\sin^2 \psi$ which can be obtained from the angle ψ formed by the normal to the surface of the sample and the measuring normal, and multiplying the gradient by the stress constant K .

In this example, it is assumed that the stress constant $K = -100$ MPa/degree. This is because, as apparent from the formula described above, the value of the gradient found with the method of least squares from the measurement result is obtained can be used as it is, since the value of the stress can be freely set according to the value of K . That is, this is because it is sufficient so long as a value of the gradient, in

other words, an index expressing a grade of deformation from a cubic in a perovskite phase is given since an absolute value of the stress constant K is not important.

The result in the example 2-1 is shown in Table 2-1.

Table 2-1

Sample No.	Composition						Electrical Characteristics			Mechanical Characteristics					
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconductor uctorizing agent	Mole % of semiconductor uctorizing agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	E ₁₀ Temperature Characteristics ΔE _{10T} (%/°C)	Thermal Crack Test (Soldering Iron Temperature °C)			Residual Compressive Stress (Mpa)
												360 °C	400 °C	450 °C	
2-1	0.30	0.35	0.35	NbO _{5/2}	3.00	0.98	0.20	None	15.8	3.7	0.01	Good	Good	Good	44
2-2	0.30	0.40	0.30	NbO _{5/2}	3.00	0.98	0.20	None	12.9	3.5	0.02	Good	Good	Good	44
2-3	0.35	0.30	0.35	NbO _{5/2}	3.00	0.98	0.20	None	16.1	4.0	0.00	Good	Good	Good	44
2-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	0.01	Good	Good	Good	45
2-5	0.35	0.40	0.25	NbO _{5/2}	3.00	0.98	0.20	None	11.6	3.5	0.02	Good	Good	Good	45
2-6	0.40	0.30	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.8	3.7	0.00	Good	Good	Good	45
2-7	0.40	0.35	0.25	NbO _{5/2}	3.00	0.98	0.20	None	10.9	3.5	0.01	Good	Good	Good	45
2-8	0.10	0.40	0.50	NbO _{5/2}	3.00	0.98	0.20	None	39.9	3.9	0.03	Good	Good	No Good	29
2-9	0.10	0.50	0.40	NbO _{5/2}	3.00	0.98	0.20	None	20.1	3.5	0.04	Good	Good	No Good	31
2-10	0.20	0.30	0.50	NbO _{5/2}	3.00	0.98	0.20	None	33.5	4.2	0.01	Good	Good	No Good	35
2-11	0.20	0.40	0.40	NbO _{5/2}	3.00	0.98	0.20	None	20.6	3.8	0.03	Good	Good	Good	43
2-12	0.20	0.50	0.30	NbO _{5/2}	3.00	0.98	0.20	None	15.7	3.4	0.04	Good	Good	Good	41
2-13	0.30	0.50	0.20	NbO _{5/2}	3.00	0.98	0.20	None	11.0	2.8	0.04	Good	Good	Good	42
2-14	0.40	0.40	0.20	NbO _{5/2}	3.00	0.98	0.20	None	10.6	2.8	0.02	Good	Good	Good	42
2-15	0.50	0.30	0.20	NbO _{5/2}	3.00	0.98	0.20	None	10.0	2.7	-0.01	Good	Good	Good	40
2-16	1.00	0.00	0.00	NbO _{5/2}	3.00	0.98	0.20	None	4.3	2.9	-0.50	Good	Good	No Good	35
2-17	0.80	0.20	0.00	NbO _{5/2}	3.00	0.98	0.20	None	4.8	3.0	-0.08	Good	Good	No Good	35
2-18	0.50	0.50	0.00	NbO _{5/2}	3.00	0.98	0.20	None	8.0	3.1	0.15	Good	Good	No Good	30
2-19	0.20	0.80	0.00	NbO _{5/2}	3.00	0.98	0.20	None	2.2	2.3	0.71	Good	Good	No Good	25
2-20	0.00	1.00	0.00	NbO _{5/2}	3.00	0.98	0.20	None	0.4	1.6	1.20	Good	No Good	No Good	23
2-21	0.00	0.80	0.20	NbO _{5/2}	3.00	0.98	0.20	None	4.6	2.5	0.23	Good	No Good	No Good	22
2-22	0.00	0.60	0.40	NbO _{5/2}	3.00	0.98	0.20	None	18.4	3.4	0.10	Good	No Good	No Good	22
2-23	0.00	0.40	0.60	NbO _{5/2}	3.00	0.98	0.20	None	74.0	3.1	0.06	Good	No Good	No Good	15
2-24	0.00	0.20	0.80	NbO _{5/2}	3.00	0.98	0.20	None	187.0	2.7	0.01	No Good	No Good	No Good	12
2-25	0.00	0.00	1.00	NbO _{5/2}	3.00	0.98	0.20	None	Isolated	—	—	No Good	No Good	No Good	10
2-26	0.80	0.00	0.20	NbO _{5/2}	3.00	0.98	0.20	None	138.0	2.4	-0.15	Good	Good	No Good	31
2-27	0.50	0.00	0.50	NbO _{5/2}	3.00	0.98	0.20	None	39.5	4.4	-0.08	Good	No Good	No Good	24
2-28	0.20	0.00	0.80	NbO _{5/2}	3.00	0.98	0.20	None	9.1	3.5	-0.01	Good	No Good	No Good	17
2-29	0.60	0.20	0.20	NbO _{5/2}	3.00	0.98	0.20	None	9.2	3.3	-0.07	Good	Good	Good	43
2-30	0.20	0.60	0.20	NbO _{5/2}	3.00	0.98	0.20	None	9.9	3.2	0.11	Good	Good	No Good	39
2-31	0.40	0.20	0.40	NbO _{5/2}	3.00	0.98	0.20	None	22.0	4.1	-0.03	Good	Good	Good	43
2-32	0.20	0.20	0.60	NbO _{5/2}	3.00	0.98	0.20	None	47.1	2.8	0.00	Good	Good	No Good	31

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO_2 is d moles, the content of $\text{NbO}_{5/2}$ is f moles, and the content of SiO_2 is g moles. The composition was fixed as $f/d \times 100 = 3.00$, $g/d \times 100 = 0.2$, and $(a + b + c)/(d + f) = 0.98$.

Mole ratios of the A site component largely affect the electrical characteristics of a varistor, and in particular, the temperature characteristic of the varistor voltage E_{10} .

In the samples 2-1 to 2-23, and 2-26 to 2-32 except for the samples 2-24 and 2-25 (the mole ratios of the A site component are $a/(a + b + c) = 0.00$, $b/(a + b + c) = 0.20$, $c/(a + b + c) = 0.80$, and $a/(a + b + c) = 0.00$, $b/(a + b + c) = 0.00$, and $c/(a + b + c) = 1.00$), a thermal crack did not arise in the test where the temperature of a soldering iron was 360°C . At this time, residual compressive stress in the composition ranges of the samples 2-1 to 2-23 and 2-26 to 2-32 where a thermal crack did not arise was 15 MPa or more without exception.

Therefore, ranges where values of the first range which is the composition range of the samples 2-1 to 2-23 and 2-26 to 2-32, i.e., $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in the trilinear coordinates shown in Fig. 4 exist on a line segment connecting a point (0.2, 0.0, 0.8) corresponding to the sample 2-28 and a point (0.0, 0.4, 0.6) corresponding to the sample 2-23, or $a/(a + b + c)$ and $b/(a + b + c)$ become larger

than this line segment are preferable ranges in the present invention. These correspond to the A site mole ratios specified in claims 15 and 32. In addition, since a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C if the residual compressive stress was 15 MPa or more, this range is also a preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 12 and 24.

In other samples 2-1 to 2-19, 2-26 and 2-29 to 2-32 except for the samples 2-20 to 2-25, 2-27 and 2-28, a thermal crack did not arise in the test where the temperature of the soldering iron was 400°C. At this time, residual compressive stress in the composition ranges of the samples 2-1 to 2-19, 2-26 and 2-29 to 2-32 where no thermal crack arose was 25 MPa or more without exception.

Hence, ranges where values of the second range which is the composition range of the samples 2-1 to 2-19, 2-26 and 2-29 to 2-32, i.e., $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in the trilinear coordinates shown in Fig. 4 exist on a first line segment connecting a point (0.5, 0.0, 0.5) corresponding to the sample 2-27 and a point (0.2, 0.2, 0.6) corresponding to the sample 2-37, a second line segment connecting this point (0.2, 0.2, 0.6) and a point (0.1, 0.4, 0.5) corresponding to the sample 2-8, a third line segment connecting this point (0.1, 0.4, 0.5) and a point (0.1, 0.5, 0.4) corresponding to the sample 2-9, or a fourth line segment connecting this point (0.1,

0.5, 0.4) and a point (0.2, 0.8, 0.0) corresponding to the sample 2-19, or $a/(a + b + c)$ becomes larger than these first to fourth line segments, which do not include a point (0.5, 0.0, 0.5) corresponding to the sample 2-27 are more preferable ranges in the present invention. These correspond to A site mole ratios specified in claims 16 and 33. In addition, since a thermal crack did not arise in the test, where the temperature of the soldering iron was 400°C, so long as residual compressive stress is 25 MPa or more. These ranges are also more preferable ranges in the present invention. These correspond to the residual compressive stress specified in claims 13 and 25.

In other samples 2-1 to 2-7, 2-11 to 2-15, 2-29 and 2-31 except for the samples 2-8 to 2-10, 2-16 to 2-28, 2-30 and 2-32, a thermal crack did not arise in the test where the temperature of the soldering iron was 450°C. At this time, residual compressive stress in the composition ranges of the samples 2-1 to 2-7, 2-11 to 2-15, 2-29 and 2-31 where a thermal crack did not arise was 40 MPa or more without exception.

Therefore, ranges where values of the third range which is a composition range of the samples 2-1 to 2-7, 2-11 to 2-15, 2-29 and 2-31, i.e., $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in the trilinear coordinates shown in Fig. 4, exist on a fifth line segment connecting a point (0.4, 0.2, 0.4) corresponding to the sample 2-31 and a point (0.2, 0.4, 0.4) corresponding to the sample 2-11, a sixth line segment connecting this point (0.2, 0.4, 0.4) and a point (0.2, 0.5,

0.3) corresponding to the sample 2-12, a seventh line segment connecting this point (0.2, 0.5, 0.3) and a point (0.3, 0.5, 0.2) corresponding to the sample 2-13, an eighth line segment connecting this point (0.3, 0.5, 0.2) and a point (0.6, 0.2, 0.2) corresponding to the sample 2-29, or a ninth line segment connecting this point (0.6, 0.2, 0.2) and a point (0.4, 0.2, 0.4) corresponding to the sample 2-31, or a range surrounded by these fifth to ninth line segments is still more preferable ranges in the present invention. These correspond to A site mole ratios specified in claims 17 and 34. In addition, since a thermal crack did not arise in the test where the temperature of the soldering iron was 450°C if the residual compressive stress was 40 MPa or more, this range is also a still more preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 14 and 26.

Example 2-2

What is performed in this example 2-2 is comparison of samples obtained by changing an amount of a semiconductorizing agent.

With fixing other parameters such as A site mole ratios, a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 2-1 except for changing the mole percent of the semiconductorizing agent as shown in Table 2-2, samples were produced, which were measured similarly to those in the example 2-1. However, the temperature characteristic of the varistor

voltage E_{10} was not measured. The result is shown in Table 2-2.

)

)

Table 2-2

Sample No.	Composition							Electrical Characteristics	Mechanical Characteristics						
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconductor uctorizing agent	Mole % of semiconductor uctorizing agent	Total A/B	SiO ₂ mol e %		Component of additive	E_{10} (V)	α	Thermal Crack Test (Soldering Iron Temperature °C)			Residual Compressive Stress (Mpa)
												360 °C	400 °C	450 °C	
2-33	0.35	0.35	0.30	NbO _{5/2}	0.10	0.98	0.20	None	30.2	3.1	No Good	No Good	No Good	14	
2-34	0.35	0.35	0.30	NbO _{5/2}	0.75	0.98	0.20	None	16.7	3.3	Good	Good	Good	40	
2-35	0.35	0.35	0.30	NbO _{5/2}	1.00	0.98	0.20	None	15.5	3.4	Good	Good	Good	45	
2-36	0.35	0.35	0.30	NbO _{5/2}	2.00	0.98	0.20	None	12.4	3.4	Good	Good	Good	45	
2-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	Good	Good	Good	45	
2-37	0.35	0.35	0.30	NbO _{5/2}	4.00	0.98	0.20	None	12.1	3.5	Good	Good	Good	41	
2-38	0.35	0.35	0.30	NbO _{6/2}	10.00	0.98	0.20	None	11.5	3.5	Good	No Good	No Good	24	
2-39	0.35	0.35	0.30	NbO _{5/2}	15.00	0.98	0.20	None	14.3	3.3	No Good	No Good	No Good	11	

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO_2 is d moles, the content of $\text{NbO}_{5/2}$ is f moles, and the content of SiO_2 is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $g/d \times 100 = 0.2$, and $(a + b + c)/(d + f) = 0.98$, but $f/d \times 100$ is changed.

The amount of a semiconductorizing agent affects the thermal crack-proof property of varistor ceramic. In other samples 2-4 and 2-34 to 2-38 except for the samples 2-33 and 2-39 where the amount of the semiconductorizing agent was too much and too few, a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C . At this time, residual compressive stress in the composition ranges of the samples 2-4 and 2-34 to 2-38 where a thermal crack did not arise was 24 MPa or more without exception.

Therefore, the mole percent range of $0.75 \leq f/d \times 100 \leq 10.00$ in the samples 2-4 and 2-34 to 2-38 is a preferable range in the present invention. This corresponds to the amount of a semiconductorizing agent specified in claims 15 and 32. In addition, since a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C if the residual compressive stress was 15 MPa or more, this range is also a preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 12 and 24.

In other samples 2-4 and 2-34 to 2-37 except for the

samples 2-33, 2-38 and 2-39, a thermal crack did not arise in the tests where the temperature of the soldering iron was 400°C and 450°C. At this time, residual compressive stress in the composition ranges of the samples 2-4 and 2-34 to 2-37 where a thermal crack did not arise was 40 MPa or more without exception.

Therefore, the mole percent range of $0.75 \leq f/d \times 100 \leq 4.00$ in the samples 2-4, and 2-34 to 2-37 is a more preferable range in the present invention. This corresponds to the amount of a semiconductorizing agent specified in claims 19 and 36. In addition, since a thermal crack did not arise in the tests where the temperature of the soldering iron was 400°C and 450°C if the residual compressive stress was 40 MPa or more, this range is also a more preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 14 and 26.

Example 2-3

What is performed in this example 2-3 is comparison of samples where a kind of semiconductorizing agent was changed. With fixing other parameters such as A site mole ratios, mole percents of semiconductorizing agents, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 2-1 except for changing the kinds of semiconductorizing agents as shown in Table 2-3, samples were produced, which were measured similarly to those in the example 2-1. However, the temperature characteristic of the varistor voltage E_{10} was not

measured. The result is shown in Table 2-3.

Table 2-3

Sample No.	Composition								Electrical Characteristics		Mechanical Characteristics			
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Thermal Crack Test (Soldering Iron Temperature °C)			Residual Compressive Stress (Mpa)
											360 °C	400 °C	450 °C	
2-4	0.35	0.35	0.30	Nb ₂ O ₅	3.00	0.98	0.20	None	11.5	3.4	Good	Good	Good	45
2-40	0.35	0.35	0.30	Ta ₂ O ₅	3.00	0.98	0.20	None	15.4	3.4	Good	Good	Good	41
2-41	0.35	0.35	0.30	Y ₂ O ₃	3.00	0.98	0.20	None	26.6	3.7	Good	Good	Good	45
2-42	0.35	0.35	0.30	La ₂ O ₃	3.00	0.98	0.20	None	15.1	3.9	Good	Good	No Good	37
2-43	0.35	0.35	0.30	CeO ₂	3.00	0.98	0.20	None	14.9	3.5	Good	Good	No Good	38
2-44	0.35	0.35	0.30	Pr ₆ O ₁₁	3.00	0.98	0.20	None	16.2	3.6	Good	Good	Good	41
2-45	0.35	0.35	0.30	Nd ₂ O ₃	3.00	0.98	0.20	None	16.8	3.7	Good	Good	Good	41
2-46	0.35	0.35	0.30	Sm ₂ O ₃	3.00	0.98	0.20	None	14.8	3.5	Good	Good	Good	40
2-47	0.35	0.35	0.30	Eu ₂ O ₃	3.00	0.98	0.20	None	19.0	3.8	Good	Good	Good	41
2-48	0.35	0.35	0.30	Gd ₂ O ₃	3.00	0.98	0.20	None	16.2	3.6	Good	Good	Good	40
2-49	0.35	0.35	0.30	Tb ₂ O ₇	3.00	0.98	0.20	None	21.3	3.8	Good	Good	No Good	37
2-50	0.35	0.35	0.30	Dy ₂ O ₃	3.00	0.98	0.20	None	18.3	3.5	Good	Good	Good	41
2-51	0.35	0.35	0.30	Ho ₂ O ₃	3.00	0.98	0.20	None	25.4	3.6	Good	Good	Good	41
2-52	0.35	0.35	0.30	Er ₂ O ₃	3.00	0.98	0.20	None	27.9	4.0	Good	Good	Good	40
2-53	0.35	0.35	0.30	Tm ₂ O ₃	3.00	0.98	0.20	None	24.1	3.9	Good	Good	Good	41
2-54	0.35	0.35	0.30	Yb ₂ O ₃	3.00	0.98	0.20	None	29.2	3.9	Good	Good	Good	40
2-55	0.35	0.35	0.30	Lu ₂ O ₃	3.00	0.98	0.20	None	28.2	4.1	Good	Good	No Good	38
2-56	0.35	0.35	0.30	Nb ₂ O ₅ + Y ₂ O ₃ Equal numbers of moles	3.00	0.98	0.20	None	22.0	4.0	Good	Good	Good	45

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO_2 is d moles, the content of $\text{YO}_{3/2}$, $\text{LaO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{NdO}_{3/2}$, $\text{SmO}_{3/2}$, $\text{EuO}_{3/2}$, $\text{GdO}_{3/2}$, $\text{TbO}_{7/4}$, $\text{DyO}_{3/2}$, $\text{HoO}_{3/2}$, $\text{ErO}_{3/2}$, $\text{TmO}_{3/2}$, $\text{YbO}_{3/2}$, $\text{LuO}_{3/2}$ or $\text{NbO}_{5/2} + \text{YO}_{3/2}$ (equal numbers of moles) is e moles, the content of $\text{TaO}_{5/2}$ or $\text{NbO}_{5/2}$ is f moles, and the content of SiO_2 is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $(e + f)/d \times 100 = 3.00$, $g/d \times 100 = 0.2$, and $(a + b + c + e)/(d + f) = 0.98$.

Since a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C in all the samples 2-4 and 2-40 to 2-56, it is preferable in the present invention to use $\text{NbO}_{5/2}$, $\text{TaO}_{5/2}$, $\text{YO}_{3/2}$, $\text{LaO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{NdO}_{3/2}$, $\text{SmO}_{3/2}$, $\text{EuO}_{3/2}$, $\text{GdO}_{3/2}$, $\text{TbO}_{7/4}$, $\text{DyO}_{3/2}$, $\text{HoO}_{3/2}$, $\text{ErO}_{3/2}$, $\text{TmO}_{3/2}$, $\text{YbO}_{3/2}$, $\text{LuO}_{3/2}$ or $\text{NbO}_{5/2} + \text{YO}_{3/2}$ (equal numbers of moles) as a semiconductorizing agent. At this time, residual compressive stress in the composition ranges of the samples 2-4 and 2-40 to 2-56 where a thermal crack did not arise was 37 MPa or more without exception.

Example 2-4

What is performed in this example 2-4 is comparison of samples obtained by changing a total A/B.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of semiconductorizing agent, and a mole percent of SiO_2 , and performing the same setup as that in

the example 2-1 except for changing the total A/B as shown in Table 2-4, samples were produced, which were measured similarly to those in the example 2-1. However, the temperature characteristic of the varistor voltage E_{10} was not measured. The result is shown in Table 2-4.

