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TITLE OF THE INVENTION

Semiconductive Ceramics Having Negative Temperature
Coefficient of Resistance

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to semiconductive ceramics
having negative temperature coefficient of resistance.

Description of the Background Art

10 In general, an element for preventing an inrush current is
prepared from an element (NTC element) having negative
temperature coefficient of resistance, whose electric resistance
value decreases with a rise in temperature. This NTC element
suppresses an inrush current due to a high resistance value at
the room temperature, and thereafter increases in temperature
15 and decreases in resistance by self heating, to reduce power
consumption in a stationary state.

In a switching power source, for example, an inrush current
flows at the instant when a switch is turned on, and hence the
so-called NTC element is employed for absorbing such an initial
20 rush current. When the switch is turned on, therefore, the NTC
element suppresses the inrush current. The NTC element
thereafter increases in temperature and decreases in resistance
by self heating, to reduce power consumption in a stationary
state.

25 When a toothed wheel of a gear which is so formed that



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supply of lubricating oil is started upon starting of a motor is immediately rotated at a high speed by the motor, the lubricating oil is so insufficiently supplied that the toothed wheel may be damaged. When a lapping machine which is employed for grinding a surface of ceramics by rotating a grindstone is rotated at a high speed immediately upon starting of a driving motor, on the other hand, the ceramics may be cracked.

In order to solve each of the aforementioned problems, it is necessary to delay the starting of the motor for a constant period. The NTC element is employed as an element for delaying the starting of the motor in such a manner.

The NTC element reduces a terminal voltage of the motor in starting, whereby it is possible to delay the starting of the motor. Thereafter the NTC element increases in temperature and decreases in resistance by self heating, so that the motor is normally rotated in a stationary state.

The aforementioned element for preventing an inrush current or delaying motor starting is generally formed by an NTC element which is prepared from a transition metal oxide having a spinel structure.

However, the conventional NTC element has such a disadvantage that the rate of reduction in resistance (constant B) caused by a temperature rise cannot be more than 3200K. Therefore, the resistance value of the NTC element cannot be sufficiently reduced in a high-temperature state, and hence



power consumption inevitably increases in a stationary state. When the NTC element is in the form of a disk, for example, the resistance value in a high-temperature can be sufficiently reduced by enlarging its diameter or making its thickness
5 thinner. However, such a countermeasure is contradictory to requirement for miniaturization of an electronic component. Further, there are limits to thinning to satisfy the strength.

In relation to an improvement in this point, known is a multilayer NTC element which is prepared by stacking a plurality
10 of ceramics layers with interposition of a plurality of internal electrodes and forming a pair of external electrodes on side surfaces of the laminate for alternately electrically connecting the internal electrodes with the pair of external electrodes.

However, the internal electrodes which are opposed to each
15 other are so close to each other that the multilayer NTC element may be broken by a current exceeding several amperes.

The inventors have made various composition experiments and practical tests to deeply study materials showing negative temperature coefficient of resistance, and noted oxides of rare
20 earth transition elements. The rare earth transition element oxides have such characteristics that B constants increase and specific resistance decrease with temperature rises. Such characteristics are described in literature (Phys. Rev. B6, [3] 1021 (1972)) by V. G. Bhide and D. S. Rajoria.

25 Although these rare earth transition element oxides exhibit



small resistance value at a high temperature as compared with the conventional transitional metal oxides having a spinel structure, the same exhibit small B constant, with no provision of practical and meritorious effects.

5 SUMMARY OF THE INVENTION

The present invention has been proposed in order to solve the aforementioned problems, and an object thereof is to provide semiconductive ceramics having negative temperature coefficient of resistance with low resistivity and a high B constant in a stationary state, to enable feeding of a heavy current.

10 Provided according to the present invention is semiconductive ceramics having negative temperature coefficient of resistance, which is mainly composed of an oxide of a rare earth transition element excluding Ce and including Y, with addition of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce.