Table 2-4

Sample No.	Composition								Electrical Characteristics		Mechanical Characteristics			
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Thermal Crack Test (Soldering Iron Temperature °C)			Residual Compressive Stress (Mpa)
											360 °C	400 °C	450 °C	
2-57	0.35	0.35	0.30	NbO _{5/2}	3.00	0.80	0.20	None	Isolated	—	No Good	No Good	No Good	5
2-58	0.35	0.35	0.30	NbO _{5/2}	3.00	0.84	0.20	None	4.4	2.6	Good	No Good	No Good	24
2-59	0.35	0.35	0.30	NbO _{5/2}	3.00	0.96	0.20	None	7.0	3.1	Good	Good	Good	45
2-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	Good	Good	Good	45
2-60	0.35	0.35	0.30	NbO _{5/2}	3.00	1.00	0.20	None	9.5	3.3	Good	Good	Good	45
2-61	0.35	0.35	0.30	NbO _{5/2}	3.00	1.01	0.20	None	6.3	3.0	Good	Good	Good	41
2-62	0.35	0.35	0.30	NbO _{5/2}	3.00	1.16	0.20	None	51.5	3.2	Good	No Good	No Good	21
2-63	0.35	0.35	0.30	NbO _{5/2}	3.00	1.20	0.20	None	Isolated	—	No Good	No Good	No Good	4

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO_2 is d moles, the content of $\text{NbO}_{5/2}$ is f moles, and the content of SiO_2 is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $f/d \times 100 = 3.00$, and $g/d \times 100 = 0.2$, but $(a + b + c)/(d + f)$ is changed.

In other samples 2-4 and 2-58 to 2-62 except for the samples 2-57 and 2-63, a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C . At this time, residual compressive stress in the composition ranges of the samples 2-4 and 2-58 to 2-62 where a thermal crack did not arise was more than 21 MPa without exception.

Therefore, the value range of $0.84 \leq (a + b + c)/(d + f) \leq 1.16$ in the samples 2-4 and 2-58 to 2-62 is a preferable range in the present invention. This corresponds to the total A/B specified in claims 15 and 32. In addition, since a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C if the residual compressive stress was 15 MPa or more, this range is also a preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 12 and 24.

In other samples 2-4 and 2-59 to 2-61 except for the samples 2-57, 2-58, 2-62 and 2-63, a thermal crack did not arise in the tests where the temperature of the soldering iron was 400°C and 450°C . At this time, residual compressive stress

in the composition ranges of the samples 2-4 and 2-59 to 2-61 where a thermal crack did not arise was more than 40 MPa without exception.

Therefore, the value range of $0.96 \leq (a + b + c)/(d + f) \leq 1.01$ in the samples 2-4 and 2-59 to 2-61 is a more preferable range in the present invention. This corresponds to the total A/B specified in claims 18 and 35. In addition, since a thermal crack did not arise in the tests where the temperature of the soldering iron was 400°C and 450°C if the residual compressive stress was 40 MPa or more, this range is also a more preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 14 and 26.

As seen from Table 2-4, in a range where there is a small amount of SiO₂ and a large amount of semiconductorizing agent is added, in order to maintain the thermal crack-proof property, it becomes indispensable in particular to control an upper limit of the total A/B. If the total A/B exceeds 1.16, a thermal crack starts arising at 360°C. If the total A/B exceeds 1.01, a thermal crack starts arising at 400°C.

Example 2-5

What is performed in this example 2-5 is comparison of samples obtained by changing a mole percent of SiO₂.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, and a total A/B, and performing the same setup as that in the example 2-1 except for changing the mole percent of SiO₂ as shown in

Table 2-5, samples were produced, which were measured similarly to those in the example 2-1. However, the temperature characteristic of the varistor voltage E_{10} was not measured. The result is shown in Table 2-5.

Table 2-5

Sample No.	Composition							Electrical Characteristics		Mechanical Characteristics				
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Thermal Crack Test (Soldering Iron Temperature °C)			Residual Compressive Stress (Mpa)
											360 °C	400 °C	450 °C	
2-64	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.00	None	7.7	3.3	Good	Good	Good	40
2-65	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.10	None	8.5	3.4	Good	Good	Good	43
2-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	Good	Good	Good	45
2-66	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.30	None	13.7	3.6	Good	Good	Good	45
2-67	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.60	None	10.4	3.4	Good	Good	No Good	32
2-68	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	1.00	None	337.0	2.9	No Good	No Good	No Good	10
2-69	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	1.50	None	Isolated	—	No Good	No Good	No Good	6

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO_2 is d moles, the content of $\text{NbO}_{5/2}$ is f moles, and the content of SiO_2 is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $f/d \times 100 = 3.00$, and $(a + b + c)/(d + f) = 0.98$, but $g/d \times 100$ was changed.

SiO_2 is added as a sintering additive. If this is contained, it becomes possible to perform stable sintering even if composition fluctuates, but, if its amount increases, it becomes easy for a thermal crack to arise.

Since a thermal crack also arose in the test where the temperature of the soldering iron was 360°C , because there was too much SiO_2 , the samples 2-68 and 2-69 are not preferable. Therefore, the samples 2-4 and 2-64 to 2-67 where a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C and 400°C are preferable in the present invention. This corresponds to the mole percent of SiO_2 specified in claims 15 and 32. At this time, residual compressive stress in the composition ranges of the samples 2-4 and 2-64 to 2-67 where a thermal crack did not arise was 32 MPa or more without exception. Although a dosage of SiO_2 in the sample 2-64 is zero nominally, in fact, SiO_2 is contained in each raw material as an impurity, and hence SiO_2 content of the sample 2-64 does not become zero.

A thermal crack arose in the sample 2-67 in the test

where the temperature of the soldering iron was 450°C. Thus, the samples 2-4 and 2-64 to 2-66 where a thermal crack did not also arise in the test at the temperature of the soldering iron of 450°C are more preferable in the present invention. This corresponds to the mole percent of SiO_2 specified in claims 20 and 37. In addition, since a thermal crack did not arise in the test where the temperature of the soldering iron was 450°C if the residual compressive stress was 40 MPa or more, this range is also a more preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 14 and 26. The mole percent of SiO_2 near that of the sample 2-4 is most preferable in the present invention.

Example 2-6

What is performed in this example 2-6 is comparison of samples where a kind and an amount of an additive were changed.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 2-1 except for changing the kind and amount of the additive as shown in Table 2-6, samples were produced, which were measured similarly to those in the example 2-1. However, the temperature characteristic of the varistor voltage E_{10} was not measured. The result is shown in Table 2-6.

Table 2-6

Sample No.	Composition										Electrical Characteristics		Mechanical Characteristics			
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	Mole % of additive	E ₁₀ (V)	α	Thermal Crack Test (Soldering Iron Temperature °C)			Residual Compressive Stress (Mpa)	
												360 °C	400 °C	450 °C		
2-70	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.01	15.6	4.0	Good	Good	Good	45	
2-71	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.03	15.0	4.1	Good	Good	Good	43	
2-72	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.60	19.6	4.2	Good	Good	Good	40	
2-73	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	1.00	26.3	4.4	Good	Good	No Good	29	
2-74	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	2.00	Isolated	—	No Good	No Good	No Good	11	
2-75	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	CoO _{4/3}	0.01	13.1	3.4	Good	Good	No Good	40	
2-76	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	CoO _{4/3}	0.50	22.1	3.7	Good	Good	Good	44	
2-77	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	CoO _{4/3}	1.00	28.8	3.7	Good	Good	No Good	32	
2-78	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	CoO _{4/3}	2.00	Isolated	—	No Good	No Good	No Good	13	
2-79	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MoO ₃	0.20	12.0	3.6	Good	Good	No Good	34	
2-80	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	WO ₃	0.20	11.8	3.6	Good	Good	No Good	39	

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO_2 is d moles, the content of $\text{NbO}_{5/2}$ is f moles, the content of SiO_2 is g moles, and the content of an additive is h moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $f/d \times 100 = 3.00$, $(a + b + c)/(d + f) = 0.98$, and $g/d \times 100 = 0.20$, but $h/d \times 100$ was changed.

An additive has the action of adjusting electrical characteristics such as the varistor voltage E_{10} and the nonlinear coefficient α . Mn enlarges the varistor voltage E_{10} and the nonlinear coefficient α , and Co enlarges varistor voltage E_{10} . In addition, it is found that Mo and W have the action of enlarging the nonlinear coefficient α . Although not shown in Table 2-6, it is found that Li, Na, Ni, Cu, Zn, Sc, Fe, Ga and In also have the same action.

Since the samples 2-74 and 2-78 had a too large amount of dosage, the degree of sintering was blocked and the ceramic was insulated by the reoxidation processing. In other samples 2-70 to 2-73, 2-75 to 2-77 and 2-79 to 2-80 except for the samples 2-74 and 2-78, a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C . At this time, residual compressive stress in the composition ranges of the samples 2-70 to 2-73, 2-75 to 2-77 and 2-79 to 2-80 where a thermal crack did not arise was 29 MPa or more without exception.

Therefore, the samples 2-70 to 2-73, 2-75 to 2-77 and 2-79 to 2-80 each having the mole percent to a principal component that is 1.00 or less are preferable in the present invention. This is included in the kind and mole percent of an additive specified in claims 21 and 38.

Example 2-7

What is performed in this example 2-7 is comparison of samples obtained by changing a temperature among reoxidation processing conditions.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 2-1 except for changing reoxidation processing conditions as shown in Table 2-7, samples were produced, which were measured similarly to those in the example 2-1. However, the temperature characteristic of the varistor voltage E_{10} was not measured. The result is shown in Table 2-7.

Table 2-7

Sample No.	Reoxidation Processing Conditions			Electrical Characteristics		Mechanical Characteristics			
	Temperature (°C)	Time (h)	Partial Pressure of Oxygen (atm.)	E ₁₀ (V)	α	Thermal Crack Test (Soldering Iron Temperature °C)			Residual Compressive Stress (Mpa)
						360 °C	400 °C	450 °C	
2-81	700	2	0.2	Less than Measuring Limit		No Good	No Good	No Good	9
2-82	800	2	0.2	2.5	2.71	No Good	No Good	No Good	14
2-83	850	2	0.2	4.0	2.83	Good	No Good	No Good	31
2-84	900	2	0.2	9.3	3.35	Good	Good	Good	41
2-4	950	2	0.2	11.5	3.40	Good	Good	Good	45
2-85	1000	2	0.2	14.5	3.42	Good	Good	Good	40
2-86	1050	2	0.2	39.0	3.35	Good	No Good	No Good	20
2-87	1100	2	0.2	121.8	2.68	No Good	No Good	No Good	10
2-88	1200	2	0.2	Not Semiconductorized		No Good	No Good	No Good	2

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO_2 is d moles, the content of $\text{NbO}_{5/2}$ is f moles, and the content of SiO_2 is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $f/d \times 100 = 3.00$, $(a + b + c)/(d + f) = 0.98$, and $g/d \times 100 = 0.20$.

Conditions at the producing samples were that time of the reoxidation processing was 2 hours, and that the processing was performed in the air (the partial pressure of oxygen was 0.2 atmospheric pressure).

The varistor voltage E_{10} changed broadly with the increase of temperature in the reoxidation processing.

In other samples 2-4 and 2-83 to 2-86 except for the samples 2-81, 2-82, 2-87 and 2-88, a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C . At this time, residual compressive stress in the composition ranges of the samples where a thermal crack did not arise was 20 MPa or more without exception.

Therefore, the samples 2-4 and 2-83 to 2-86 where temperature in the reoxidation processing was 850°C to 1050°C are preferable in the present invention. This corresponds to claim 27. In addition, since a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C if the residual compressive stress was 15 MPa or more, this range can also be called a preferable range in the present

invention. This corresponds to the residual compressive stress specified in claims 12 and 24.

In the samples 2-4, 2-84 and 2-85, a thermal crack did not arise in the tests where the temperature of the soldering iron was 400°C and 450°C. At this time, residual compressive stress in the composition ranges of the samples where a thermal crack did not arise was 40 MPa or more without exception.

Therefore, the samples 2-4, 2-84 and 2-85 where temperature in the reoxidation processing was 900°C to 1000°C are more preferable in the present invention. This corresponds to claim 28. In addition, since a thermal crack did not arise in the test where the temperature of the soldering iron was 450°C if the residual compressive stress was 40 MPa or more, this range is also a more preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 14 and 26.

Thus, it is possible to secure a wide range of varistor voltage values and sufficient nonlinear coefficient α with keeping large surface residual compressive stress by controlling a varistor voltage value through changing temperature in the reoxidation processing without changing the composition. In consequence, with maintaining the high strength and high heat-resisting property by the large surface residual compressive stress, a wide range of varistor voltage and practical α can be obtained by the same composition. Hence it becomes unnecessary to prepare various types of material, and

hence, material control becomes easy.

Example 2-8

What is performed in this example 2-8 is comparison of samples obtained by changing a time among reoxidation processing conditions.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 2-1 except for changing reoxidation processing conditions as shown in Table 2-8, samples were produced, which were measured similarly to those in the example 2-1. However, the temperature characteristic of the varistor voltage E_{10} was not measured. The result is shown in Table 2-8.

Table 2-8

Sample No.	Reoxidation Processing Conditions			Electrical Characteristics		Mechanical Characteristics			
	Temperature (°C)	Time (h)	Partial Pressure of Oxygen (atm.)	E ₁₀ (V)	α	Thermal Crack Test (Soldering Iron Temperature °C)			Residual Compressive Stress (Mpa)
						360 °C	400 °C	450 °C	
2-89	950	0.10	0.2	3.1	2.78	Good	No Good	No Good	24
2-90	950	0.25	0.2	4.9	3.03	Good	Good	Good	39
2-91	950	0.50	0.2	7.1	3.27	Good	Good	Good	42
2-92	950	1.00	0.2	10.4	3.34	Good	Good	Good	44
2-4	950	2.00	0.2	11.5	3.40	Good	Good	Good	45
2-93	950	4.00	0.2	20.2	3.80	Good	Good	Good	44
2-94	950	8.00	0.2	28.6	3.85	Good	Good	Good	41
2-95	950	16.00	0.2	40.6	3.94	Good	Good	No Good	38
2-96	950	32.00	0.2	57.7	3.67	Good	No Good	No Good	24
2-97	950	64.00	0.2	81.8	3.33	No Good	No Good	No Good	14

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO_2 is d moles, the content of $\text{NbO}_{5/2}$ is f moles, and the content of SiO_2 is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $f/d \times 100 = 3.00$, $(a + b + c)/(d + f) = 0.98$, and $g/d \times 100 = 0.20$.

Conditions at the producing samples were that temperature in the reoxidation processing was 950°C , and that the processing was performed in the air (the partial pressure of oxygen was 0.2 atmospheric pressure).

The varistor voltage E_{10} monotonously increased with a lapse of the time of the reoxidation processing. When the time of the reoxidation processing exceeded 32 hours, the residual compressive stress reduced rapidly. In other samples 2-4 and 2-89 to 2-96 except for the sample 2-97, a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C . At this time, residual compressive stress in the composition ranges of the samples where a thermal crack did not arise was 24 MPa or more without exception.

Therefore, the samples 2-4 and 2-89 to 2-96 where time of the reoxidation processing was 32 hours or shorter are preferable in the present invention. This corresponds to claim 29. In addition, since a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C if the residual compressive stress was 15 MPa or more, this range

is also a preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 12 and 24.

In the samples 2-4 and 2-90 to 2-95, a thermal crack did not arise in the tests where the temperature of the soldering iron was 400°C. At this time, residual compressive stress in the composition ranges of the samples where a thermal crack did not arise was 38 MPa or more without exception.

Therefore, the samples 2-4 and 2-90 to 2-95 where time of the reoxidation processing was 0.25 to 16 hours are more preferable in the present invention. This corresponds to claim 30. In addition, since a thermal crack did not arise in the test where the temperature of the soldering iron was 400°C if the residual compressive stress was 25 MPa or more, this range is also a more preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 13 and 25.

In addition, in the samples 2-4 and 2-91 to 2-94, a thermal crack did not arise in the tests where the temperature of the soldering iron was 450°C. At this time, residual compressive stress in the composition ranges of the samples where a thermal crack did not arise was 41 MPa or more without exception.

Therefore, the samples 2-4 and 2-91 to 2-94 where time of the reoxidation processing was 0.5 to 8 hours are still more preferable in the present invention. In addition, since a

thermal crack did not arise in the test where the temperature of the soldering iron was 450°C if the residual compressive stress was 40 MPa or more, this range is also a more preferable range in the present invention. This corresponds to the residual compressive stress specified in claims 14 and 26.

Example 2-9

What is performed in this example 2-9 is comparison of samples obtained by changing a partial pressure of oxygen among reoxidation processing conditions.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO₂, and performing the same setup as that in the example 2-1 except for changing reoxidation processing conditions as shown in Table 2-9, samples were produced, which were measured similarly to those in the example 2-1. However, the temperature characteristic of the varistor voltage E_{10} was not measured. The result is shown in Table 2-9.

Table 2-9

Sample No.	Reoxidation Processing Conditions			Electrical Characteristics		Mechanical Characteristics			
	Temperature (°C)	Time (h)	Partial Pressure of Oxygen (atm.)	E ₁₀ (V)	α	Thermal Crack Test (Soldering Iron Temperature °C)			Residual Compressive Stress (Mpa)
						360 °C	400 °C	450 °C	
2-98	950	2	0.00	Less than Measuring Limit		No Good	No Good	No Good	7
2-99	950	2	0.05	5.2	1.97	No Good	No Good	No Good	14
2-100	950	2	0.10	8.3	3.03	Good	Good	Good	41
2-4	950	2	0.20	11.5	3.40	Good	Good	Good	45
2-101	950	2	0.50	14.3	3.95	Good	Good	Good	46
2-102	950	2	1.00	16.0	4.23	Good	Good	Good	48

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO_2 is d moles, the content of $\text{NbO}_{5/2}$ is f moles, and the content of SiO_2 is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $f/d \times 100 = 3.00$, $(a + b + c)/(d + f) = 0.98$, and $g/d \times 100 = 0.20$.

The reoxidation processing was performed at 950°C for 2 hours, and samples were produced with changing the partial pressure of oxygen.

In the samples 2-98 and 2-99, the coefficient α was small, and residual compressive stress was also small. In other samples 2-4 and 2-100 to 2-102 except for these samples, a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C, 400°C and 450°C. At this time, residual compressive stress in the composition ranges of the samples where a thermal crack did not arise was 40 MPa or more without exception.

Therefore, the samples 2-4 and 2-100 to 2-102 where the partial pressure of oxygen in reoxidation processing was 0.10 atmospheric pressure or higher are preferable in the present invention. This corresponds to claim 31. In addition, since a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C, 400°C and 450°C when the residual compressive stress was 40 MPa or more, this range is also a more preferable range in the present invention. This

corresponds to the residual compressive stress specified in claims 14 and 26.

According to the above Tables 2-1 to 2-9, if the composition, content and reoxidation processing conditions of each component are within the range of the present invention, the residual compressive stress within the preferable range described above can be obtained. Hence it is possible to provide varistor ceramic, which has high bending strength and is excellent in the thermal shock-proof property, and its manufacturing method.

Third Embodiment

Hereafter, the composition of the varistor ceramic 10 in this third embodiment will be described.

The varistor ceramic 10 contains a first component of the composite perovskite which consists of oxides of Sr, Ba, Ca and Ti, at least one component of a second component which consists of at least one kind of oxide selected from oxides of R (Y and lanthanoids (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu)) and a third component which consists of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component which consists of an oxide of Si, and does not contain Mg substantially. It is assumed that a is the number of moles calculated for Sr of the first component as SrO , b is the number of moles calculated for Ba of the first component as BaO , c is the number of moles calculated for Ca of the first

component as CaO, d is the number of moles calculated for Ti of the first component as TiO_2 , e is the number of moles calculated for R of the second component as $\text{YO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{TbO}_{7/4}$ and $\text{RO}_{3/2}$ (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as $\text{NbO}_{5/2}$ and $\text{TaO}_{5/2}$ respectively, and g is the number of moles calculated for Si of the fourth component as SiO_2 . Then, the component of this varistor ceramic is $0.30 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.40$, $0.25 \leq c/(a + b + c) \leq 0.35$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$. More preferable ranges of this composition are $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$, $0.75 \leq (e + f)/d \times 100 \leq 4.0$, and $g/d \times 100 \leq 0.3$.