The rare earth transition element oxide, such as LaCoO_3 or SmNiO_3 , is not restricted in particular. LaCoO_3 exhibits such practical characteristics that its B constant extremely increases with a temperature rise, with small resistivity at the room temperature. Among rare earth elements, Ce is excluded since it is difficult to obtain an oxide with a transition metal. On the other hand, Y is included in the group of rare earth elements in the present invention since this element can attain characteristics and effects which are similar to those of the



rare earth elements.

According to the present invention, preferably 0.001 to 10 mole percent, more preferably 0.1 to 5 mole percent of the aforementioned additive is added to the main component.

5 It is possible to obtain a high B constant by adding at least 0.001 mole percent of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce to the main component of a rare earth transition element oxide, since the resistance value at a room temperature can be increased with maintaining low resistance
10 value at a high temperature. If the content of the additive exceeds 10 mole percent, however, the B constant at a high temperature is reduced below that of an NTC element which is composed of a transition metal oxide having a spinel structure. Therefore, the content of the additive is preferably set in a
15 range of 0.001 to 10 mole percent.

As to the rare earth transition element oxide, the mole ratio of a rare earth element to a transition element is not restricted to 1:1 but may be varied. Even if the mole ratio is varied within a range of 0.6 to 1.1, it is possible to obtain a B
20 constant which is substantially identical to that obtained at the mole ratio of 1:1. If the mole ratio is less than 0.6 or in excess of 1.1, however, power consumption in a stationary state so increases that the semiconductive ceramics cannot be applied to a circuit which is supplied with a heavy current, since the
25 resistance value will not decrease upon a temperature rise.



As hereinabove described, the inventive semiconductive ceramics having negative temperature coefficient of resistance is composed of a rare earth transition element oxide with addition of a prescribed element, whereby it is possible to obtain an
5 element having a high B constant at a high temperature, since the resistance value at a room temperature can be increased with maintaining low resistance value at a high temperature.

Therefore, it is possible to sufficiently reduce a resistance value in a temperature rise state for reducing power consumption
10 in a stationary state, so that the element can be applied to a circuit which is supplied with a heavy current.

Thus, the semiconductive ceramics according to the present invention is applicable to an NTC element for preventing an
15 inrush current in a switching power source which is supplied with a heavy current, or that for delaying motor starting.

While the semiconductive ceramics having negative temperature coefficient of resistance according to the present invention is applied to an element for preventing a rush current
20 or that for delaying motor starting, the present invention is not restricted to such application.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

25 BRIEF DESCRIPTION OF THE DRAWINGS



Fig. 1 is a characteristic diagram showing results of a test which was made by series-connecting an NTC element to a switching power source and measuring time change of a switching power source current upon power supply at a temperature of 25°C; and

5 Fig. 2 is a characteristic diagram showing relation between the number of times of a repetitive energization test and resistance values at a temperature of 25°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(Example 1)

10 This Example was carried out on a rare earth transition element oxide of LaCoO_3 .

First, LaCoO_3 powder materials were prepared in the following manner: Respective powder materials of Co_3O_4 and La_2O_3 were weighed so that La was at a mole ratio of 0.95 to Co.
15 Prescribed amounts of additives shown in Tables 1, 2 and 3 were added to the powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours. Referring to Table 1, asterisked (*) amounts are
20 out of the scope of the present invention.

Thus obtained calcined powder materials were pulverized by jet mills. Binders were added to the powder materials, which in turn were again wet-blended for 5 hours in ball mills employing nylon balls, filtered, dried and thereafter pressure-molded into
25 the form of disks. The disks were fired in the atmosphere at



1400°C for 2 hours, to obtain sintered bodies. Both major surfaces of the sintered bodies were coated with platinum paste by screen printing, and baked at 1000°C for 2 hours, to be provided with electrodes. NTC elements were thus obtained.