The first component is a main component of the varistor ceramic 10. This first component consists of, in composite perovskite, an A site component of Sr, Ba and Ca, and a B site component of Ti. The second and third components are metallic oxides that contribute to semiconductorization, and the fourth component is mainly added for the improvement of a degree of sintering.

Electrical characteristics as a varistor are mainly expressed with a temperature characteristic of the varistor voltage E_{10} and a nonlinear coefficient α . The varistor voltage E_{10} expresses an applied voltage value at the time of 10-mA electric current flowing in the varistor, and the nonlinear coefficient α is generally expressed in $\alpha = 1/\log(E_{10}/E_1)$. Where,

E_1 is an applied voltage value at the time of 1-mA electric current flowing in the varistor.

As for mole ratios of Sr, Ba and Ca which are contents of the A site component, it is preferable that Sr is set between 0.30 and 0.40 inclusive, Ba is between 0.30 and 0.40 inclusive, and Ca is between 0.25 and 0.35 inclusive. Then, it becomes possible to enhance electrical characteristics such as the controllability of the varistor voltage E_{10} , the of the E_{10} temperature characteristics, and the nonlinear coefficient α , and to enhance the thermal shock-proof property of the varistor. That is, if there is too much Sr, the temperature characteristic of E_{10} will become negative, and if too few, strength will drop. In addition, if there is too much Ba, the positive trend of temperature characteristic of E_{10} becomes strong too much, and if too few, the temperature characteristic of E_{10} becomes negative. Furthermore, even if there is too much Ca or too few Ca, the nonlinear coefficient α to the varistor voltage E_{10} becomes small. In addition, if there is too much Ca, the varistor voltage E_{10} becomes extremely large to become difficult of control, and a base is made an insulator by reoxidation.

The thermal shock-proof property of a varistor can be enhanced by setting the mole percent (calculated with the number of moles of metal ions) of a semiconductorizing agent (the second and/or third components) to the principal component (TiO_2) to be between 0.75 and 10.0 inclusive, or more preferably

to be between 0.75 and 4.0 inclusive. That is, even if the semiconductorizing agent is too much or too few, strength is lowered and a thermal crack easily arises.

Even if an amount of the fourth component (SiO_2) is reduced by performing setup so that the total A/B may become between 0.84 and 1.16 inclusive, or may more preferably become between 0.96 and 1.01 inclusive, it is possible as described later to improve a degree of sintering. That is, this is because sintering is blocked even if the total A/B is too large or too small, and hence the base is made an insulator owing to reoxidation. In addition, even if the total A/B is too large or too small, strength is lowered and a thermal crack easily arises. In a range where an amount of SiO_2 is few and a lot of semiconductorizing agent is added as described above, in order to maintain the thermal crack-proof property, it becomes indispensable to restrict an upper limit of the total A/B to be 1.16 or less, or more preferably, to be 1.01 or less.

The thermal shock-proof property of a varistor can be sharply enhanced by setting the mole percent of the fourth component (SiO_2) to the principal component (TiO_2) to be 0.6 or less, or more preferably, to be 0.3 or less. In other words, SiO_2 is added as a sintering additive and it is possible to stably perform sintering even if composition fluctuates, but however, if the amount of SiO_2 increases, it becomes easy for a thermal crack to arise. It should be noted that the content (mole percent) of SiO_2 of 0.6 or less or of 0.3 or less also

includes the case where its dosage is zero.

The varistor ceramic 10 may also contain an additive that consist of at least one kind of oxide selected from among oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W. Supposing the content is the number of moles obtained by converting Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W into $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 , it is preferable that the composition is $0 < h/d \times 100 \leq 1.000$. Thereby, there is an effect of improving the nonlinear coefficient α .

In addition, the varistor ceramic 10 may also contain other elements such as P, S, K, Al and Zr as unavoidable impurities besides such additives. Such elements usually exist as oxides.

As described above, the varistor ceramic 10 is a polycrystal consisting of perovskite type crystals. A part of each component is contained in the perovskite type crystals with being solidly solved in grains, and another part exists in crystal grain boundaries as oxides or complex oxides. For example, Ba, Ca, Sr, Ti, Nb, Ta, Y, lanthanoids and the like exist mostly in grains, and Mo, W, Mn, Si, Co and the like exist mostly in crystal grain boundaries.

A mean grain diameter of the varistor ceramic 10 usually is about 0.5 to 10 μm , and in particular, 1 to 6 μm .

Since the electrodes 11 are formed with the material made of Cu or mainly made of Cu, they are hard to be corroded even

under high temperature, and hence, this can endure hot solder work.

Next, a method of manufacturing this varistor ceramic 10 will be described simply.

The varistor ceramic 10 is obtained by processing raw material powder in order of mixing, calcining, grinding, forming, binder removal, reduction sintering, and reoxidation.

The powder of a compound of each structural element of ceramic is usually used for the raw material powder. An oxide or a compound which becomes an oxide by sintering, such as carbonate and a hydroxide can be used for the raw material powder. With citing an example about Ba, at least one kind of barium compounds such as BaCO_3 , BaSiO_3 , BaO , BaCl_2 , Ba(OH)_2 and $\text{Ba(NO}_3)_2$, and alkoxide (for example, $(\text{CH}_3\text{O})_2\text{Ba}$) can be used as the raw material. The mean particle diameter of raw material powder may be usually about 0.2 to 5 μm .

First, the weighing of the raw material powder is performed so that the final composition may become the above-described composition, and usually, wet blending is performed. Subsequently, after performing dehydration processing, the raw material powder is dried and calcining is performed at about 1080 to 1250°C for about 2 to 4 hours. Next, after grinding a calcining object, an organic binder is added, and further, water, a pH regulator, a moisturizer, etc. are added and mixed. Subsequently, a mixture is molded, and is sintered at about 1250-1400°C in a reducing atmosphere for about 2 to 4 hours

after performing binder removal processing for semiconductor ceramic to be obtained.

Each raw material powder such as Nb, Ta, Y, lanthanoids, Mo, W, Mn, Si, Co and the like may be added at the time of mixing after the calcining.

The semiconductor ceramic obtained in this manner is given heat treatment (reoxidation processing) in an oxidizing atmosphere such as air, so that a suitable varistor voltage according to an object may be obtained. The temperature TEM_{rox} and Time TIM_{rox} in this reoxidation processing are controlled as follows:

- (1) $850^{\circ}\text{C} \leq TEM_{rox} \leq 900^{\circ}\text{C}$, $0.25 \text{ hour} \leq TIM_{rox} \leq 32 \text{ hours}$,
- (2) $900^{\circ}\text{C} < TEM_{rox} \leq 1050^{\circ}\text{C}$, $0.1 \text{ hour} \leq TIM_{rox} \leq 32 \text{ hours}$,
- (3) $900^{\circ}\text{C} \leq TEM_{rox} < 950^{\circ}\text{C}$, $0.5 \text{ hour} \leq TIM_{rox} \leq 16 \text{ hours}$, or
- (4) $950^{\circ}\text{C} \leq TEM_{rox} \leq 1000^{\circ}\text{C}$, $0.25 \text{ hour} \leq TIM_{rox} \leq 16 \text{ hours}$.

The insulating layer 10b is formed on a surface portion by this reoxidation processing. Varistor characteristics appear owing to the presence of this insulating layer. Generally, the nonlinear coefficient α and varistor voltage become large if this insulating layer is thick, and they become small if thin.

It is possible to secure a sufficient nonlinear coefficient α , a sufficient bending strength, and a sufficient thermal shock-proof property in a wide range of varistor voltage, and also to reduce the dependency of the varistor voltage to a change of heat treatment temperature, by thus controlling the temperature TEM_{rox} and time TIM_{rox} in such

reoxidation processing. Since the practical nonlinear coefficient α and the sufficient strength in a wide range of varistor voltages can be obtained in the single composition, it becomes unnecessary to prepare various materials and it becomes easy to control materials. With considering the influence of a change of the reoxidation processing conditions over a varistor voltage, the time of the reoxidation processing TIM_{rox} has less impact than the temperature in the reoxidation processing TEM_{rox} . Hence, by controlling a varistor voltage value through finally adjusting the time of the reoxidation processing TIM_{rox} , the shift of the varistor voltage due to the change of reoxidation processing conditions becomes small, and hence a yield improves and the control of reoxidation processing conditions becomes easy.

Electrodes 11 are formed on one surface of the varistor ceramic after reoxidation processing with Cu or material mainly made of Cu, and a varistor is obtained. The material mainly made of CU is the same as that in the first embodiment.

In the third embodiment described above, although the electrodes are provided in one surface of varistor ceramic, an electrode(s) may be provided in top and back faces or sides of the varistor ceramic.

In addition, varistor ceramic may be manufactured by adding a minor component later. Namely, it is also possible to weigh and mix raw material powder, to add a part of contents after performing calcining, to adjust the contents so that the

powder may have a composition predetermined, to grind and form the powder, and to perform the reduction sintering of this formed object, and the reoxidation.

Hereafter, the present invention is described still in detail according to examples according to the third embodiment.

Example 3-1

What is performed in this example 3-1 is comparison of samples obtained by changing A site mole ratios with fixing other parameters such as reoxidation processing conditions, a mole percent and a kind of a semiconductorizing agent, and a total A/B.

First, after respectively weighing by conversion and blending SrCO_3 , BaCO_3 , CaCO_3 , TiO_2 , $\text{NbO}_{5/2}$ and SiO_2 as raw material so that the raw material might have the composition shown in Table 3-1, they were mixed for 10 to 20 hours with using an wet media mill, dehydrated and dried.

After calcining a mixture obtained, at 1150°C , the mixture was rough-ground, and again, dehydrated and dried after being mixed with a wet media mill for 10 to 20 hours. Subsequently, 1.0 to 1.5 wt% of polyvinyl alcohol was mixed to the mixture as an organic binder to be granulated, and the granulated mixture was formed at forming pressure of 2 t/cm^2 to become a formed object having an outer diameter of 12 mm, an inside diameter of 9 mm and a thickness of 1.0 mm.

After performing the binder removal processing of this forming object at about 600°C in an air atmosphere, sintering

was performed for 2 hours at about 1350°C in a reducing atmosphere of N₂ (95 volume percent) + H₂ (5 volume percent) for the semiconductor ceramic to be obtained. Subsequently, two-hours reoxidation processing of the semiconductor ceramic was performed at 950°C in the air in the rise and fall temperature speed of 100 to 600°C/h for the varistor ceramic to be obtained.

Next, Cu paste was applied to one surface of the varistor ceramic 10 as shown in Figs. 1a and 1b, in a neutral atmosphere, three Cu electrodes, although the five electrodes are shown in these figures, were formed by baking the Cu paste at 750°C to obtain test samples of the varistors for measuring.

Then, after measuring the voltages E_1 and E_{10} of each sample at 20°C, the nonlinear coefficient α was obtained from $\alpha = 1/\log(E_{10}/E_1)$ with using the measured voltages E_1 and E_{10} . Furthermore, the temperature characteristic (temperature coefficient) of the varistor voltage E_{10} was also obtained. Moreover, while performing the thermal crack test of each sample, a transverse rupture strength of each sample was measured.

The voltages E_1 and E_{10} were measured with using a measuring circuit shown in Fig. 3. In this measuring circuit, an ammeter 30 is connected in series between a varistor 31 and a DC constant current source 32, and a voltmeter 33 is connected in parallel with the varistor 31. The voltages E_1 and E_{10} were measured by measuring the voltage values between both terminals of the varistor 31 when electric current of 1 mA and

10 mA flows in the varistor 21 respectively with using the ammeter 30 and the voltmeter 33.

Temperature characteristics (temperature coefficient)

ΔE_{10T} of the varistor voltage E_{10} were obtained with $\Delta E_{10T} = \{E_{10}(85) - E_{10}(20)\} / \{E_{10}(20) \times (85 - 20)\} \times 100$ [%/°C] about each sample. The voltages $E_{10}(20)$ and $E_{10}(85)$ are the varistor voltages E_{10} at the temperature of 20°C and 85°C, respectively. These were measured with using a thermostat oven.

The transverse rupture strength was measured by a transverse rupture strength tester such as MODEL-1311D of AIKOH ENGINEERING Co., Ltd..

The thermal crack test was performed by contacting a soldering iron, where temperature was set beforehand, to the electrode side of the sample left at the room temperature, for 3 seconds with supplying eutectic solder. The temperature of a soldering iron was two kinds of temperature, that is, 360°C, and 400°C were used. Thirty samples were visually inspected for cracks with using alcohol. The result is shown in Table 3-1.

Table 3-1

Sample No.	Composition							Electrical Characteristics			Mechanical Characteristics		Thermal Crack Test	
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	E ₁₀ Temperature Characteristics ΔE _{10T} (%/°C)	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
													360 °C	400 °C
3-1	0.30	0.35	0.35	NbO _{5/2}	3.00	0.98	0.20	None	15.8	3.7	0.01	30.1	Good	Good
3-2	0.30	0.40	0.30	NbO _{5/2}	3.00	0.98	0.20	None	12.9	3.5	0.02	29.9	Good	Good
3-3	0.35	0.30	0.35	NbO _{5/2}	3.00	0.98	0.20	None	16.1	4.0	0.00	32.7	Good	Good
3-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	0.01	33.5	Good	Good
3-5	0.35	0.40	0.25	NbO _{5/2}	3.00	0.98	0.20	None	11.6	3.5	0.02	31.8	Good	Good
3-6	0.40	0.30	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.8	3.7	0.00	31.4	Good	Good
3-7	0.40	0.35	0.25	NbO _{5/2}	3.00	0.98	0.20	None	10.9	3.5	0.01	33.0	Good	Good
3-8	0.10	0.40	0.50	NbO _{5/2}	3.00	0.98	0.20	None	39.9	3.9	0.03	24.0	Good	Good
3-9	0.10	0.50	0.40	NbO _{5/2}	3.00	0.98	0.20	None	20.1	3.5	0.04	24.8	Good	Good
3-10	0.20	0.30	0.50	NbO _{5/2}	3.00	0.98	0.20	None	33.5	4.2	0.01	25.1	Good	Good
3-11	0.20	0.40	0.40	NbO _{5/2}	3.00	0.98	0.20	None	20.6	3.8	0.03	26.0	Good	Good
3-12	0.20	0.50	0.30	NbO _{5/2}	3.00	0.98	0.20	None	15.7	3.4	0.04	27.6	Good	Good
3-13	0.30	0.50	0.20	NbO _{5/2}	3.00	0.98	0.20	None	11.0	2.8	0.04	28.3	Good	Good
3-14	0.40	0.40	0.20	NbO _{5/2}	3.00	0.98	0.20	None	10.6	2.8	0.02	29.1	Good	Good
3-15	0.50	0.30	0.20	NbO _{5/2}	3.00	0.98	0.20	None	10.0	2.7	-0.01	28.0	Good	Good
3-16	1.00	0.00	0.00	NbO _{5/2}	3.00	0.98	0.20	None	4.3	2.9	-0.50	24.9	Good	Good
3-17	0.80	0.20	0.00	NbO _{5/2}	3.00	0.98	0.20	None	4.8	3.0	-0.08	24.4	Good	Good
3-18	0.50	0.50	0.00	NbO _{5/2}	3.00	0.98	0.20	None	8.0	3.1	0.15	24.2	Good	Good
3-19	0.20	0.80	0.00	NbO _{5/2}	3.00	0.98	0.20	None	2.2	2.3	0.71	23.0	Good	Good
3-20	0.00	1.00	0.00	NbO _{5/2}	3.00	0.98	0.20	None	0.4	1.6	1.20	19.8	Good	No Good
3-21	0.00	0.80	0.20	NbO _{5/2}	3.00	0.98	0.20	None	4.6	2.5	0.23	18.5	Good	No Good
3-22	0.00	0.60	0.40	NbO _{5/2}	3.00	0.98	0.20	None	18.4	3.4	0.10	18.3	Good	No Good
3-23	0.00	0.40	0.60	NbO _{5/2}	3.00	0.98	0.20	None	74.0	3.1	0.06	18.1	Good	No Good
3-24	0.00	0.20	0.80	NbO _{5/2}	3.00	0.98	0.20	None	187.0	2.7	0.01	16.8	No Good	No Good
3-25	0.00	0.00	1.00	NbO _{5/2}	3.00	0.98	0.20	None	Isolated	—	—	16.5	No Good	No Good
3-26	0.80	0.00	0.20	NbO _{5/2}	3.00	0.98	0.20	None	138.0	2.4	-0.15	25.4	Good	Good
3-27	0.50	0.00	0.50	NbO _{5/2}	3.00	0.98	0.20	None	39.5	4.4	-0.08	20.1	Good	No Good
3-28	0.20	0.00	0.80	NbO _{5/2}	3.00	0.98	0.20	None	9.1	3.5	-0.01	18.6	Good	No Good
3-29	0.60	0.20	0.20	NbO _{5/2}	3.00	0.98	0.20	None	9.2	3.3	-0.07	26.1	Good	Good
3-30	0.20	0.60	0.20	NbO _{5/2}	3.00	0.98	0.20	None	9.9	3.2	0.11	24.9	Good	Good
3-31	0.40	0.20	0.40	NbO _{5/2}	3.00	0.98	0.20	None	22.0	4.1	-0.03	26.0	Good	Good
3-32	0.20	0.20	0.60	NbO _{5/2}	3.00	0.98	0.20	None	47.1	2.8	0.00	24.1	Good	Good

Mole ratios of the A site component largely affect the electrical characteristics of a varistor, and in particular, to the temperature characteristic of the varistor voltage E_{10} . When the temperature characteristic of the voltage E_{10} is negative, the varistor voltage drops in connection with the rise of operating temperature, and hence, excessive electric current flows to the varistor or a possibility of causing a thermal runaway exists. Therefore, this is not adoptable. Therefore, the samples 3-15 to 3-17, 3-26 to 3-29 and 3-31 are in ranges where they cannot be used as varistors respectively.

Even if the temperature characteristic of the voltage E_{10} is zero or positive, it is not desirable to exceed 0.06, and hence, the samples 3-18 to 3-23 and 3-30 are not preferable as varistors.

Since being insulated as a whole by reoxidation processing, the sample 3-25 does not operate as a varistor. In addition, since the samples 3-24 and 3-26 contain too much Ca, their varistor voltages E_{10} are extremely high, and hence, control is difficult.

Since Ca contained is too few although the E_{10} characteristics of the samples 3-13, 3-14 and 3-32 are 0.06 or less, their nonlinear coefficients α to the varistor voltage E_{10} are low, and hence they are not preferable.

Therefore, the samples 3-1 to 3-12 are preferable because the temperature characteristics of the varistor voltages E_{10} are 0.06 or less and the coefficients α to the varistor voltages E_{10}

are not so low. Furthermore, the samples 3-1 to 3-7 where the temperature characteristic of the voltage E_{10} is 0.02 or less is more preferable in the present invention. This corresponds to the A site mole ratio specified in claim 47. In this range, no crack arose at the thermal crack test where the temperature of the soldering iron was 360°C, and furthermore, no crack also arose at the thermal crack test where the temperature of the soldering iron was 400°C. In particular, the sample 3-4 has the best balance of the temperature characteristic of the voltage E_{10} and the nonlinear coefficient α , and the mole ratios of the A site component near that of this sample are most preferable in the present invention.

Example 3-2

What is performed in this example 3-2 is comparison of samples obtained by changing an amount of a semiconductorizing agent.

With fixing other parameters such as reoxidation processing conditions, A site mole ratios, a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 and performing the same setup as that in the example 3-1 except for changing the mole percent of the semiconductorizing agent as shown in Table 3-2, samples were produced, which were measured similarly to those in the example 3-1. The result is shown in Table 3-2.