5 The NTC elements were subjected to measurement of electric characteristics of specific resistance values and B constants. Tables 1 to 3 as well as Tables 4 to 10 described later show resistivity values which were measured at a temperature of 25°C. Assuming that $\rho(T)$ and $\rho(T_0)$ represent resistivity values at
10 temperatures T and T_0 respectively and $\ln$ represents a natural logarithm, each B constant, which is a constant showing resistance change caused by temperature change, is defined as follows:

$$B(T) = [\ln \rho(T_0) - \ln \rho(T)] / (1/T_0 - 1/T)$$

15 Temperature change caused by the temperature increases with this value.

Referring to Tables 1, 2 and 3, the B constants at -10°C and 140°C are defined as follows:

20 B constant (-10°C) = $[\ln \rho(-10^\circ\text{C}) - \ln \rho(25^\circ\text{C})] / [1/(-10 + 273.15) - 1/(25 + 273.5)]$

B constant (140°C) = $[\ln \rho(25^\circ\text{C}) - \ln \rho(140^\circ\text{C})] / [1/(25 + 273.15) - 1/(140 + 273.5)]$

Figs. 1 and 2 show results of a repetitive energization test which was made on a sample according to Example 1, containing 1
25 mole percent of Zr. Fig. 1 shows the results of the test which



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was made by series-connecting an NTC element to a switching power source and measuring time change of a switching power source current upon power supply at a temperature of 25°C. Fig. 2 is a characteristic diagram showing relation between the number of
5 times of the repetitive energization test and resistance values at a temperature of 25°C. In this repetitive energization test, the NTC element was energized with a current for 1 minute and thereafter the power source was turned off for 30 minutes to cool the element to 25°C every cycle. As clearly understood from
10 Figs. 1 and 2, no characteristic change was recognized even after 10000 cycles. Further, no NTC element was broken when currents of 200 A were continuously applied to 100 NTC elements. Thus, it was confirmed that the inventive NTC element is applicable to a heavy current.

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Table 1

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-1	Zr	0 *	4.9	520	1590
1-2	Zr	0.0005*	8.4	890	2510
1-3	Zr	0.001	11.1	1220	3020
1-4	Zr	0.01	14.8	1650	3780
1-5	Zr	0.1	18.7	2150	4480
1-6	Zr	1	19.8	2620	4730
1-7	Zr	10	13.6	1600	3290
1-8	Zr	20*	4.7	790	1790

Table 2

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-9	Si	0.05	17.4	2010	4290
1-10	Mo	0.05	16.7	1820	4580
1-11	Sn	0.5	20.5	2400	4680
1-12	Sb	1	17.3	1970	4450
1-13	Te	1	20.2	2630	4530
1-14	Hf	5	18.4	2260	4310
1-15	Ta	5	17.5	2100	4570
1-16	W	10	16.4	1990	4320
1-17	Ce	10	17.0	2090	4480

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Table 3

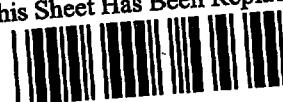
No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-18	Zr	0.05	19.6	2280	4230
	Mo	0.05			
1-19	Zr	1	18.3	2570	4550
	Sn	0.5			
1-20	Zr	0.05	17.8	2130	4510
	Sn	0.05			
	W	0.05			
1-21	Zr	1	16.2	2460	4290
	Mo	0.5			
	Ce	0.5			

(Example 2)

This Example was carried out on a rare earth transition element oxide of LaCrO_3 .

First, LaCrO_3 powder materials were prepared in the following manner: Respective powder materials of La_2O_3 and Cr_2O_3 were weighed so that Co was at a mole ratio of 0.95 to Cr. Additives shown in Table 4 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly



to Example 1, to obtain NTC elements.

Table 4 also shows results of respective electric characteristics of the as-obtained NTC elements, which were measured similarly to Example 1.