Table 3-2

Sample No.	Composition								Electrical Characteristics		Mechanical Characteristics		
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
												360 °C	400 °C
3-33	0.35	0.35	0.30	NbO _{5/2}	0.10	0.98	0.20	None	30.2	3.1	17.2	No Good	No Good
3-34	0.35	0.35	0.30	NbO _{5/2}	0.75	0.98	0.20	None	16.7	3.3	27.3	Good	Good
3-35	0.35	0.35	0.30	NbO _{5/2}	1.00	0.98	0.20	None	15.5	3.4	28.6	Good	Good
3-36	0.35	0.35	0.30	NbO _{5/2}	2.00	0.98	0.20	None	12.4	3.4	32.2	Good	Good
3-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	33.5	Good	Good
3-37	0.35	0.35	0.30	NbO _{5/2}	4.00	0.98	0.20	None	12.1	3.5	30.5	Good	Good
3-38	0.35	0.35	0.30	NbO _{5/2}	10.00	0.98	0.20	None	11.5	3.5	19.6	Good	No Good
3-39	0.35	0.35	0.30	NbO _{5/2}	15.00	0.98	0.20	None	14.3	3.3	9.9	No Good	No Good

The amount of a semiconductorizing agent affects the thermal crack-proof property of varistor ceramic. Since the amount of semiconductorizing agent in the samples 3-33 and 3-39 are too few and too much respectively, thermal cracks arose in the test where the temperature of the soldering iron was 360°C, and hence, these are not preferable. Therefore, the samples 3-4 and 3-34 to 3-38 where thermal cracks did not arise in the test where the temperature of the soldering iron was 360°C and the traverse rupture strength was 18 kgf/mm² or more are preferable in the present invention. This corresponds to the mole percent of the semiconductorizing agent specified in claim 47.

Since a thermal crack arose in the sample 3-38 in the test where the temperature of the soldering iron was 400°C, the samples 3-4 and 3-34 to 3-37 where a thermal crack did not also arise in the test where the temperature of the soldering iron was 400°C are more preferable in the present invention. This corresponds to the mole percent of the semiconductorizing agent specified in claim 49. In addition, the mole percent of the semiconductorizing agent near that of the sample 3-4 is most preferable in the present invention.

Example 3-3

What is performed in this example 3-3 is comparison of samples where a kind of semiconductorizing agent was changed.

With fixing other parameters such as reoxidation processing conditions, A site mole ratios, a mole percent of a semiconductorizing agent, a total A/B, and a mole percent of

SiO_2 and performing the same setup as that in the example 3-1 except for changing the mole percent of SiO_2 as shown in Table 3-3, samples were produced, which were measured similarly to those in the example 3-1. The result is shown in Table 3-3.

Table 3-3

Sample No.	Composition								Electrical Characteristics		Mechanical Characteristics		
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
												360 °C	400 °C
3-4	0.35	0.35	0.30	Nb ₂ O ₅	3.00	0.98	0.20	None	11.5	3.4	33.5	Good	Good
3-40	0.35	0.35	0.30	Ta ₂ O ₅	3.00	0.98	0.20	None	15.4	3.4	27.5	Good	Good
3-41	0.35	0.35	0.30	Y ₂ O ₃	3.00	0.98	0.20	None	26.6	3.7	32.3	Good	Good
3-42	0.35	0.35	0.30	La ₂ O ₃	3.00	0.98	0.20	None	15.1	3.9	24.6	Good	Good
3-43	0.35	0.35	0.30	CeO ₂	3.00	0.98	0.20	None	14.9	3.5	24.9	Good	Good
3-44	0.35	0.35	0.30	Pr ₆ O ₁₁	3.00	0.98	0.20	None	16.2	3.6	26.5	Good	Good
3-45	0.35	0.35	0.30	Nd ₂ O ₃	3.00	0.98	0.20	None	16.8	3.7	26.1	Good	Good
3-46	0.35	0.35	0.30	Sm ₂ O ₃	3.00	0.98	0.20	None	14.8	3.5	26.9	Good	Good
3-47	0.35	0.35	0.30	Eu ₂ O ₃	3.00	0.98	0.20	None	19.0	3.8	26.4	Good	Good
3-48	0.35	0.35	0.30	Gd ₂ O ₃	3.00	0.98	0.20	None	16.2	3.6	26.7	Good	Good
3-49	0.35	0.35	0.30	Tb ₂ O ₃	3.00	0.98	0.20	None	21.3	3.8	25.1	Good	Good
3-50	0.35	0.35	0.30	Dy ₂ O ₃	3.00	0.98	0.20	None	18.3	3.5	26.9	Good	Good
3-51	0.35	0.35	0.30	Ho ₂ O ₃	3.00	0.98	0.20	None	25.4	3.6	27.5	Good	Good
3-52	0.35	0.35	0.30	Er ₂ O ₃	3.00	0.98	0.20	None	27.9	4.0	27.9	Good	Good
3-53	0.35	0.35	0.30	Tm ₂ O ₃	3.00	0.98	0.20	None	24.1	3.9	27.3	Good	Good
3-54	0.35	0.35	0.30	Yb ₂ O ₃	3.00	0.98	0.20	None	29.2	3.9	26.3	Good	Good
3-55	0.35	0.35	0.30	Lu ₂ O ₃	3.00	0.98	0.20	None	28.2	4.1	24.4	Good	Good
3-56	0.35	0.35	0.30	Nb ₂ O ₅ + Y ₂ O ₃ Equal numbers of moles	3.00	0.98	0.20	None	22.0	4.0	31.7	Good	Good

A thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C, and the transverse rupture strength was 18 kgf/mm² or more in all the samples 3-4 and 3-40 to 3-56. Hence, it is preferable in the present invention to use NbO_{5/2}, TaO_{5/2}, YO_{3/2}, LaO_{3/2}, CeO₂, PrO_{11/6}, NdO_{3/2}, SmO_{3/2}, EuO_{3/2}, GdO_{3/2}, TbO_{7/4}, DyO_{3/2}, HoO_{3/2}, ErO_{3/2}, TmO_{3/2}, YbO_{3/2}, LuO_{3/2} or NbO_{5/2} + YO_{3/2} (equal numbers of moles) as a semiconductorizing agent. This corresponds to the kind of semiconductorizing agent specified in claim 47.

Example 3-4

What is performed in this example 3-4 is comparison of samples obtained by changing a total A/B.

With fixing other parameters such as reoxidation processing conditions, A site mole ratios, a mole percent and a kind of a semiconductorizing agent, and a mole percent of SiO₂ and performing the same setup as that in the example 3-1 except for changing the total A/B as shown in Table 3-4, samples were produced, which were measured similarly to those in the example 3-1. The result is shown in Table 3-4.

Table 3-4

Sample No.	Composition								Electrical Characteristics		Mechanical Characteristics		
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
												360 °C	400 °C
3-57	0.35	0.35	0.30	NbO _{5/2}	3.00	0.80	0.20	None	Isolated	—	5.0	No Good	No Good
3-58	0.35	0.35	0.30	NbO _{5/2}	3.00	0.84	0.20	None	4.4	2.6	23.6	Good	No Good
3-59	0.35	0.35	0.30	NbO _{5/2}	3.00	0.96	0.20	None	7.0	3.1	31.7	Good	Good
3-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	33.5	Good	Good
3-60	0.35	0.35	0.30	NbO _{5/2}	3.00	1.00	0.20	None	9.5	3.3	32.0	Good	Good
3-61	0.35	0.35	0.30	NbO _{5/2}	3.00	1.02	0.20	None	6.3	3.0	27.7	Good	Good
3-62	0.35	0.35	0.30	NbO _{5/2}	3.00	1.16	0.20	None	51.5	3.2	18.1	Good	No Good
3-63	0.35	0.35	0.30	NbO _{5/2}	3.00	1.20	0.20	None	Isolated	—	7.7	No Good	No Good

The value of the total A/B affects the degree of sintering of ceramic. The samples 3-57 and 3-63 have too small and too large total A/B respectively, these could not operate as varistors because it was impossible to sinter precise ceramic and they were insulated as a whole by reoxidation processing. Furthermore, thermal cracks arose when the temperature of the soldering iron was 360°C.

As shown in Table 3-4, in a range where an amount of SiO_2 is few and a lot of semiconductorizing agent is added, in order to maintain the thermal crack-proof property, it is indispensable to especially control an upper limit of the total A/B. If the total A/B exceeds 1.16, a thermal crack starts arising at 360°C. If the total A/B exceeds 1.01, a thermal crack starts arising at 400°C.

That is, since a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C, and transverse rupture strength was 18 kgf/mm² or more, the samples 3-4 and 3-58 to 3-62 are preferable in the present invention. This corresponds to a range of the total A/B specified in claim 47.

Furthermore, since a thermal crack did not arise in the test where the temperature of the soldering iron was 400°C, the samples 3-4 and 3-59 to 3-61 are more preferable in the present invention. This corresponds to a range of the total A/B specified in claim 48. In addition, the vicinity of the total A/B where the B site component is a little rich like the sample

3-4 is a most preferable range of the present invention.

Example 3-5

What is performed in this example 3-5 is comparison of samples obtained by changing a mole percent of SiO_2 .

With fixing other parameters such as reoxidation processing conditions, A site mole ratios, a mole percent and a kind of a semiconductorizing agent, and a total A/B, and performing the same setup as that in the example 3-1 except for changing the mole percent of SiO_2 as shown in Table 3-5, samples were produced, which were measured similarly to those in the example 3-1. The temperature of a soldering iron in a thermal crack test was three kinds of temperature, that is, 360°C , 400°C and 450°C . The result is shown in Table 3-5.

Table 3-5

Sample No.	Composition								Electrical Characteristics		Mechanical Characteristics			
	Sr mole ratio a/(a+b+c)	Ba mole ratio b/(a+b+c)	Ca mole ratio c/(a+b+c)	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)		
												360 °C	400 °C	450 °C
3-64	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.00	None	7.7	3.3	27.2	Good	Good	Good
3-65	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.10	None	8.5	3.4	31.8	Good	Good	Good
3-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	33.5	Good	Good	Good
3-66	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.30	None	13.7	3.6	33.1	Good	Good	Good
3-67	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.60	None	10.4	3.4	24.2	Good	Good	No Good
3-68	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	1.00	None	337.0	2.9	16.5	No Good	No Good	No Good
3-69	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	1.50	None	Isolated	—	8.3	No Good	No Good	No Good

SiO_2 is added as a sintering additive. If SiO_2 is contained, it becomes possible to perform stable sintering even if composition fluctuates. However, if its amount increases, it becomes easy for a thermal crack to arise.

Since a thermal crack also arose in the test where the temperature of the soldering iron was 360°C , because there was too much SiO_2 , the samples 3-68 and 3-69 are not preferable. Therefore, the samples 3-4 and 3-64 to 3-67 where thermal cracks did not arise in the test at the temperature of the soldering iron of 360°C and 400°C and the transverse rupture strength is 18 kgf/mm^2 or more, are preferable in the present invention. This corresponds to the mole percent of SiO_2 specified in claim 47.

Since a thermal crack arose in the sample 3-67 in the test where the temperature of the soldering iron was 450°C , the samples 3-4 and 3-64 to 3-66 where a thermal crack did not arise even in the test at this temperature are more preferable in the present invention. This corresponds to the mole percent of SiO_2 specified in claim 50. In addition, the mole percent of SiO_2 near that of the sample 3-4 is most preferable in the present invention. Although a dosage of SiO_2 in the sample 3-64 is zero nominally, in fact, SiO_2 is contained in each raw material as an impurity, and hence SiO_2 content of the sample 3-64 does not become zero.

Example 3-6

What is performed in this example 3-6 is comparison of

samples where a kind and an amount of an additive were changed.

With fixing other parameters such as reoxidation processing conditions, A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 3-1 except for changing the kind and amount of an additive as shown in Table 3-6, samples were produced, which were measured similarly to those in the example 3-1. The result is shown in Table 3-6.

Table 3-6

Sample No.	Composition										Electrical Characteristics		Mechanical Characteristics	
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	Mole % of additive	E ₁₀ (V)	α	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
													360 °C	400 °C
3-70	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.01	15.6	4.0	30.7	Good	Good
3-71	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.03	15.0	4.1	31.3	Good	Good
3-72	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.60	19.6	4.2	31.1	Good	Good
3-73	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	1.00	26.3	4.4	24.6	Good	Good
3-74	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	2.00	Isolated	—	17.3	No Good	No Good
3-75	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	Co ₃ O ₄	0.01	13.1	3.4	25.4	Good	Good
3-76	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	Co ₃ O ₄	0.50	22.1	3.7	32.4	Good	Good
3-77	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	Co ₃ O ₄	1.00	28.8	3.7	24.8	Good	Good
3-78	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	Co ₃ O ₄	2.00	Isolated	—	16.9	No Good	No Good
3-79	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MoO ₃	0.20	12.0	3.6	24.7	Good	Good
3-80	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	WO ₃	0.20	11.8	3.6	25.1	Good	Good

An additive has the action of adjusting electrical characteristics such as the varistor voltage E_{10} and the nonlinear coefficient α . Mn enlarges the varistor voltage E_{10} and the nonlinear coefficient α , and Co enlarges varistor voltage E_{10} . In addition, it is found that Mo and W have the action of enlarging the nonlinear coefficient α . Although not shown in Table 3-6, it is found that other elements such as Li, Na, Ni, Cu, Zn, Sc, Fe, Ga and In also have the same action.

Since the samples 3-74 and 3-78 had a too large amount of dosage, the degree of sintering was blocked and the ceramic was insulated by the reoxidation processing. Therefore, the samples 3-70 to 3-73, 3-75 to 3-77 and 3-79 to 3-80 each having the mole percent to a principal component that is 1.00 or less, and the transverse rupture strength is 18 kgf/mm² or more are preferable in the present invention. This is included in a kind and the mole percent of an additive specified in claim 51.

Example 3-7

What is performed in this example 3-7 is comparison of samples obtained by changing a temperature TEM_{tox} and a time TIM_{tox} among reoxidation processing conditions.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO₂, and performing the same setup as that in the example 3-1 except for changing the reoxidation processing conditions as shown in Table 3-8, samples were produced, which were measured similarly to those

in the example 3-1. The result is shown in Tables 3-7 and 3-8.

Table 3-7

Sample No.	Reoxidation Processing Conditions		Electrical Characteristics		Mechanical Characteristics		
	Temperature TEM _{rox} (°C)	Time TIM _{ro} x (h)	E ₁₀ (V)	α	Transverse Rupture Strength (Kgf/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
						360 °C	400 °C
3-81	800	0.10	0.68	1.62	10.15	No Good	No Good
3-82	800	0.25	1.07	1.71	10.94	No Good	No Good
3-83	800	0.50	1.53	1.78	11.93	No Good	No Good
3-84	800	1	2.27	2.37	12.47	No Good	No Good
3-85	800	2	2.50	2.71	12.53	No Good	No Good
3-86	800	4	4.38	2.87	13.45	No Good	No Good
3-87	800	8	6.22	3.04	13.69	No Good	No Good
3-88	800	16	8.83	3.08	12.35	No Good	No Good
3-89	800	32	12.53	3.47	11.74	No Good	No Good
3-90	800	64	17.78	3.55	10.53	No Good	No Good
3-91	850	0.10	1.10	1.73	15.31	No Good	No Good
3-92	850	0.25	1.73	1.81	18.31	Good	No Good
3-93	850	0.50	2.48	2.41	19.37	Good	No Good
3-94	850	1	3.67	2.68	20.25	Good	No Good
3-95	850	2	4.04	2.83	20.35	Good	No Good
3-96	850	4	7.09	3.12	21.84	Good	No Good
3-97	850	8	10.06	3.56	22.24	Good	No Good
3-98	850	16	14.28	3.63	20.06	Good	No Good
3-99	850	32	20.26	3.73	18.42	Good	No Good
3-100	850	64	28.75	3.85	12.36	No Good	No Good
3-101	900	0.10	2.54	2.72	17.45	No Good	No Good
3-102	900	0.25	3.99	2.74	21.42	Good	No Good
3-103	900	0.50	5.73	3.09	24.13	Good	Good
3-104	900	1	8.47	3.21	24.40	Good	Good
3-105	900	2	9.33	3.35	24.53	Good	Good
3-106	900	4	16.37	3.75	26.32	Good	Good
3-107	900	8	23.23	3.80	26.81	Good	Good
3-108	900	16	32.97	3.85	24.18	Good	Good
3-109	900	32	46.79	3.71	20.28	Good	No Good
3-110	900	64	66.40	3.58	14.90	No Good	No Good
3-111	950	0.10	3.13	2.78	22.13	Good	No Good
3-112	950	0.25	4.92	3.03	25.69	Good	Good
3-113	950	0.50	7.06	3.27	28.00	Good	Good
3-114	950	1	10.45	3.34	29.27	Good	Good
3-115	950	2	11.50	3.40	29.42	Good	Good
3-116	950	4	20.18	3.80	31.57	Good	Good
3-117	950	8	28.63	3.85	32.15	Good	Good
3-118	950	16	40.64	3.94	29.00	Good	Good
3-119	950	32	57.67	3.67	22.55	Good	No Good
3-120	950	64	81.85	3.33	17.87	No Good	No Good

Table 3-8

Sample No.	Reoxidation Processing Conditions		Electrical Characteristics		Mechanical Characteristics		
	Temperature TEM_{rox} (°C)	Time TIM_{rox} (h)	E_{10} (V)	α	Transverse Rupture Strength (Kgf/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
						360 °C	400 °C
3-121	1000	0.10	3.94	2.99	22.96	Good	No Good
3-122	1000	0.25	6.19	3.08	26.66	Good	Good
3-123	1000	0.50	8.88	3.58	29.06	Good	Good
3-124	1000	1	13.14	3.75	30.37	Good	Good
3-125	1000	2	14.47	3.42	30.53	Good	Good
3-126	1000	4	25.39	2.87	32.76	Good	Good
3-127	1000	8	36.03	3.83	33.36	Good	Good
3-128	1000	16	51.13	3.89	30.09	Good	Good
3-129	1000	32	72.57	3.47	23.40	Good	No Good
3-130	1000	64	102.99	3.06	17.54	No Good	No Good
3-131	1050	0.10	10.62	3.71	18.69	Good	No Good
3-132	1050	0.25	16.70	3.77	20.54	Good	No Good
3-133	1050	0.50	23.94	3.81	22.38	Good	No Good
3-134	1050	1	35.43	3.87	23.40	Good	No Good
3-135	1050	2	39.00	3.35	23.52	Good	No Good
3-136	1050	4	68.42	3.54	23.68	Good	No Good
3-137	1050	8	97.10	3.22	23.31	Good	No Good
3-138	1050	16	137.81	2.98	23.18	Good	No Good
3-139	1050	32	195.58	2.79	20.51	Good	No Good
3-140	1050	64	277.58	2.54	14.29	No Good	No Good
3-141	1100	0.10	33.15	3.85	10.39	No Good	No Good
3-142	1100	0.25	52.14	3.71	12.06	No Good	No Good
3-143	1100	0.50	74.75	3.46	13.14	No Good	No Good
3-144	1100	1	110.63	3.10	13.74	No Good	No Good
3-145	1100	2	121.79	2.68	13.81	No Good	No Good
3-146	1100	4	213.66	2.82	14.82	No Good	No Good
3-147	1100	8	303.23	2.31	15.09	No Good	No Good
3-148	1100	16	Upper than Measuring Limit		12.61	No Good	No Good
3-149	1100	32	Upper than Measuring Limit		10.59	No Good	No Good
3-150	1100	64	Upper than Measuring Limit		10.29	No Good	No Good

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO₂ is d moles, the content of NbO_{5/2} is f moles, and the content of SiO₂ is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $f/d \times 100 = 3.00$, $(a + b + c)/(d + f) = 0.98$, and $g/d \times 100 = 0.20$. In addition, the samples were produced under the processing atmosphere that was in the air (the partial pressure of oxygen was 0.2 atmospheric pressure).

The varistor voltage E_{10} was controlled under this reoxidation processing conditions. When the varistor voltage E_{10} was controlled with making the temperature in the reoxidation processing TEM_{rox} be a parameter, for example, when the time of the reoxidation processing TIM_{rox} was fixed at two hours and the temperature TEM_{rox} was changed from 800°C to 1100°C like the samples 3-85, 3-95, 3-105, 3-115, 3-125, 3-135 and 3-145. The varistor voltages E_{10} obtained was between about 2.5 and 122 V inclusive. Here, if conditions were limited to those that a thermal crack did not arise even in the test where the temperature of the soldering iron was 400°C and the transverse rupture strength to bending stress was 18 kgf/mm² or more, the varistor voltage E_{10} obtained was between 9.3 and 14.5 V inclusive.

However, when the varistor voltage E_{10} was controlled with making the time TIM_{rox} be a parameter, for example, when the

temperature in the reoxidation processing TEM_{rox} was fixed at 950°C and the time TIM_{rox} was changed from 0.1 to 64 hours like the samples 3-111 to 3-120, the varistor voltages E_{10} obtained was between about 3.1 and 81.9 V inclusive. Here, if conditions were limited to those that a thermal crack did not arise even in the test where the temperature of the soldering iron was 400°C and the transverse rupture strength to bending stress was 18 kgf/mm^2 or more, the varistor voltage E_{10} obtained was between 4.9 and 40.6 V inclusive.

Namely, by controlling the time of the reoxidation processing TIM_{rox} as a parameter, it becomes possible to obtain ceramic having a wide acquisition range of the varistor voltage E_{10} with maintaining sufficient strength to stress at the time of soldering. This corresponds to claim 42.

Since the samples 3-81 to 3-91, 3-100, 3-101, 3-110, 3-120, 3-130 and 3-140 to 3-150 had the transverse rupture strength to bending stress being less than 18 kgf/mm^2 , these are not desirable in respect of strength.

In the samples 3-92 to 3-99, 3-102 to 3-109, 3-111 to 3-119, 3-121 to 3-129 and 3-131 to 3-139 except for these samples, the transverse rupture strength was 18 kgf/mm^2 and a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C . Therefore, preferable ranges in the present invention are those that correspond to these samples, that is, $850^{\circ}\text{C} \leq TEM_{\text{rox}} \leq 900^{\circ}\text{C}$ and $0.25 \text{ hour} \leq TIM_{\text{rox}} \leq 32 \text{ hours}$, and $900^{\circ}\text{C} < TEM_{\text{rox}} \leq 1050^{\circ}\text{C}$ and $0.1 \text{ hour} \leq TIM_{\text{rox}} \leq 32 \text{ hours}$. This

corresponds to claim 40.

In the samples 3-103 to 3-108, 3-112 to 3-118 and 3-122 to 3-128, a thermal crack did not arise in the test where the temperature of the soldering iron was 400°C. Therefore, more preferable ranges in the present invention are those that correspond to these samples, that is, $900^{\circ}\text{C} \leq \text{TEM}_{\text{rox}} \leq 950^{\circ}\text{C}$ and $0.5 \text{ hour} \leq \text{TIM}_{\text{rox}} \leq 16 \text{ hours}$, and $950^{\circ}\text{C} \leq \text{TEM}_{\text{rox}} \leq 1000^{\circ}\text{C}$ and $0.25 \text{ hour} \leq \text{TIM}_{\text{rox}} \leq 16 \text{ hours}$. These correspond to claim 41.

Thus, if a value of the varistor voltage is controlled by changing reoxidation processing conditions without changing the composition, it is possible to maintain the strength of the ceramic itself in a high level, and to obtain sufficient bending strength to bending stress and sufficient resistance over a local thermal shock at the time of soldering. Of course, it is possible to secure a sufficient nonlinear coefficient α in a wide range of varistor voltages, and to lessen the dependency of the varistor voltage to the change of heat treatment temperature. Thus, since practical nonlinear coefficient α and sufficient strength in a wide range of varistor voltages can be obtained in the single composition, it becomes unnecessary to prepare various materials and it becomes easy to control materials.

Example 3-8

What is performed in this example 3-8 is comparison of samples obtained by changing a repeat count of thermal treatment steps in reoxidation processing.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 and performing the same setup as that in the example 3-1 except for changing the reoxidation processing conditions as shown in Table 3-9, samples were produced, which were measured similarly to those in the example 3-1. The composition of each sample is the same as that in the example 3-7. The result is shown in Table 3-9.

Table 3-9

Sample No.	Reoxidation Processing Conditions				Electrical Characteristics		Mechanical Characteristics		
	Temperature TEM _{rox} (°C)	Time TIM _{rox} (h)	Unit Time (h)	Repeat Count	E ₁₀ (V)	α	Transverse Rupture Strength (Kgf/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
								360 °C	400 °C
3-151	900	4	4	1	16.37	3.75	26.32	Good	Good
3-152	900	8	8	1	23.23	3.80	26.81	Good	Good
3-153	900	12	12	1	28.51	3.83	25.88	Good	Good
3-154	900	16	16	1	32.97	3.85	24.18	Good	Good
3-155	900	20	20	1	36.90	3.89	20.26	Good	No Good
3-156	900	24	24	1	40.46	3.74	19.04	Good	No Good
3-157	900	8	4	2	23.15	3.75	26.73	Good	Good
3-158	900	12	4	3	27.39	3.76	25.72	Good	Good
3-159	900	16	4	4	31.74	3.75	24.03	Good	Good
3-160	900	20	4	5	35.83	3.88	20.29	Good	No Good
3-161	900	24	4	6	38.69	3.73	19.23	No Good	No Good
3-162	950	4	4	1	20.18	3.80	31.57	Good	Good
3-163	950	8	8	1	28.63	3.85	32.15	Good	Good
3-164	950	12	12	1	35.14	3.89	31.04	Good	Good
3-165	950	16	16	1	40.64	3.94	29.00	Good	Good
3-166	950	20	20	1	45.48	3.87	24.30	Good	Good
3-167	950	24	24	1	49.87	3.83	22.83	Good	No Good
3-168	950	8	4	2	28.89	3.84	32.07	Good	Good
3-169	950	12	4	3	36.32	3.87	30.75	Good	Good
3-170	950	16	4	4	40.53	3.92	29.15	Good	Good
3-171	950	20	4	5	45.39	3.81	24.22	Good	Good
3-172	950	24	4	6	48.79	3.82	22.95	Good	No Good
3-173	1000	4	4	1	25.38	3.83	32.76	Good	Good
3-174	1000	8	8	1	36.02	3.89	33.36	Good	Good
3-175	1000	12	12	1	44.21	3.73	32.21	Good	Good
3-176	1000	16	16	1	51.13	3.69	30.09	Good	Good
3-177	1000	20	20	1	57.22	3.55	25.21	Good	No Good
3-178	1000	24	24	1	62.74	3.53	23.69	Good	No Good
3-179	1000	8	4	2	28.89	3.84	32.07	Good	Good
3-180	1000	12	4	3	44.18	3.78	32.19	Good	Good
3-181	1000	16	4	4	51.38	3.64	30.13	Good	Good
3-182	1000	20	4	5	57.37	3.58	25.37	Good	Good
3-183	1000	24	4	6	61.46	3.52	23.97	Good	No Good

With fixing the temperature in the reoxidation processing TEM_{rox} at 950°C and setting the cumulative time TIM_{rox} at 12 hours, the sample 3-164 produced through a single continuous heat treatment step was compared for the varistor voltage E₁₀ with the sample 3-169 produced through three times of independent heat treatment steps, where each processing time was 4 hours. In consequence, the varistor voltages E₁₀, transverse rupture

strengths, and thermal crack test results that were obtained were almost the same. In addition, the comparison of the sample 3-153 and the sample 3-158 that were produced with fixing the temperature TEM_{rox} at 900°C and setting the cumulative time TIM_{rox} at 12 hours was also similar to this.

Therefore, in case of setting the time when the transverse rupture strength to a bending stress becomes 18 kgf/mm^2 or more when the varistor voltage E_{10} is controlled with making the time of the reoxidation processing TIM_{rox} be a parameter, so long as the cumulative time is the same, it is possible to obtain ceramic with an wide acquisition range of varistor voltage E_{10} regardless of the repeat count of the heat treatment step with maintaining sufficient strength to the stress at the time of soldering. This corresponds to claim 46.

According to the above Tables 3-1 to 3-9, it is possible to provide a manufacturing method of obtaining varistor ceramic, which has the above-described preferable range of transverse rupture strength and is excellent in the thermal shock-proof property, so long as the composition, content, and reoxidation processing conditions of each component are within the range of the present invention.

Fourth Embodiment

Hereafter, the composition of the varistor ceramic 10 in this fourth embodiment will be described.

The varistor ceramic 10 contains a first component of the

composite perovskite which consists of oxides of Sr, Ba, Ca and Ti, at least one component of a second component which consists of at least one kind of oxide selected from oxides of R (Y and lanthanoids (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu)) and a third component which consists of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component which consists of an oxide of Si. It is assumed that a is the number of moles calculated for Sr of the first component as SrO, b is the number of moles calculated for Ba of the first component as BaO, c is the number of moles calculated for Ca of the first component as CaO, d is the number of moles calculated for Ti of the first component as TiO₂, e is the number of moles calculated for R of the second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4} and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of the fourth component as SiO₂. Then, the component of this varistor ceramic is $0.10 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.50$, $0.20 < c/(a + b + c) \leq 0.50$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$.

More preferable ranges of this composition are $0.30 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.40$, $0.25 \leq c/(a + b + c) \leq 0.35$, $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$, $0.75 \leq (e + f)/d \times 100 \leq 4.0$, and $g/d \times 100 \leq 0.3$.

The first component is a main component of the varistor

ceramic 10. This first component consists of, in composite perovskite, an A site component of Sr, Ba and Ca, and a B site component of Ti. The second and third components are metallic oxides that contribute to semiconductorization, and the fourth component is mainly added for the improvement of a degree of sintering.

Electrical characteristics as a varistor are mainly expressed with a temperature characteristic of a varistor voltage E_{10} and a nonlinear coefficient α . The varistor voltage E_{10} expresses an applied voltage value at the time of 10-mA electric current flowing in the varistor, and the nonlinear coefficient α is generally expressed in $\alpha=1/\log (E_{10}/E_1)$. Where, E_1 is an applied voltage value at the time of 1-mA electric current flowing in the varistor.

As for mole ratios of Sr, Ba and Ca which are contents of the A site component, it is preferable that Sr is set 0.1 or more but 0.40 or less, Ba is 0.30 or more but 0.50 or less, and Ca is more than 0.20 but 0.5 or less. It is more preferable that Sr is set 0.30 or more but 0.40 or less, Ba is 0.30 or more but 0.40 or less, and Ca is 0.25 or more but 0.35 or less. Then, it becomes possible to enhance the electrical characteristics such as the controllability of the varistor voltage E_{10} , the temperature characteristics of the varistor voltage E_{10} , and the nonlinear coefficient α , and to enhance the thermal shock-proof property of the varistor. That is, if there is too much Sr, the temperature characteristic of E_{10} will

become negative, and if too few, strength will drop. In addition, if there is too much Ba, the positive trend of temperature characteristic of E_{10} becomes strong too much, and if too few, the temperature characteristic of E_{10} becomes negative. Furthermore, even if there is too much Ca or too few Ca, the nonlinear coefficient α to the varistor voltage E_{10} becomes small. In addition, if there is too much Ca, the varistor voltage E_{10} becomes extremely large to become difficult of control, and a base is made an insulator by reoxidation.

The thermal shock-proof property of a varistor can be enhanced by setting the mole percent (calculated with the number of moles of metal ions) of a semiconductorizing agent (the second and/or third components) to the principal component (TiO_2) to be between 0.75 and 10.0 inclusive, or more preferably to be between 0.75 and 4.0 inclusive. That is, even if the semiconductorizing agent is too much or too few, strength is lowered and a thermal crack easily arises.

Even if an amount of the fourth component (SiO_2) is reduced by performing setup so that the total A/B may become between 0.84 and 1.16 inclusive, or may more preferably become between 0.96 and 1.01 inclusive, it is possible as described later to improve a degree of sintering. That is, this is because sintering is blocked even if the total A/B is too large or too small, and hence the base is made an insulator owing to reoxidation. In addition, even if the total A/B is too large or too small, strength is lowered and a thermal crack easily

arises. In a range where an amount of SiO_2 is few and a lot of semiconductorizing agent is added as described above, in order to maintain the thermal crack-proof property, it becomes indispensable to restrict an upper limit of the total A/B to be 1.16 or less, or more preferably, to be 1.01 or less.

The thermal shock-proof property of a varistor can be sharply enhanced by setting the mole percent of the fourth component (SiO_2) to the principal component (TiO_2) to be 0.6 or less, or more preferably to be 0.3 or less. That is, SiO_2 is added as a sintering additive and it is possible to stably perform sintering even if composition fluctuates, but however, if the amount of SiO_2 increases, it becomes easy for a thermal crack to arise. It should be noted that the content (mole percent) of SiO_2 of 0.6 or less or of 0.3 or less also includes the case where its dosage is zero.

The varistor ceramic 10 may also contain a fifth component (an additive) which consist of at least one kind of oxide selected from among oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W. Supposing the content is the number of moles obtained by converting Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W into $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 , it is preferable that the composition is $0 < h/d \times 100 \leq 1.000$. Thereby, there is an effect of improving the nonlinear coefficient α .

In addition, the varistor ceramic 10 may also contain other elements such as P, S, K, Al and Zr as unavoidable

impurities besides such additives. Such elements usually exist as oxides.

As described above, the varistor ceramic 10 is a polycrystal consisting of perovskite type crystals. A part of each component is contained in the perovskite type crystals with being solidly solved in grains, and another part exists in crystal grain boundaries as oxides or complex oxides. For example, Ba, Ca, Sr, Ti, Nb, Ta, Y, lanthanoids and the like exist mostly in grains, and Mo, W, Mn, Si, Co and the like exist mostly in crystal grain boundaries.

A mean grain diameter of the varistor ceramic 10 usually is about 0.5 to 10 μm , and in particular, 1 to 6 μm .

Since the electrodes 11 are formed with the material made of Cu or mainly made of Cu, they are hard to be corroded even under high temperature, and hence, this can endure hot solder work.

Next, a method of manufacturing this varistor ceramic 10 will be described.

The varistor ceramic 10 is obtained by processing raw material powder in order of mixing, calcining, grinding, forming, binder removal, reduction sintering, and reoxidation.

The powder of a compound of each structural element of ceramic is usually used for the raw material powder. An oxide or a compound which becomes an oxide by sintering, such as carbonate and a hydroxide can be used for the raw material powder. With citing an example about Ba, at least one kind of

barium compounds such as BaCO_3 , BaSiO_3 , BaO , BaCl_2 , Ba(OH)_2 and $\text{Ba(NO}_3)_2$, and alkoxide (for example, $(\text{CH}_3\text{O})_2\text{Ba}$) can be used as the raw material. The mean particle diameter of raw material powder may be usually about 0.2 to 5 μm .

First, the weighing of the raw material powder is performed so that the final composition may become the above-described composition, and usually, wet blending is performed. Subsequently, after performing dehydration processing, the raw material powder is dried and calcining is performed at about 1080 to 1250°C for about 2 to 4 hours. Next, this calcining object is ground.

The grinding time in this grinding is set so that the specific surface area of each grain after grinding may become between 0.5 and 5.0 m^2/g inclusive. Specifically, it is about 1 to 25 hours. Since the composition-heterogeneity or the composition concentration gradient of material do not arise so long as the specific surface area of each grain after grinding is 0.5 m^2/g or more, it is possible to obtain the sufficient bending strength and thermal shock-proof property of sintered ceramic. When the specific surface area exceeds 5.0 m^2/g , the grinding time becomes long too much, and hence it is inefficient on manufacturing. In addition, since it becomes easy for Ti-rich liquid phase to arise, it becomes easy for the partial heterogeneity of composition to arise. Hence the specific surface area is made to be 5.0 m^2/g or less.

Thereafter, an organic binder is added to grains after

this grinding, and further, water, a pH regulator, a moisturizer, etc. are added and mixed. Subsequently, a mixture is molded.

This forming is performed in conditions where the density of a formed object may become between 2.80 and 3.40 g/cm³ inclusive. If the density of a formed object is 2.80 g/cm³ or more, a fault never arises in manufacturing processes since the strength of a formed object becomes enough. If the density of a formed object exceeds 3.40 g/cm³, the lifetime of forming equipment and dies becomes short, and hence maintenance cost increases to be inefficient on manufacturing. Hence the density of a formed object is made to be 3.40 g/cm³ or less.

Next, the formed object is sintered at about 1250 to 1400°C in a reducing atmosphere for about 2 to 4 hours after performing binder removal processing for semiconductor ceramic to be obtained.

Each raw material powder such as Nb, Ta, Y, lanthanoids, Mo, W, Mn, Si, Co and the like may be added at the time of mixing after the calcining.

The semiconductor ceramic obtained in this manner is given heat treatment (reoxidation processing) in an oxidizing atmosphere such as air at the temperature, for example, 800 to 1000°C, so that a suitable varistor voltage according to an object may be obtained. The insulating layer 10b is formed on a surface portion by this reoxidation processing. Varistor characteristics appear owing to the presence of this insulating

layer. Generally, the nonlinear coefficient α and varistor voltage become large if this insulating layer is thick, and they become small if thin.

Electrodes are formed on one surface of the varistor ceramic after reoxidation processing with the material made of Cu or mainly made of Cu, and a varistor is obtained. In the embodiment described above, although the electrodes are provided in one surface of varistor ceramic, electrodes may be provided in top and back faces or side faces of the varistor ceramic.

Thus, by performing the grinding so that the specific surface area of each grain after grinding may be made to be 0.5 to 5.0 m²/g and forming the grains so that the density of a formed object may become 2.80 to 3.40 g/cm³, it becomes possible to maintain the strength of the ceramic itself in a high level and to obtain sufficient bending strength to a bending stress and sufficient resistance over a local thermal shock at the time of soldering.

In addition, varistor ceramic may be manufactured by adding a minor component later. Namely, it is also possible to weigh and mix raw material powder, to add a part of contents after performing calcining, to adjust the contents so that the powder may have a composition predetermined, to grind and form the powder, and to perform the reduction sintering of this formed object, and the reoxidation.

Hereinafter, the present invention will be described

further in detail with reference to examples according to the fourth embodiment.

Example 4-1

What is performed in this example 4-1 is comparison of samples obtained by fixing other parameters such as a grinding time after calcining, a density of a formed object, a mole percent and a kind of a semiconductorizing agent, a total A/B ratio, and a mole percent of SiO_2 , and changing mole ratios of an A site component.

First, after respectively weighing by conversion and blending SrCO_3 , BaCO_3 , CaCO_3 , TiO_2 , $\text{NbO}_{5/2}$ and SiO_2 as raw material so that they might have the composition shown in Table 4-1, they were mixed for 10 to 20 hours with using a wet media mill, dehydrated and dried.

After calcining a mixture obtained, at 1150°C , the mixture was rough-ground, and again, dehydrated and dried after being mixed with a wet media mill for 10 to 20 hours. With setting the grinding time after calcining at 16 hours, the specific surface area of each grain after grinding was fixed at $4.00 \text{ m}^2/\text{g}$.

Subsequently, 1.0 to 1.5 wt% of polyvinyl alcohol was mixed to the mixture as an organic binder to be granulated, and the granulated mixture was formed at forming pressure of $2 \text{ t}/\text{cm}^2$ to become a formed object having an outer diameter of 12 mm, an inside diameter of 9 mm and a thickness of 1.0 mm. The density ρ_g of a formed object was fixed at $3.10 \text{ g}/\text{cm}^3$.

After performing the binder removal processing of this forming object at about 600°C in an air atmosphere, sintering was performed for 2 hours at about 1350°C in a reducing atmosphere of N₂ (95 volume percent) + H₂ (5 volume percent) for the semiconductor ceramic to be obtained. Subsequently, 2 hours reoxidation processing of the semiconductor ceramic was performed at 950°C in the air in the rise and fall temperature speed of 100 to 600°C/h for the varistor ceramic to be obtained.

Next, Cu paste was applied to one surface of the varistor ceramic 10 as shown in Figs. 1a and 1b, in a neutral atmosphere, three Cu electrodes, although the five electrodes are shown in these figures, were formed by baking the Cu paste at 750°C to obtain test samples of the varistors for measuring.

Then, after measuring the voltages E_1 and E_{10} of each sample at 20°C, the nonlinear coefficient α was obtained from $\alpha = 1/\log(E_{10}/E_1)$ with using the measured voltages E_1 and E_{10} . Furthermore, the temperature characteristic (temperature coefficient) of the varistor voltage E_{10} was obtained. Moreover, while performing the thermal crack test of each sample, the transverse rupture strength of each sample was measured.