Table 4

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
2-1	Zr	1	19.1	2670	4060
2-2	Mo	1	20.0	2710	4320
2-3	Sb	1	18.9	2430	4070
2-4	Hf	0.5	16.8	2610	4150
2-5	Ta	0.5	18.3	2420	4270
2-6	Ce	0.5	20.0	2590	4010
2-7	Sb	1	18.2	2530	3970
	Hf	1			
2-8	Zr	0.05	17.0	2680	4190
	Ta	0.1			
2-9	Sn	0.5	16.1	2420	3870
	Ce	0.5			
2-10	Si	0.05	17.3	2700	4260
	Mo	0.05			
	W	0.1			

(Example 3)

This Example was carried out on a rare earth transition



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element oxide of SmNiO_3 .

First, SmNiO_3 powder materials were prepared in the following manner: Respective powder materials of Sm_2O_3 and NiO were weighed so that Sm was at a mole ratio of 0.95 to Ni.

5 Additives shown in Tables 5 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

10 Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 5 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.



Table 5

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
3-1	Zr	0.05	14.8	2240	3920
3-2	Mo	0.05	14.0	2340	3870
3-3	Sb	1	13.8	2290	3790
3-4	Hf	1	12.1	2150	3740
3-5	Ta	0.5	14.3	2230	3800
3-6	W	0.5	15.0	2090	3750
3-7	Sb	0.5	12.9	2410	3930
	Ce	0.5			
3-8	Zr	0.05	14.3	2060	3620
	Ta	0.05			
3-9	Sn	1	12.0	2220	3890
	W	1			
3-10	Si	0.1	13.7	2390	3990
	Mo	0.1			
	W	0.1			

(Example 4)

This Example was carried out on a rare earth transition element oxide of NdNiO_3 .

First, NdNiO_3 powder materials were prepared in the following manner: Respective powder materials of Nd_2O_3 and NiO were weighed so that Nd was at a mole ratio of 0.95 to Ni.



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Additives shown in Tables 6 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

5 Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 6 also shows results of respective electric characteristics of the obtained NTC elements, which were measured similarly to Example 1.

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Table 6

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
4-1	Si	0.5	24.3	2030	3860
4-2	Zr	0.5	24.0	2170	3790
4-3	Mo	5	25.8	2100	3910
4-4	Sn	5	24.1	2090	3730
4-5	Sb	1	23.6	2160	3850
4-6	Ce	1	22.6	2240	3930
4-7	Si	1	25.9	2120	3710
	Sn	1			
4-8	Zr	0.5	25.4	1990	3790
	W	0.5			
4-9	Mo	0.5	24.3	1970	3860
	Ta	0.5			
4-10	Zr	0.1	24.6	2080	3900
	Sn	0.1			
	Ta	0.1			

(Example 5)

This Example was carried out on a rare earth transition element oxide of PrNiO_3 .

First, PrNiO_3 powder materials were prepared in the following manner: Respective powder materials of Pr_6P_{11} and NiO were weighed so that Pr was at a mole ratio of 0.95 to Ni. Additives shown in Tables 7 were added to the weighed powder

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materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly
5 to Example 1, to obtain NTC elements.

Table 7 also shows results of respective electric characteristics of the obtained NTC elements, which were measured similarly to Example 1.



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Table 7

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
5-1	Zr	1	10.6	1960	3650
5-2	Mo	1	9.8	2100	3590
5-3	Sb	0.5	11.6	2060	3710
5-4	Te	0.5	8.9	1980	3690
5-5	Ta	0.05	10.3	2030	3740
5-6	W	0.05	12.0	2210	3820
5-7	Zr	1	9.7	2120	3640
	Hf	1			
5-8	Zr	0.5	9.6	1990	3630
	W	0.1			
5-9	Mo	0.1	11.3	1970	3670
	Sb	0.1			
5-10	Sb	0.5	10.2	2090	3710
	Hf	0.5			
	W	0.5			

(Example 6)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$.