The voltages E_1 and E_{10} were measured with using a measuring circuit shown in Fig. 3. In this measuring circuit, an ammeter 30 is connected in series between a varistor 31 and a DC constant current source 32, and a voltmeter 33 is connected in parallel with the varistor 31. The voltages E_1 and E_{10} were measured by measuring the voltage values between both

terminals of the varistor 31 when electric current of 1 mA and 10 mA flows in the varistor 31 respectively with using the ammeter 30 and the voltmeter 33.

Temperature characteristics (temperature coefficient)

ΔE_{10T} of the varistor voltage E_{10} were obtained with $\Delta E_{10T} = \{E_{10}(85) - E_{10}(20)\} / \{E_{10}(20) \times (85 - 20)\} \times 100$ [%/°C] about each sample. The voltages $E_{10}(20)$ and $E_{10}(85)$ are the varistor voltages E_{10} at the temperature of 20°C and 85°C respectively. These were measured with using a thermostat oven.

The transverse rupture strength was measured by a transverse rupture strength tester such as MODEL-1311D of AIKOH ENGINEERING Co., Ltd..

The thermal crack test was performed by contacting a soldering iron, where temperature was set beforehand, to the electrode side of the sample left at the room temperature, for 3 seconds with supplying eutectic solder. The temperature of a soldering iron was two kinds of temperature, that is, 360°C, and 400°C were used. Thirty samples were visually inspected for cracks with using alcohol. The result is shown in Table 4-1.

Table 4-1

Sample No.	Composition							Electrical Characteristics			Mechanical Characteristics			
	Sr mole ratio a/(a+b+c)	Ba mole ratio b/(a+b+c)	Ca mole ratio c/(a+b+c)	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	E ₁₀ Temperature Characteristics ΔE _{10T} (%/°C)	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
													360 °C	400 °C
4-1	0.30	0.35	0.35	NbO _{5/2}	3.00	0.98	0.20	None	15.8	3.7	0.01	30.1	Good	Good
4-2	0.30	0.40	0.30	NbO _{5/2}	3.00	0.98	0.20	None	12.9	3.5	0.02	29.9	Good	Good
4-3	0.35	0.30	0.35	NbO _{5/2}	3.00	0.98	0.20	None	16.1	4.0	0.00	32.7	Good	Good
4-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	0.01	33.5	Good	Good
4-5	0.35	0.40	0.25	NbO _{5/2}	3.00	0.98	0.20	None	11.6	3.5	0.02	31.8	Good	Good
4-6	0.40	0.30	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.8	3.7	0.00	31.4	Good	Good
4-7	0.40	0.35	0.25	NbO _{5/2}	3.00	0.98	0.20	None	10.9	3.5	0.01	33.0	Good	Good
4-8	0.10	0.40	0.50	NbO _{5/2}	3.00	0.98	0.20	None	39.9	3.9	0.03	24.0	Good	Good
4-9	0.10	0.50	0.40	NbO _{5/2}	3.00	0.98	0.20	None	20.1	3.5	0.04	24.8	Good	Good
4-10	0.20	0.30	0.50	NbO _{5/2}	3.00	0.98	0.20	None	33.5	4.2	0.01	25.1	Good	Good
4-11	0.20	0.40	0.40	NbO _{5/2}	3.00	0.98	0.20	None	20.6	3.8	0.03	26.0	Good	Good
4-12	0.20	0.50	0.30	NbO _{5/2}	3.00	0.98	0.20	None	15.7	3.4	0.04	27.6	Good	Good
4-13	0.30	0.50	0.20	NbO _{5/2}	3.00	0.98	0.20	None	11.0	2.8	0.04	28.3	Good	Good
4-14	0.40	0.40	0.20	NbO _{5/2}	3.00	0.98	0.20	None	10.6	2.8	0.02	29.1	Good	Good
4-15	0.50	0.30	0.20	NbO _{5/2}	3.00	0.98	0.20	None	10.0	2.7	-0.01	28.0	Good	Good
4-16	1.00	0.00	0.00	NbO _{5/2}	3.00	0.98	0.20	None	4.3	2.9	-0.50	24.9	Good	Good
4-17	0.80	0.20	0.00	NbO _{5/2}	3.00	0.98	0.20	None	4.8	3.0	-0.08	24.4	Good	Good
4-18	0.50	0.50	0.00	NbO _{5/2}	3.00	0.98	0.20	None	8.0	3.1	0.15	24.2	Good	Good
4-19	0.20	0.80	0.00	NbO _{5/2}	3.00	0.98	0.20	None	2.2	2.3	0.71	23.0	Good	Good
4-20	0.00	1.00	0.00	NbO _{5/2}	3.00	0.98	0.20	None	0.4	1.6	1.20	19.8	Good	No Good
4-21	0.00	0.80	0.20	NbO _{5/2}	3.00	0.98	0.20	None	4.6	2.5	0.23	18.5	Good	No Good
4-22	0.00	0.60	0.40	NbO _{5/2}	3.00	0.98	0.20	None	18.4	3.4	0.10	18.3	Good	No Good
4-23	0.00	0.40	0.60	NbO _{5/2}	3.00	0.98	0.20	None	74.0	3.1	0.06	18.1	Good	No Good
4-24	0.00	0.20	0.80	NbO _{5/2}	3.00	0.98	0.20	None	187.0	2.7	0.01	16.8	No Good	No Good
4-25	0.00	0.00	1.00	NbO _{5/2}	3.00	0.98	0.20	None	Isolated	-	-	16.5	No Good	No Good
4-26	0.80	0.00	0.20	NbO _{5/2}	3.00	0.98	0.20	None	138.0	2.4	-0.15	25.4	Good	Good
4-27	0.50	0.00	0.50	NbO _{5/2}	3.00	0.98	0.20	None	39.5	4.4	-0.08	20.1	Good	No Good
4-28	0.20	0.00	0.80	NbO _{5/2}	3.00	0.98	0.20	None	9.1	3.5	-0.01	18.6	Good	No Good
4-29	0.60	0.20	0.20	NbO _{5/2}	3.00	0.98	0.20	None	9.2	3.3	-0.07	26.1	Good	Good
4-30	0.20	0.60	0.20	NbO _{5/2}	3.00	0.98	0.20	None	9.9	3.2	0.11	24.9	Good	Good
4-31	0.40	0.20	0.40	NbO _{5/2}	3.00	0.98	0.20	None	22.0	4.1	-0.03	26.0	Good	Good
4-32	0.20	0.20	0.60	NbO _{5/2}	3.00	0.98	0.20	None	47.1	2.8	0.00	24.1	Good	Good

Mole ratios of the A site component have large influence on the electrical characteristic of a varistor, and in particular, to the temperature characteristics of the varistor voltage E_{10} . When the temperature characteristic of the voltage E_{10} is negative, the varistor voltage drops in connection with the rise of operating temperature, and hence, excessive electric current flows to the varistor or a possibility of causing a thermal runaway exists. Therefore, this is not adoptable. Therefore, the samples 4-15 to 4-17, 4-26 to 4-29 and 4-31 are in ranges where they cannot be used as varistors respectively.

Even if the temperature characteristic of the voltage E_{10} is zero or positive, it is not desirable to exceed 0.06, and hence, the samples 4-18 to 4-23 and 4-30 are not preferable as varistors.

Since being insulated as a whole by reoxidation processing, the sample 4-25 does not operate as a varistor. In addition, since the samples 4-24 and 4-26 contain too much Ca, their varistor voltages E_{10} are extremely high, and hence, control is difficult.

Since Ca contained is too much or too little although the E_{10} characteristics of the samples 4-13, 4-14 and 4-32 are 0.06 or less, their nonlinear coefficients α to the varistor voltage E_{10} are low, and hence they are not preferable.

Therefore, it can be said that the samples 4-1 to 4-12 are preferable because the temperature characteristics of the

varistor voltages E_{10} are 0.06 or less and the coefficients α to the varistor voltages E_{10} are not so low. This corresponds to A site mole ratios specified in claim 54. In this range, no crack arose at the thermal crack test where the temperature of the soldering iron was 360°C, and furthermore, no crack also arose at the thermal crack test where the temperature of the soldering iron was 400°C.

Furthermore, the samples 4-1 to 4-7 whose temperature characteristics of the voltages E_{10} are 0.02 or less are more preferable in the present invention. This corresponds to A site mole ratios specified in claim 55. In particular, the sample 4-4 has the best balance of the temperature characteristic of the voltage E_{10} and the nonlinear coefficient α , and the mole ratios of the A site component near that of this sample are most preferable in the present invention.

Example 4-2

What is performed in this example 4-2 is comparison of samples obtained by changing an amount of a semiconductorizing agent.

With fixing other parameters such as a grinding time after calcining, a density of a formed object, A site mole ratios, a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 and performing the same setup as that in the example 4-1 except for changing the mole percent of the semiconductorizing agent as shown in Table 4-2, samples were produced, which were measured similarly to those in the example

4-1. The result is shown in Table 4-2.

Table 4-2

Sample No.	Composition							Electrical Characteristics		Mechanical Characteristics	
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	E ₁₀ (V)	α	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)
											360 °C 400 °C
4-33	0.35	0.35	0.30	NbO _{5/2}	0.10	0.98	0.20	30.2	3.1	17.2	No Good No Good
4-34	0.35	0.35	0.30	NbO _{5/2}	0.75	0.98	0.20	16.7	3.3	27.3	Good Good
4-35	0.35	0.35	0.30	NbO _{5/2}	1.00	0.98	0.20	15.5	3.4	28.6	Good Good
4-36	0.35	0.35	0.30	NbO _{5/2}	2.00	0.98	0.20	12.4	3.4	32.2	Good Good
4-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	11.5	3.4	33.5	Good Good
4-37	0.35	0.35	0.30	NbO _{5/2}	4.00	0.98	0.20	12.1	3.5	30.5	Good Good
4-38	0.35	0.35	0.30	NbO _{5/2}	10.00	0.98	0.20	11.5	3.5	19.6	Good No Good
4-39	0.35	0.35	0.30	NbO _{5/2}	15.00	0.98	0.20	14.3	3.3	9.9	No Good No Good

The amount of a semiconductorizing agent affects the thermal crack-proof property of varistor ceramic. Since the samples 4-33 and 4-39 have too few and too much semiconductorizing agent respectively, thermal cracks arose in the test where the temperature of the soldering iron was 360°C, and hence, these are not preferable. Therefore, the samples 4-4 and 4-34 to 4-38 where thermal cracks did not arise in the test where the temperature of the soldering iron was 360°C and the traverse rupture strength was 18 kgf/mm² or more are preferable in the present invention. This corresponds to the mole percent of the semiconductorizing agent specified in claim 54.

Furthermore, since a thermal crack arose in the sample 4-38 in the test where the temperature of the soldering iron is 400°C, the samples 4-4 and 4-34 to 4-37 where a thermal crack did not also arise in the test where the temperature of the soldering iron was 400°C are more preferable in the present invention. This corresponds to the mole percent of the semiconductorizing agent specified in claim 57. In addition, the mole percent of the semiconductorizing agent near that of the sample 4-4 is most preferable in the present invention.

Example 4-3

What is performed in this example 4-3 is comparison of samples where a kind of semiconductorizing agent was changed.

With fixing other parameters such as a grinding time after calcining, a density of a formed object, A site mole ratios, a mole percent of a semiconductorizing agent, a total

A/B, and a mole percent of SiO_2 and performing the same setup as that in the example 4-1 except for changing the kind of the semiconductorizing agent as shown in Table 4-3, samples were produced, which were measured similarly to those in the example 4-1. The result is shown in Table 4-3.

Table 4-3

Sample No.	Composition								Electrical Characteristics		Mechanical Characteristics		
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
												360 °C	400 °C
4-4	0.35	0.35	0.30	Nb ₂ O ₅	3.00	0.98	0.20	None	11.5	3.4	33.5	Good	Good
4-40	0.35	0.35	0.30	Ta ₂ O ₅	3.00	0.98	0.20	None	15.4	3.4	27.5	Good	Good
4-41	0.35	0.35	0.30	Y ₂ O ₃	3.00	0.98	0.20	None	26.6	3.7	32.3	Good	Good
4-42	0.35	0.35	0.30	La ₂ O ₃	3.00	0.98	0.20	None	15.1	3.9	24.6	Good	Good
4-43	0.35	0.35	0.30	CeO ₂	3.00	0.98	0.20	None	14.9	3.5	24.9	Good	Good
4-44	0.35	0.35	0.30	Pr ₆ O ₁₁	3.00	0.98	0.20	None	16.2	3.6	26.5	Good	Good
4-45	0.35	0.35	0.30	Nd ₂ O ₃	3.00	0.98	0.20	None	16.8	3.7	26.1	Good	Good
4-46	0.35	0.35	0.30	Sm ₂ O ₃	3.00	0.98	0.20	None	14.8	3.5	26.9	Good	Good
4-47	0.35	0.35	0.30	Eu ₂ O ₃	3.00	0.98	0.20	None	19.0	3.8	26.4	Good	Good
4-48	0.35	0.35	0.30	Gd ₂ O ₃	3.00	0.98	0.20	None	16.2	3.6	26.7	Good	Good
4-49	0.35	0.35	0.30	Tb ₄ O ₇	3.00	0.98	0.20	None	21.3	3.8	25.1	Good	Good
4-50	0.35	0.35	0.30	Dy ₂ O ₃	3.00	0.98	0.20	None	18.3	3.5	26.9	Good	Good
4-51	0.35	0.35	0.30	Ho ₂ O ₃	3.00	0.98	0.20	None	25.4	3.6	27.5	Good	Good
4-52	0.35	0.35	0.30	Er ₂ O ₃	3.00	0.98	0.20	None	27.9	4.0	27.9	Good	Good
4-53	0.35	0.35	0.30	Tm ₂ O ₃	3.00	0.98	0.20	None	24.1	3.9	27.3	Good	Good
4-54	0.35	0.35	0.30	Yb ₂ O ₃	3.00	0.98	0.20	None	29.2	3.9	26.3	Good	Good
4-55	0.35	0.35	0.30	Lu ₂ O ₃	3.00	0.98	0.20	None	28.2	4.1	24.4	Good	Good
4-56	0.35	0.35	0.30	Nb ₂ O ₅ + Y ₂ O ₃ Equal numbers of moles	3.00	0.98	0.20	None	22.0	4.0	31.7	Good	Good

Since a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C and the transverse rupture strength was 18 kgf/mm² or more in all the samples 4-4 and 4-40 to 4-56. Hence, it is preferable in the present invention to use NbO_{5/2}, TaO_{5/2}, YO_{3/2}, LaO_{3/2}, CeO₂, PrO_{11/6}, NdO_{3/2}, SmO_{3/2}, EuO_{3/2}, GdO_{3/2}, TbO_{7/4}, DyO_{3/2}, HoO_{3/2}, ErO_{3/2}, TmO_{3/2}, YbO_{3/2}, LuO_{3/2} or NbO_{5/2} + YO_{3/2} (equal numbers of moles) as a semiconductorizing agent. This corresponds to the kind of semiconductorizing agent specified in claim 54.

Example 4-4

What is performed in this example 4-4 is comparison of samples obtained by changing a total A/B.

With fixing other parameters such as a grinding time after calcining, a density of a formed object, A site mole ratios, a mole percent and a kind of a semiconductorizing agent, and a mole percent of SiO₂, and performing the same setup as that in the example 4-1 except for changing the total A/B as shown in Table 4-4, samples were produced, which were measured similarly to those in the example 4-1. The result is shown in Table 4-4.

Table 4-4

Sample No.	Composition								Electrical Characteristics		Mechanical Characteristics		
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
												360 °C	400 °C
4-57	0.35	0.35	0.30	NbO _{5/2}	3.00	0.80	0.20	None	Isolated	—	5.0	No Good	No Good
4-58	0.35	0.35	0.30	NbO _{5/2}	3.00	0.84	0.20	None	4.4	2.6	23.6	Good	No Good
4-59	0.35	0.35	0.30	NbO _{5/2}	3.00	0.96	0.20	None	7.0	3.1	31.7	Good	Good
4-60	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	33.5	Good	Good
4-61	0.35	0.35	0.30	NbO _{5/2}	3.00	1.00	0.20	None	9.5	3.3	32.0	Good	Good
4-62	0.35	0.35	0.30	NbO _{5/2}	3.00	1.02	0.20	None	6.3	3.0	27.7	Good	Good
4-63	0.35	0.35	0.30	NbO _{5/2}	3.00	1.16	0.20	None	51.5	3.2	18.1	Good	No Good
4-63	0.35	0.35	0.30	NbO _{5/2}	3.00	1.20	0.20	None	Isolated	—	7.7	No Good	No Good

The value of the total A/B affects the degree of sintering of ceramic. The samples 4-57 and 4-63 have too small and too large total A/B respectively, these could not operate as varistors because it was impossible to sinter precise ceramic and they were insulated as a whole by reoxidation processing. Furthermore, a thermal crack arose when the temperature of the soldering iron was 360°C.

As shown in Table 4-4, in a range where an amount of SiO_2 is few and a lot of semiconductorizing agent is added, in order to maintain the thermal crack-proof property, it is indispensable to especially control an upper limit of the total A/B. If the total A/B exceeds 1.16, a thermal crack starts arising at 360°C. If the total A/B exceeds 1.01, a thermal crack starts arising at 400°C.

That is, since a thermal crack did not arise in the test where the temperature of the soldering iron was 360°C, and the transverse rupture strength was 18 kgf/mm² or more, the samples 4-4 and 4-58 to 4-62 are preferable in the present invention. This corresponds to a range of the total A/B specified in claim 54.

Furthermore, since a thermal crack did not arise in the test where the temperature of the soldering iron was 400°C, the samples 4-4 and 4-59 to 4-61 are more preferable in the present invention. This corresponds to a range of the total A/B specified in claim 56. In addition, the vicinity of the total A/B where the B site component is a little rich like the sample

4-4 is a most preferable range of the present invention.

Example 4-5

What is performed in this example 4-5 is comparison of samples obtained by changing a mole percent of SiO_2 .

With fixing other parameters such as a grinding time after calcining, a density of a formed object, A site mole ratios, a mole percent and a kind of a semiconductorizing agent, and a total A/B, and performing the same setup as that in the example 4-1 except for changing the mole percent of SiO_2 as shown in Table 4-5, samples were produced, which were measured similarly to those in the example 4-1. The temperature of a soldering iron in a thermal crack test was three kinds of temperature, that is, 360°C , 400°C and 450°C . The result is shown in Table 4-5.

Table 4-5

Sample No.	Composition							Electrical Characteristics		Mechanical Characteristics				
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	E ₁₀ (V)	α	Transverse Rupture Strength (Kgf/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)		
												360 °C	400 °C	450 °C
4-64	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.00	None	7.7	3.3	27.2	Good	Good	Good
4-65	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.10	None	8.5	3.4	31.8	Good	Good	Good
4-4	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	None	11.5	3.4	33.5	Good	Good	Good
4-66	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.30	None	13.7	3.6	33.1	Good	Good	Good
4-67	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.60	None	10.4	3.4	24.2	Good	Good	No Good
4-68	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	1.00	None	337.0	2.9	16.5	No Good	No Good	No Good
4-69	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	1.50	None	Isolated	—	8.3	No Good	No Good	No Good

SiO_2 is added as a sintering additive. If SiO_2 is contained, it becomes possible to stably perform sintering even if composition fluctuates. However, if its amount increases, it becomes easy for a thermal crack to arise.

Since a thermal crack also arose in the test where the temperature of the soldering iron was 360°C , because there was too much SiO_2 , the samples 4-68 and 4-69 are not preferable. Therefore, the samples 4-4 and 4-64 to 4-67 where thermal cracks did not arise in the test at the temperature of the soldering iron of 360°C and 400°C and the transverse rupture strength was 18 kgf/mm^2 or more are preferable in the present invention. This corresponds to the mole percent of SiO_2 specified in claim 54.