First, respective powder materials of La_2O_3 , Nd_2O_3 and Co_3O_4 were weighed to obtain $\text{La}_{0.2}\text{Nd}_{0.1}\text{CoO}_3$ semiconductive ceramic materials. Additives shown in Tables 8 were added to the weighed powder materials, which in turn were wet-blended for 16



hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 8 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 8

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
6-1	Zr	0.5	26.1	1870	3630
6-2	Sb	1	25.7	1720	3690
6-3	W	5	26.4	1910	3590
6-4	Si	1	24.0	1860	3540
	Hf	1			
6-5	Zr	0.5	25.6	1790	3680
	Mo	0.5			
	Ta	0.5			

(Example 7)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$.

First, respective powder materials of La_2O_3 , Gd_2O_3 and



Co₃O₄ were weighed to obtain La_{0.2}Gd_{0.1}CoO₃ semiconductive ceramic materials. Additives shown in Tables 8 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 9 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 9

No.	Additional Element	Content (mol%)	Resistivity (Ω·cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
7-1	Sn	0.01	22.0	2010	3750
7-2	Ta	0.5	21.9	1960	3710
7-3	Ce	1	23.7	1840	3860
7-4	Zr	0.1	22.4	2020	3650
	Mo	0.1			
7-5	Zr	0.5	23.7	1970	3700
	Te	0.5			
	Hf	0.5			



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(Example 8)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.99}\text{Y}_{0.01}\text{MnO}_3$.

First, respective powder materials of La_2O_3 , Y_2O_3 and MnO were weighed to obtain $\text{La}_{0.99}\text{Y}_{0.01}\text{MnO}_3$ semiconductive ceramic materials. Additives shown in Tables 8 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 10 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.



Table 10

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
8-1	Sn	5	20.6	2190	3970
8-2	Mo	1	21.5	2290	3860
8-3	W	0.5	19.7	2200	3900
8-4	Sb	0.5	20.1	2260	3840
	Ta	0.5			
8-5	Zr	1	20.6	2270	3820
	Sb	1			
	Mo	1			

Although the aforementioned Examples were carried out on oxides of LaCoO_3 , LaCrO_3 , SmNiO_3 , NdNiO_3 and PrNiO_3 respectively, the present invention is also applicable to other rare earth transition element oxides, to attain similar effects.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.





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WHAT IS CLAIMED IS:

1. Semiconductive ceramics having negative temperature coefficient of resistance, being mainly composed of an oxide of a rare earth transition element excluding Ce and including Y, with
5 addition of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce.

2. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1, wherein
10 0.001 to 10 mole percent of said additive is added to said main component.

3. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1, wherein
15 0.1 to 5 mole percent of said additive is added to said main component.

4. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1, wherein
20 said rare earth transition element oxide is an oxide being selected from a group of respective oxides of LaCoO_3 , LaCrO_3 , LaMnO_3 , SmNiO_3 , NdNiO_3 and PrNiO_3 .

25 5. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 4, wherein





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said rare earth transition element oxide of LaCoO_3 is
 $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$.

6. Semiconductive ceramics having negative temperature
5 coefficient of resistance in accordance with claim 4, wherein
said rare earth transition element oxide of LaCoO_3 is
 $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$.

7. Semiconductive ceramics having negative temperature
10 coefficient of resistance in accordance with claim 4, wherein
said rare earth transition element oxide of LaCoO_3 is
 $\text{La}_{0.99}\text{Y}_{0.01}\text{CoO}_3$.

8. Semiconductive ceramics having negative temperature
15 coefficient of resistance in accordance with claim 1, being
applied to an element for preventing a rush current.

9. Semiconductive ceramics having negative temperature
coefficient of resistance in accordance with claim 1, being
20 applied to an element for delaying motor starting.