Since a thermal crack arose in the sample 4-67 in the test where the temperature of the soldering iron was 450°C , the samples 4-4 and 4-64 to 4-66 where a thermal crack did not arise even in the test at the temperature of the soldering iron of 450°C are more preferable in the present invention. This corresponds to the mole percent of SiO_2 specified in claim 58. In addition, the mole percent of SiO_2 near that of the sample 4-4 is most preferable in the present invention. In addition, although a dosage of SiO_2 in the sample 4-64 is zero nominally, in fact, SiO_2 is contained in each raw material as an impurity, and hence actual SiO_2 content of the sample 4-64 does not become zero.

Example 4-6

What is performed in this example 4-6 is comparison of samples where a kind and an amount of an additive were changed. With fixing other parameters such as a grinding time after calcining, a density of a formed object, A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO_2 , and performing the same setup as that in the example 4-1 except for changing the kind and amount of an additive as shown in Table 4-6, samples were produced, which were measured similarly to those in the example 4-1. The result is shown in Table 4-6.

Table 4-6

Sample No.	Composition										Electrical Characteristics		Mechanical Characteristics		
	Sr mole ratio $a/(a+b+c)$	Ba mole ratio $b/(a+b+c)$	Ca mole ratio $c/(a+b+c)$	Component of semiconducting agent	Mole % of semiconducting agent	Total A/B	SiO ₂ mole %	Component of additive	Mole % of additive	E ₁₀ (V)	α	Transverse Rupture Strength (Kg/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)		
													360 °C	400 °C	
4-70	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.01	15.6	4.0	30.7	Good	Good	
4-71	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.03	15.0	4.1	31.3	Good	Good	
4-72	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	0.60	19.6	4.2	31.1	Good	Good	
4-73	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	1.00	26.3	4.4	24.6	Good	Good	
4-74	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MnO	2.00	Isolated	—	17.3	No Good	No Good	
4-75	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	Co ₃ O ₄	0.01	13.1	3.4	25.4	Good	Good	
4-76	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	Co ₃ O ₄	0.50	22.1	3.7	32.4	Good	Good	
4-77	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	Co ₃ O ₄	1.00	28.8	3.7	24.8	Good	Good	
4-78	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	Co ₃ O ₄	2.00	Isolated	—	16.9	No Good	No Good	
4-79	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	MoO ₃	0.20	12.0	3.6	24.7	Good	Good	
4-80	0.35	0.35	0.30	NbO _{5/2}	3.00	0.98	0.20	WO ₃	0.20	11.8	3.6	25.1	Good	Good	

An additive has the action of adjusting electrical characteristics such as the varistor voltage E_{10} and the nonlinear coefficient α . Mn enlarges the varistor voltage E_{10} and the nonlinear coefficient α , and Co enlarges varistor voltage E_{10} . In addition, it is found that Mo and W have the action of enlarging the nonlinear coefficient α . Although not shown in Table 4-6, it is found that other elements such as Li, Na, Ni, Cu, Zn, Sc, Fe, Ga and In also have the same action.

Since the samples 4-74 and 4-78 had a too large amount of dosage, the degree of sintering was blocked and the ceramic was insulated by the reoxidation processing. Therefore, the samples 4-70 to 4-73, 4-75 to 4-77 and 4-79 to 4-80 each having the mole percent to a principal component, which is 1.00 or less and the transverse rupture strength is 18 kgf/mm² or more are preferable in the present invention. This is included in the kind and mole percent of an additive specified in claim 59.

Example 4-7

What is performed in this example 4-7 is comparison of samples where a grinding time after calcining, that is, a specific surface area of each grain after grinding, and a density of a formed object were changed.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO₂, and performing the same setup as that in the example 4-1 except for changing the grinding and forming conditions as shown in Table 4-7, samples

were produced, which were measured similarly to those in the example 4-1. The result is shown in Table 4-7.

Table 4-7

Sample No.	Grinding Time After Presintering (h)	Specific Surface Area (m ² /g)	Density of Formed Object ρ_g (g/cm ³)	Density of Sintered Object ρ_s (g/cm ³)	Transverse Rupture Strength (Kgf/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
						360 °C	400 °C
4-81	1	0.53	2.60	4.58	15.13	No Good	No Good
4-82	5	2.33	2.60	4.55	15.60	No Good	No Good
4-83	24	4.52	2.60	4.57	14.35	No Good	No Good
4-84	50	7.29	2.60	4.66	14.83	No Good	No Good
4-85	100	10.43	2.60	4.54	12.91	No Good	No Good
4-86	1	0.53	2.80	4.85	19.02	No Good	No Good
4-87	5	2.33	2.80	4.92	18.08	No Good	No Good
4-88	24	4.52	2.80	4.92	19.11	No Good	No Good
4-89	50	7.29	2.80	4.86	19.27	No Good	No Good
4-90	0	0.23	3.00	4.99	22.57	Good	No Good
4-91	1	0.53	3.00	5.02	23.60	Good	Good
4-92	5	2.33	3.00	5.01	23.35	Good	Good
4-93	10	3.32	3.00	5.09	24.82	Good	Good
4-94	24	4.52	3.00	5.12	25.41	Good	Good
4-95	50	7.29	3.00	5.11	21.83	Good	Good
4-96	100	10.43	3.00	5.03	22.81	Good	No Good
4-97	0	0.23	3.20	5.03	25.00	Good	No Good
4-98	1	0.53	3.20	5.10	26.22	Good	Good
4-99	5	2.33	3.20	5.03	25.80	Good	Good
4-100	24	4.52	3.20	5.11	24.65	Good	Good
4-101	50	7.29	3.20	5.16	23.48	Good	Good
4-102	0	0.23	3.40	5.14	26.72	Good	No Good
4-103	1	0.53	3.40	5.23	26.92	Good	Good
4-104	5	2.33	3.40	5.31	28.83	Good	Good
4-105	24	4.52	3.40	5.19	29.88	Good	Good
4-106	50	7.29	3.40	5.34	27.93	Good	Good
4-107	1	0.53	3.60	5.11	22.93	Good	Good
4-108	5	2.33	3.60	5.22	22.85	Good	Good
4-109	24	4.52	3.60	5.13	23.92	Good	Good
4-110	50	7.29	3.60	5.28	21.86	Good	Good
4-111	100	10.43	3.60	5.13	23.55	Good	No Good

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO₂ is d moles, the

content of $\text{NbO}_{5/2}$ is f moles, and the content of SiO_2 is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b + c) = 0.35$, $c/(a + b + c) = 0.30$, $f/d \times 100 = 3.00$, $(a + b + c)/(d + f) = 1.16$, and $g/d \times 100 = 0.30$ to produce samples.

In each sample in this example, the total A/B has comparatively large composition as 1.16.

In the samples 4-81 to 4-85, by changing the grinding time after the calcining with 1 to 100 hours with making the density of a formed object ρ_g be 2.60 g/cm^3 lower than usual. The specific surface area of the grain after grinding is changed with 0.53 to $10.43 \text{ m}^2/\text{g}$. In these samples, the transverse rupture strength was lower than 18 kgf/mm^2 , and thermal cracks arose also in the test where the temperature of the soldering iron was 360°C and 400°C . This may be because sufficient bending strength cannot be obtained since the density of a sintered object after sintering considerably dropped to 4.66 g/cm^3 or less due to the low density ρ_g of a formed object.

In the samples 4-86 to 4-89, the density ρ_g of each formed object was made to be 2.80 g/cm^3 as is usual, and the specific surface area of each grain after grinding was changed with 0.53 to $7.29 \text{ m}^2/\text{g}$. Although bending strength was secured as the transverse rupture strength was over 18 kgf/mm^2 in these samples, thermal cracks arose in the tests where the temperature of the soldering iron was 360°C and 400°C . Since requiring the grinding time of 50 hours, the sample 4-89 is not

preferable from the point of manufacturing efficiency.

In the samples 4-90 to 4-96, the density ρ_g of each formed object was made to be 3.00 g/cm^3 , and the specific surface area of each grain after grinding was changed with 0.23 to $10.43 \text{ m}^2/\text{g}$. In these samples, since the transverse rupture strength greatly exceeded 18 kgf/mm^2 , the bending strength was secured. Furthermore, a thermal crack did not arise in the tests, where the temperature of the soldering iron was 360°C and 400°C , except for the samples 4-90 and 4-96. Since requiring the grinding time of 50 hours, the samples 4-95 and 4-96 are not preferable from the point of manufacturing efficiency.

In the samples 4-97 to 4-101, the density ρ_g of each formed object was made to be 3.20 g/cm^3 as is usual, and the specific surface area of each grain after grinding was changed with 0.23 to $7.29 \text{ m}^2/\text{g}$. In these samples, the transverse rupture strength greatly exceeded 18 kgf/mm^2 , the bending strength was secured. Furthermore, a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C , except for the sample 4-97. Since requiring the grinding time of 50 hours, the sample 4-101 is not preferable from the point of manufacturing efficiency.

In the samples 4-102 to 4-106, the density ρ_g of each formed object was made to be 3.40 g/cm^3 , and the specific surface area of each grain after grinding was changed with 0.23 to $7.29 \text{ m}^2/\text{g}$. In these samples, since the transverse rupture strength greatly exceeded 18 kgf/mm^2 , the bending strength was

secured. Furthermore, a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C, except for the sample 4-102. Since requiring the grinding time of 50 hours, the sample 4-106 is not preferable from the point of manufacturing efficiency.

In the samples 4-107 to 4-111, the density ρ_g of each formed object was made to be 3.60 g/cm³, and the specific surface area of each grain after grinding was changed with 0.53 to 10.43 m²/g. In these samples, the transverse rupture strength greatly exceeded 18 kgf/mm², the bending strength was secured. Furthermore, a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C, except for the sample 4-111. However, since it remarkably reduces the life of dies to make the density of a formed object be 3.60 g/cm³, these samples 4-107 to 4-111 are not preferable.

Therefore, by performing the grinding so that the specific surface area of each grain after the grinding may become between 0.53 and 4.52 m²/g inclusive, and making the density of a formed object be between 2.80 and 3.40 g/cm³ inclusive, it becomes possible to obtain the sufficient bending strength and thermal shock-proof property of the sintered ceramic. In addition, it becomes possible to avoid such inconvenience that manufacturing becomes inefficient because the grinding time becomes long too much, and maintenance cost increases due to the shortening of life of forming equipment

and dies.

Furthermore, in this example, although a range of the specific surface area is between 0.53 and 4.52 m²/g inclusive, in consideration of an error range of specific surface area measurement, the preferable range in the present invention becomes between 0.5 and 5.0 m²/g inclusive. This corresponds to claims 52 and 53.

Example 4-8

What is performed in this example 4-8 is comparison of samples where a grinding time after calcining, that is, a specific surface area of each grain after grinding, and a density of a formed object were changed.

With fixing other parameters such as A site mole ratios, a mole percent and a kind of a semiconductorizing agent, a total A/B, and a mole percent of SiO₂, and performing the same setup as that in the example 4-1 except for changing the grinding and forming conditions as shown in Table 4-8, samples were produced, which were measured similarly to those in the example 4-1. The result is shown in Table 4-8.

Table 4-8

Sample No.	Grinding Time After Presintering (h)	Specific Surface Area (m ² /g)	Density of Formed Object ρ_g (g/cm ³)	Density of Sintered Object ρ_s (g/cm ³)	Transverse Rupture Strength (Kgf/mm ²)	Thermal Crack Test (Soldering Iron Temperature °C)	
						360 °C	400 °C
4-112	1	0.52	2.60	4.55	18.76	No Good	No Good
4-113	5	2.89	2.60	4.61	19.23	No Good	No Good
4-114	24	4.83	2.60	4.59	17.98	No Good	No Good
4-115	50	7.26	2.60	4.63	18.46	No Good	No Good
4-116	100	11.06	2.60	4.70	16.54	No Good	No Good
4-117	1	0.52	2.80	4.83	22.65	Good	Good
4-118	5	2.89	2.80	4.98	24.67	Good	Good
4-119	24	4.83	2.80	4.92	26.31	Good	Good
4-120	50	7.26	2.80	4.89	22.90	Good	Good
4-121	0	0.30	3.00	4.98	23.20	Good	Good
4-122	1	0.52	3.00	5.05	27.23	Good	Good
4-123	5	2.89	3.00	4.99	26.98	Good	Good
4-124	10	3.32	3.00	5.13	28.45	Good	Good
4-125	24	4.83	3.00	5.08	29.04	Good	Good
4-126	50	7.26	3.00	5.11	25.46	Good	Good
4-127	100	11.06	3.00	4.99	22.44	Good	Good
4-128	0	0.30	3.20	5.02	28.63	Good	Good
4-129	1	0.52	3.20	5.12	29.85	Good	Good
4-130	5	2.89	3.20	5.09	29.43	Good	Good
4-131	24	4.83	3.20	5.21	28.28	Good	Good
4-132	50	7.26	3.20	5.16	22.41	Good	Good
4-133	0	0.30	3.40	5.14	30.35	Good	Good
4-134	1	0.52	3.40	5.22	30.55	Good	Good
4-135	5	2.89	3.40	5.25	32.46	Good	Good
4-136	24	4.83	3.40	5.19	33.51	Good	Good
4-137	50	7.26	3.40	5.06	24.38	Good	Good
4-138	1	0.52	3.60	5.44	26.56	Good	Good
4-139	5	2.89	3.60	5.38	26.48	Good	Good
4-140	24	4.83	3.60	5.41	27.55	Good	Good
4-141	50	7.26	3.60	5.13	25.49	Good	Good
4-142	100	11.06	3.60	5.22	23.54	Good	Good

As for the notation of composition, the content of SrO is expressed as a moles, the content of BaO is b moles, the content of CaO is c moles, the content of TiO₂ is d moles, the content of NbO_{5/2} is f moles, and the content of SiO₂ is g moles. The composition was fixed as $a/(a + b + c) = 0.35$, $b/(a + b +$

$c) = 0.35$, $c/(a + b + c) = 0.30$, $f/d \times 100 = 3.00$, $(a + b + c)/(d + f) = 0.98$, and $g/d \times 100 = 0.20$ to produce samples.

Each sample in this example 4-8 has the improved composition that the total A/B is 0.98 that is quite lower than those of the samples in the example 4-7, and that the mole percent of SiO_2 is 0.2 which is lower than that of the samples in the example 4-7.

In the samples 4-112 to 4-116, the density ρ_g of each formed object was made to be 2.60 g/cm^3 lower than usual, and the specific surface area of each grain after grinding is changed with 0.52 to $11.06 \text{ m}^2/\text{g}$ by changing the grinding time after calcining with 1 to 100 hours. In these samples, the transverse rupture strength was near 18 kgf/mm^2 , and thermal cracks arose also in the test where the temperature of the soldering iron was 360°C and 400°C . This may be because sufficient bending strength could not be obtained since the density of a sintered object after sintering considerably dropped to 4.70 g/cm^3 or less due to the low density ρ_g of a formed object.

In the samples 4-117 to 4-120, the density ρ_g of each formed object was made to be 2.80 g/cm^3 as is usual, and the specific surface area of each grain after grinding was changed with 0.52 to $7.26 \text{ m}^2/\text{g}$. The bending strength was secured since the transverse rupture strength was over 18 kgf/mm^2 in these samples, and a thermal crack did not arise even in the tests where the temperature of the soldering iron was 360°C and 400°C .

However, since requiring the grinding time of 50 hours, the sample 4-120 is not preferable from the point of manufacturing efficiency.

In the samples 4-121 to 4-127, the density ρ_g of each formed object was made to be 3.00 g/cm^3 , and the specific surface area of each grain after grinding was changed with 0.30 to $11.06 \text{ m}^2/\text{g}$. In these samples, since the transverse rupture strength greatly exceeded 18 kgf/mm^2 , the bending strength was secured. Furthermore, a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C . Nevertheless, since requiring the grinding time of 50 hours, the samples 4-126 and 4-127 are not preferable from the point of manufacturing efficiency.

In the samples 4-128 to 4-132, the density ρ_g of each formed object was made to be 3.20 g/cm^3 as is usual, and the specific surface area of each grain after grinding was changed with 0.30 to $7.26 \text{ m}^2/\text{g}$. In these samples, since the transverse rupture strength greatly exceeded 18 kgf/mm^2 , the bending strength was secured. Furthermore, a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C . Since requiring the grinding time of 50 hours, the sample 4-132 is not preferable from the point of manufacturing efficiency.

In the samples 4-133 to 4-137, the density ρ_g of each formed object was made to be 3.40 g/cm^3 , and the specific surface area of each grain after grinding was changed with 0.30

to $7.26 \text{ m}^2/\text{g}$. In these samples, since the transverse rupture strength greatly exceeded 18 kgf/mm^2 , the bending strength was secured. Furthermore, a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C . Since requiring the grinding time of 50 hours, the sample 4-137 is not preferable from the point of manufacturing efficiency.

In the samples 4-138 to 4-142, the density ρ_g of each formed object was made to be 3.60 g/cm^3 , and the specific surface area of each grain after grinding was changed with 0.52 to $11.06 \text{ m}^2/\text{g}$. In these samples, since the transverse rupture strength greatly exceeded 18 kgf/mm^2 , the bending strength was secured. Furthermore, a thermal crack did not arise in the tests where the temperature of the soldering iron was 360°C and 400°C . However, since it remarkably reduces the life of dies to make the density of a formed object be 3.60 g/cm^3 , these samples 4-138 to 4-142 are not preferable.

Therefore, by performing the grinding so that the specific surface area of each grain after the grinding may become 0.52 to $4.83 \text{ m}^2/\text{g}$, and making the density of a formed object be between 2.80 and 3.40 g/cm^3 inclusive, it becomes possible to obtain the sufficient bending strength and thermal shock-proof property of the sintered ceramic. In addition, it becomes possible to avoid such inconvenience that manufacturing becomes inefficient because the grinding time becomes long too much, and maintenance cost increases due to the shortening of

life of forming equipment and dies.

Furthermore, in this example, although a range of the specific surface area is between 0.52 and 4.83 m²/g inclusive, in consideration of an error range of specific surface area measurement, the preferable range in the present invention becomes between 0.5 and 5.0 m²/g inclusive. This corresponds to claims 52 and 53.

According to the above Tables 4-1 to 4-8, it is possible to provide a manufacturing method of obtaining varistor ceramic which is provided with the above-described preferable range of transverse rupture strength and is excellent in the thermal shock-proof property, so long as the composition, content, grinding time after calcining, that is, specific surface area of each grain after the grinding, and density of each formed object of each component are within the range of the present invention.

Many widely different embodiments and examples of the present invention may be constructed without departing from the spirit and scope of the present invention. It should be understood that the present invention is not limited to the specific embodiments and examples described in the specification, except as defined in the appended claims.

09 JAN 2004

WHAT IS CLAIMED IS:

1. A voltage-dependent nonlinear resistor ceramic of a composite perovskite-based semiconductor ceramic containing a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, said ceramic substantially containing no Mg and having a composition of $0.10 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.50$, $0.20 < c/(a + b + c) \leq 0.50$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $1.0 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of said first component as SrO, b is the number of moles calculated for Ba of said first component as BaO, c is the number of moles calculated for Ca of said first component as CaO, d is the number of moles calculated for Ti of said first component as TiO₂, e is the number of moles calculated for R of said second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4} and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of said third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of said fourth component as SiO₂.

2. The voltage-dependent nonlinear resistor ceramic as claimed in claim 1, wherein a composition of said first component is $0.30 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.40$, and $0.25 \leq c/(a + b + c) \leq 0.35$.

3. The voltage-dependent nonlinear resistor ceramic as claimed in claim 1 or 2, wherein a composition of said first component and of said at least one component of said second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$.

09 JAN 2004
30 JUN 20

4. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 1 to 3, wherein a composition of said at least one component of said second and third components is $1.0 \leq (e + f)/d \times 100 \leq 4.0$.
5. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 1 to 4, wherein a composition of said fourth component is $g/d \times 100 \leq 0.3$.
6. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 1 to 5, wherein said ceramic further contains a fifth component consisting of at least one kind of oxide selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W, and wherein a composition of said fifth component is $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of said fifth component, as $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 .
7. A voltage-dependent nonlinear resistor comprising said ceramic as claimed in any one of claims 1 to 6.
8. The voltage-dependent nonlinear resistor as claimed in claim 7, wherein said resistor comprises electrodes formed on at least one surface of said ceramic, and wherein said electrodes consist of Cu or material mainly made of Cu.
9. The voltage-dependent nonlinear resistor as claimed in claim 8, wherein said electrodes consists of a Cu alloy.
10. The voltage-dependent nonlinear resistor as claimed in claim 8, wherein said electrodes consist of Cu containing glass frit.

09 JAN 2004

11. A voltage-dependent nonlinear resistor ceramic containing oxides consisting of at least one of Sr, Ba and Ca and consisting of Ti, said ceramic comprising a surface provided with a compressive stress of 15 MPa or more when an X-ray stress constant is -100 MPa/degree.

12. The voltage-dependent nonlinear resistor ceramic as claimed in claim 11, wherein said compressive stress is 25 MPa or more when an X-ray stress constant is -100 MPa/degree.

13. The voltage-dependent nonlinear resistor ceramic as claimed in claim 11, wherein said compressive stress is 40 MPa or more when an X-ray stress constant is -100 MPa/degree.

14. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 11 to 13, wherein said ceramic contains a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, wherein values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in trilinear coordinates exist on a line segment connecting a point (0.2, 0.0, 0.8) and a point (0.0, 0.4, 0.6), or in a range where $a/(a + b + c)$ and $b/(a + b + c)$ are larger than said line segment, and wherein a composition of said ceramic is $0.84 \leq (a + b + c +$

09 JAN 2004

$e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of said first component as SrO, b is the number of moles calculated for Ba of said first component as BaO, c is the number of moles calculated for Ca of said first component as CaO, d is the number of moles calculated for Ti of said first component as TiO_2 , e is the number of moles calculated for R of said second component as $YO_{3/2}$, CeO_2 , $PrO_{11/6}$, $TbO_{7/4}$ and $RO_{3/2}$ (other lanthanoids) respectively, f is the number of moles calculated for M of said third component as $NbO_{5/2}$ and $TaO_{5/2}$ respectively, and g is the number of moles calculated for Si of said fourth component as SiO_2 .

15. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 11 to 13, wherein said ceramic contains a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, wherein values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in trilinear coordinates exist on a first line segment connecting a point (0.5, 0.0, 0.5) and a point (0.2, 0.2, 0.6), a second line segment connecting a point (0.2, 0.2, 0.6) and a point (0.1, 0.4, 0.5), a third line segment connecting a point (0.1, 0.4, 0.5) and a point (0.1, 0.5, 0.4), or a fourth line segment connecting a point (0.1, 0.5, 0.4) and a point (0.2, 0.8, 0.0), or a value of $a/(a + b + c)$ exists in a range larger than said first to

09 JAN 2004

fourth line segments, and wherein a composition of said ceramic is $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of said first component as SrO, b is the number of moles calculated for Ba of said first component as BaO, c is the number of moles calculated for Ca of said first component as CaO, d is the number of moles calculated for Ti of said first component as TiO₂, e is the number of moles calculated for R of said second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4} and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of said third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of said fourth component as SiO₂.

16. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 11 to 13, wherein said ceramic contains a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, wherein values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in trilinear coordinates exist on a fifth line segment connecting a point (0.4, 0.2, 0.4) and a point (0.2, 0.4, 0.4), a sixth line segment connecting a point (0.2, 0.4, 0.4) and a point (0.2, 0.5, 0.3), a seventh line segment connecting a point (0.2, 0.5, 0.3) and a point (0.3, 0.5, 0.2), an eighth line segment connecting a point (0.3, 0.5, 0.2) and a point (0.6, 0.2, 0.2), or a ninth

09 JAN 2004

line segment connecting a point (0.6, 0.2, 0.2) and a point (0.4, 0.2, 0.4), or in a range surrounded by said fifth to ninth line segments, and wherein a composition of said ceramic is $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of said first component as SrO, b is the number of moles calculated for Ba of said first component as BaO, c is the number of moles calculated for Ca of said first component as CaO, d is the number of moles calculated for Ti of said first component as TiO₂, e is the number of moles calculated for R of said second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4} and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of said third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of said fourth component as SiO₂.

17. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 14 to 16, wherein a composition of said first component and said at least one component of said second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$.

18. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 14 to 17, wherein a composition of said at least one component of said second and third components is $0.75 \leq (e + f)/d \times 100 \leq 4.0$.

19. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 14 to 18, wherein a composition of

said fourth component is $g/d \times 100 \leq 0.3$.

20. The voltage-dependent nonlinear resistor ceramic as claimed in any one of claims 14 to 19, wherein said ceramic further contains a fifth component consisting of at least one kind of oxide selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W, and wherein a composition of said fifth component is $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of said fifth component, as $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 .

21. A manufacturing method of a voltage-dependent nonlinear resistor ceramic, comprising a step of performing reduction sintering to obtain a ceramic containing oxides consisting of at least one of Sr, Ba and Ca and consisting of Ti, and a step of performing reoxidation of said obtained ceramic to generate a compressive stress in a surface of said ceramic, said reduction sintering performing step and said reoxidation performing step generating a compressive stress of 15 MPa or more in the surface of said ceramic when an X-ray stress constant is -100 MPa/degree.

22. The manufacturing method as claimed in claim 21, wherein said method further comprises a step of weighing raw material powder so that a weighed powder has a predetermined composition, a step of mixing the weighed powder, a step of performing calcining of the mixed powder, a step of grinding a calcined object, a step of forming the ground object, a step of

performing the reduction sintering of the formed object, and a step of performing the reoxidation of the reduction sintered object.

23. The manufacturing method as claimed in claim 21 or 22, wherein said reduction sintering performing step and said reoxidation performing step generate a compressive stress of 25 MPa or more in the surface of said ceramic when an X-ray stress constant is -100 MPa/degree.

24. The manufacturing method as claimed in claim 21 or 22, wherein said reduction sintering performing step and said reoxidation performing step generate a compressive stress of 40 MPa or more in the surface of said ceramic when an X-ray stress constant is -100 MPa/degree.

25. The manufacturing method as claimed in any one of claims 21 to 24, wherein a temperature in said reoxidation performing step is between 850°C and 1050°C inclusive.

26. The manufacturing method as claimed in any one of claims 21 to 24, wherein a temperature in said reoxidation performing step is between 900°C and 1000°C inclusive.

27. The manufacturing method as claimed in any one of claims 21 to 26, wherein a time of said reoxidation performing step is 32 hours or less.

28. The manufacturing method as claimed in any one of claims

09 JAN 2004

21 to 26, wherein a time of said reoxidation performing step is between 0.25 hour and 16 hours inclusive.

29. The manufacturing method as claimed in any one of claims 21 to 26, wherein a time of said reoxidation performing step is between 0.5 hour and 8 hours inclusive.

30. The manufacturing method as claimed in any one of claims 21 to 29, wherein a partial pressure of oxygen in said reoxidation performing step is 0.1 atmospheric pressure or more.

31. The manufacturing method as claimed in any one of claims 21 to 30, wherein said ceramic contains a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, wherein values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in trilinear coordinates exist on a line segment connecting a point (0.2, 0.0, 0.8) and a point (0.0, 0.4, 0.6), or in a range where $a/(a + b + c)$ and $b/(a + b + c)$ are larger than said line segment, and wherein a composition of said ceramic is $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of said first component as SrO, b is the number of moles calculated for Ba of said first component as BaO, c is the number of moles calculated for Ca of said first component as CaO, d is the number of moles

09 JAN 2004

calculated for Ti of said first component as TiO_2 , e is the number of moles calculated for R of said second component as $\text{YO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{TbO}_{7/4}$ and $\text{RO}_{3/2}$ (other lanthanoids) respectively, f is the number of moles calculated for M of said third component as $\text{NbO}_{5/2}$ and $\text{TaO}_{3/2}$ respectively, and g is the number of moles calculated for Si of said fourth component as SiO_2 .

32. The manufacturing method as claimed in any one of claims 21 to 30, wherein said ceramic contains a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, wherein values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in trilinear coordinates exist on a first line segment connecting a point (0.5, 0.0, 0.5) and a point (0.2, 0.2, 0.6), a second line segment connecting a point (0.2, 0.2, 0.6) and a point (0.1, 0.4, 0.5), a third line segment connecting a point (0.1, 0.4, 0.5) and a point (0.1, 0.5, 0.4), or a fourth line segment connecting a point (0.1, 0.5, 0.4) and a point (0.2, 0.8, 0.0), or a value of $a/(a + b + c)$ exists in a range larger than said first to fourth line segments, and wherein a composition of said ceramic is $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of said first component as SrO , b is the number of moles calculated for Ba of said first component as BaO , c is the number of moles

09 JAN 2004

calculated for Ca of said first component as CaO, d is the number of moles calculated for Ti of said first component as TiO_2 , e is the number of moles calculated for R of said second component as $\text{YO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{TbO}_{7/4}$ and $\text{RO}_{3/2}$ (other lanthanoids) respectively, f is the number of moles calculated for M of said third component as $\text{NbO}_{5/2}$ and $\text{TaO}_{5/2}$ respectively, and g is the number of moles calculated for Si of said fourth component as SiO_2 .

33. The manufacturing method as claimed in any one of claims 21 to 30, wherein said ceramic contains a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, wherein values of $a/(a + b + c)$, $b/(a + b + c)$ and $c/(a + b + c)$ in trilinear coordinates exist on a fifth line segment connecting a point (0.4, 0.2, 0.4) and a point (0.2, 0.4, 0.4), a sixth line segment connecting a point (0.2, 0.4, 0.4) and a point (0.2, 0.5, 0.3), a seventh line segment connecting a point (0.2, 0.5, 0.3) and a point (0.3, 0.5, 0.2), an eighth line segment connecting a point (0.3, 0.5, 0.2) and a point (0.6, 0.2, 0.2), or a ninth line segment connecting a point (0.6, 0.2, 0.2) and a point (0.4, 0.2, 0.4), or in a range surrounded by said fifth to ninth line segments, and wherein a composition of said ceramic is $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of said

first component as SrO , b is the number of moles calculated for Ba of said first component as BaO , c is the number of moles calculated for Ca of said first component as CaO , d is the number of moles calculated for Ti of said first component as TiO_2 , e is the number of moles calculated for R of said second component as $\text{YO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{TbO}_{7/4}$ and $\text{RO}_{3/2}$ (other lanthanoids) respectively, f is the number of moles calculated for M of said third component as $\text{NbO}_{5/2}$ and $\text{TaO}_{5/2}$ respectively, and g is the number of moles calculated for Si of said fourth component as SiO_2 .

34. The manufacturing method as claimed in any one of claims 31 to 33, wherein a composition of said first component and said at least one component of said second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$.

35. The manufacturing method as claimed in any one of claims 31 to 34, wherein a composition of said at least one component of said second and third components is $0.75 \leq (e + f)/d \times 100 \leq 4.0$.

36. The manufacturing method as claimed in any one of claims 31 to 35, wherein a composition of said fourth component is $g/d \times 100 \leq 0.3$.

37. The manufacturing method as claimed in any one of claims 31 to 36, wherein said ceramic further contains a fifth component consisting of at least one kind of oxide selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W,

09 JAN 2004

and wherein a composition of said fifth component is $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of said fifth component, as $\text{LiO}_{1/2}$, $\text{NaO}_{1/2}$, MnO , $\text{CoO}_{4/3}$, NiO , CuO , ZnO , $\text{ScO}_{3/2}$, $\text{FeO}_{3/2}$, $\text{GaO}_{3/2}$, $\text{InO}_{3/2}$, MoO_3 and WO_3 .

38. A manufacturing method of a voltage-dependent nonlinear resistor ceramic, comprising a step of performing reduction sintering to obtain a ceramic, and a step of performing reoxidation of said obtained ceramic, said ceramic containing a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, and wherein a composition of said ceramic is $0.30 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.40$, $0.25 \leq c/(a + b + c) \leq 0.35$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of said first component as SrO , b is the number of moles calculated for Ba of said first component as BaO , c is the number of moles calculated for Ca of said first component as CaO , d is the number of moles calculated for Ti of said first component as TiO_2 , e is the number of moles calculated for R of said second component as $\text{YO}_{3/2}$, CeO_2 , $\text{PrO}_{11/6}$, $\text{TbO}_{7/4}$ and $\text{RO}_{3/2}$ (other lanthanoids) respectively, f is the number of moles calculated for M of said third component as $\text{NbO}_{5/2}$ and $\text{TaO}_{5/2}$ respectively, and g is the number of moles calculated for Si of said fourth component as

SiO₂.

39. The manufacturing method as claimed in claim 38, wherein a composition of said first component and said at least one component of said second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$.

40. The manufacturing method as claimed claim 38 or 39, wherein a composition of said at least one component of said second and third components is $0.75 \leq (e + f)/d \times 100 \leq 4.0$.

41. The manufacturing method as claimed in any one of claims 38 to 40, wherein a composition of said fourth component is $g/d \times 100 \leq 0.3$.

42. The manufacturing method as claimed in any one of claims 38 to 41, wherein said ceramic further contains a fifth component consisting of at least one kind of oxide selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W, and wherein a composition of said fifth component is $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of said fifth component, as LiO_{1/2}, NaO_{1/2}, MnO, CoO_{4/3}, NiO, CuO, ZnO, ScO_{3/2}, FeO_{3/2}, GaO_{3/2}, InO_{3/2}, MoO₃ and WO₃.

43. The manufacturing method as claimed in any one of claims 38 to 42, wherein a temperature in said reoxidation performing step is between 850°C and 900°C inclusive and a time of said reoxidation performing step being between 0.25 hour and 32 hours

inclusive.

44. The manufacturing method as claimed in any one of claims 38 to 42, wherein a temperature in said reoxidation performing step is between 900°C and 1050°C inclusive and a time of said reoxidation performing step being between 0.1 hour and 32 hours inclusive.

45. The manufacturing method as claimed in any one of claims 38 to 42, wherein a temperature in said reoxidation performing step is between 900°C and 950°C inclusive and a time of said reoxidation performing step is between 0.5 hour and 16 hours inclusive

46. The manufacturing method as claimed in any one of claims 38 to 42, wherein a temperature in said reoxidation performing step is between 950°C and 1000°C inclusive and a time of said reoxidation performing step is between 0.25 hour and 16 hours inclusive.

47. The manufacturing method as claimed in any one of claims 38 to 46, wherein a time of said reoxidation performing step is adjusted to control a varistor voltage value.

48. The manufacturing method as claimed in any one of claims 38 to 46, wherein said method further comprises a step of weighing raw material powder so that a weighed powder has a predetermined composition, a step of mixing the weighed powder, a step of performing calcining of the mixed powder, a step of

30 JUN 20
09 JAN 2004

grinding a calcined object, a step of forming the ground object, a step of performing the reduction sintering of the formed object, and a step of performing the reoxidation of the reduction sintered object.

49. The manufacturing method as claimed in any one of claims 38 to 47, wherein said method further comprises a step of weighing raw material powder, a step of mixing the weighed powder, a step of performing calcining of the mixed powder, a step of adding a part of contents so as to adjust a composition of a calcined object to a predetermined component, a step of grinding the adjusted object, a step of forming the ground object, a step of performing the reduction sintering of the formed object, and a step of performing the reoxidation of the reduction sintered object.

50. The manufacturing method as claimed in any one of claims 38 to 49, wherein said reoxidation performing step comprises a single continuous heat treatment process.

51. The manufacturing method as claimed in any one of claims 38 to 49, wherein said reoxidation performing step comprises a plurality of separate heat treatment processes.

52. A manufacturing method of a voltage-dependent nonlinear resistor ceramic, comprising a step of weighing raw material powder containing oxides consisting of at least one of Sr, Ba and Ca and consisting of Ti so that a weighed powder has a predetermined composition, a step of mixing the weighed powder,

a step of performing calcining of the mixed powder, a step of grinding a calcined object, a step of forming the ground object, a step of performing reduction sintering of the formed object, and a step of performing reoxidation of the reduction sintered object, said grinding step being performed so that a specific surface area of each grain after the grinding becomes between 0.5 and 5.0 m²/g inclusive, said forming step being performed so that a density of the formed object becomes between 2.80 and 3.40 g/cm³ inclusive.

53. A manufacturing method of a voltage-dependent nonlinear resistor ceramic, comprising a step of weighing raw material powder containing oxides consisting of at least one of Sr, Ba and Ca and consisting of Ti so that a weighed powder has a predetermined composition, a step of mixing the weighed powder, a step of performing calcining of the mixed powder, a step of adding a part of contents so as to adjust a composition of a calcined object to a predetermined component, a step of grinding the adjusted object, a step of forming the ground object, a step of performing reduction sintering of the formed object, and a step of performing reoxidation of the reduction sintered object, said grinding step being performed so that a specific surface area of each grain after the grinding becomes between 0.5 and 5.0 m²/g inclusive, said forming step being performed so that a density of the formed object becomes between 2.80 and 3.40 g/cm³ inclusive.

54. The manufacturing method as claimed in claim 52 or 53, wherein said ceramic contains a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si, and wherein a composition of said ceramic is $0.10 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.50$, $0.20 < c/(a + b + c) \leq 0.50$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $0.75 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of said first component as SrO, b is the number of moles calculated for Ba of said first component as BaO, c is the number of moles calculated for Ca of said first component as CaO, d is the number of moles calculated for Ti of said first component as TiO₂, e is the number of moles calculated for R of said second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4} and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of said third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of said fourth component as SiO₂.

55. The manufacturing method as claimed in claim 54, wherein a composition of said first component is $0.30 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.40$, and $0.25 \leq c/(a + b + c) \leq 0.35$.

56. The manufacturing method as claimed in claim 54 or 55, wherein a composition of said first component and said at least one component of said second and third components is $0.96 \leq (a + b + c + e)/(d + f) \leq 1.01$.

57. The manufacturing method as claimed in any one of claims 54 to 56, wherein a composition of said at least one component of said second and third components is $0.75 \leq (e + f)/d \times 100 \leq$

09 JAN 2004

4.0.

58. The manufacturing method as claimed in any one of claims 54 to 57, wherein a composition of said fourth component is $g/d \times 100 \leq 0.3$.

59. The manufacturing method as claimed in any one of claims 54 to 58, wherein said ceramic further contains a fifth component consisting of at least one kind of oxide selected from oxides of Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W, and wherein a composition of said fifth component is $0 < h/d \times 100 \leq 1.000$, where h is the number of moles calculated for Li, Na, Mn, Co, Ni, Cu, Zn, Sc, Fe, Ga, In, Mo and W which are contents of said fifth component, as $LiO_{1/2}$, $NaO_{1/2}$, MnO, $CoO_{4/3}$, NiO, CuO, ZnO, $ScO_{3/2}$, $FeO_{3/2}$, $GaO_{3/2}$, $InO_{3/2}$, MoO_3 and WO_3 .

09 JAN 2004

ABSTRACT OF THE DISCLOSURE

A composite perovskite-based semiconductor varistor ceramic and a varistor may contain a first component consisting of oxides of Sr, Ba, Ca and Ti, at least one component of a second component consisting of at least one kind of oxide selected from oxides of R (Y and lanthanoids) and a third component consisting of at least one kind of oxide selected from oxides of M (Nb and Ta), and a fourth component consisting of an oxide of Si. The ceramic substantially containing no Mg. A composition of the ceramic is $0.10 \leq a/(a + b + c) \leq 0.40$, $0.30 \leq b/(a + b + c) \leq 0.50$, $0.20 < c/(a + b + c) \leq 0.50$, $0.84 \leq (a + b + c + e)/(d + f) \leq 1.16$, $1.0 \leq (e + f)/d \times 100 \leq 10.0$, and $g/d \times 100 \leq 0.6$, where a is the number of moles calculated for Sr of the first component as SrO, b is the number of moles calculated for Ba of the first component as BaO, c is the number of moles calculated for Ca of the first component as CaO, d is the number of moles calculated for Ti of the first component as TiO₂, e is the number of moles calculated for R of the second component as YO_{3/2}, CeO₂, PrO_{11/6}, TbO_{7/4} and RO_{3/2} (other lanthanoids) respectively, f is the number of moles calculated for M of the third component as NbO_{5/2} and TaO_{5/2} respectively, and g is the number of moles calculated for Si of the fourth component as SiO₂. A composite perovskite-based semiconductor varistor ceramic and a varistor may consist of at least one kind of Sr, Ba and Ca, and Ti, and have a surface provided with a compressive stress.