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ABSTRACT OF THE DISCLOSURE

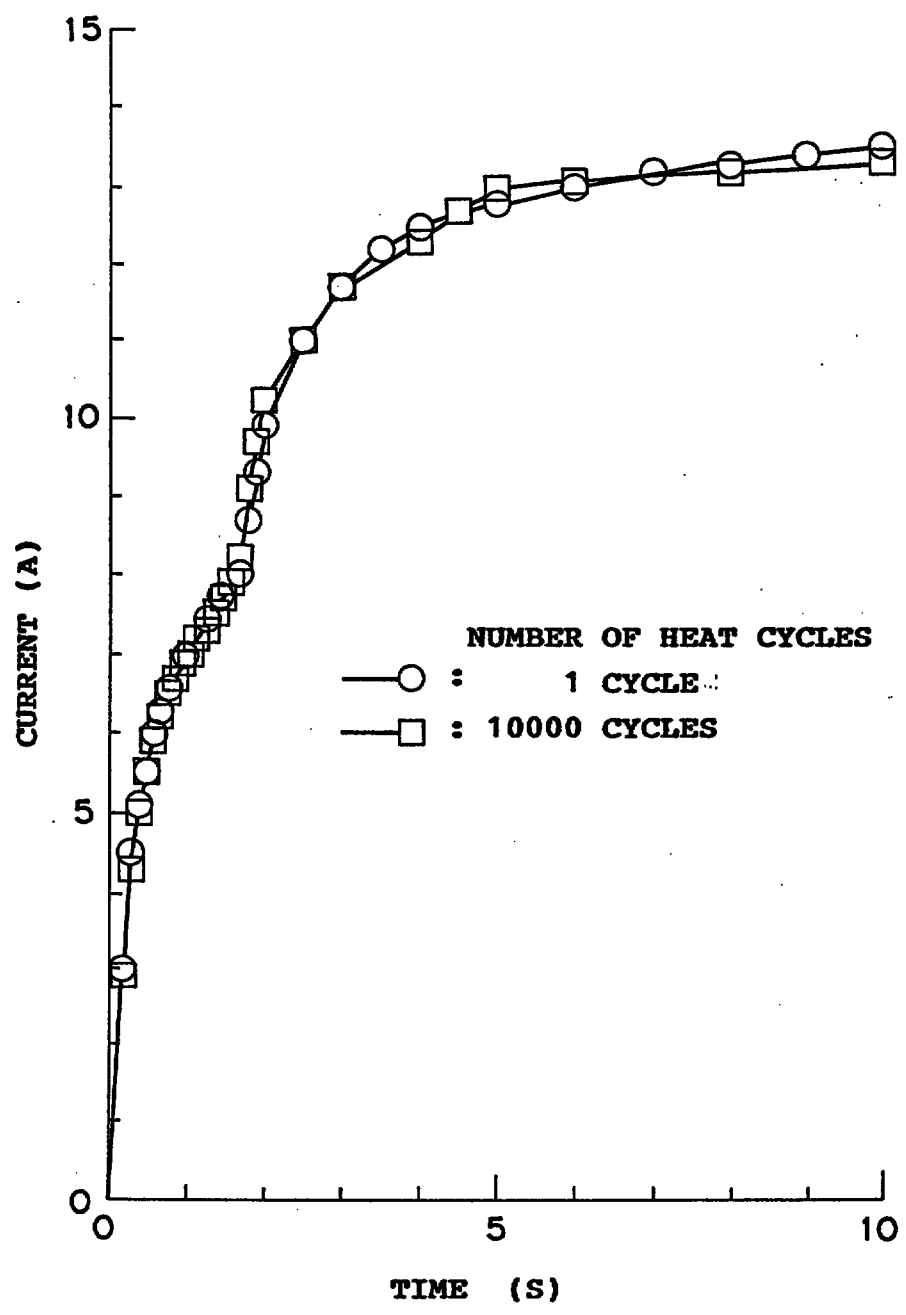
Semiconductive ceramics having negative temperature
coefficient of resistance, which is mainly composed of an oxide of
a rare earth transition element excluding Ce and including Y,
5 with addition of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te
and Ce.

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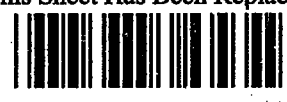


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FIG. 1

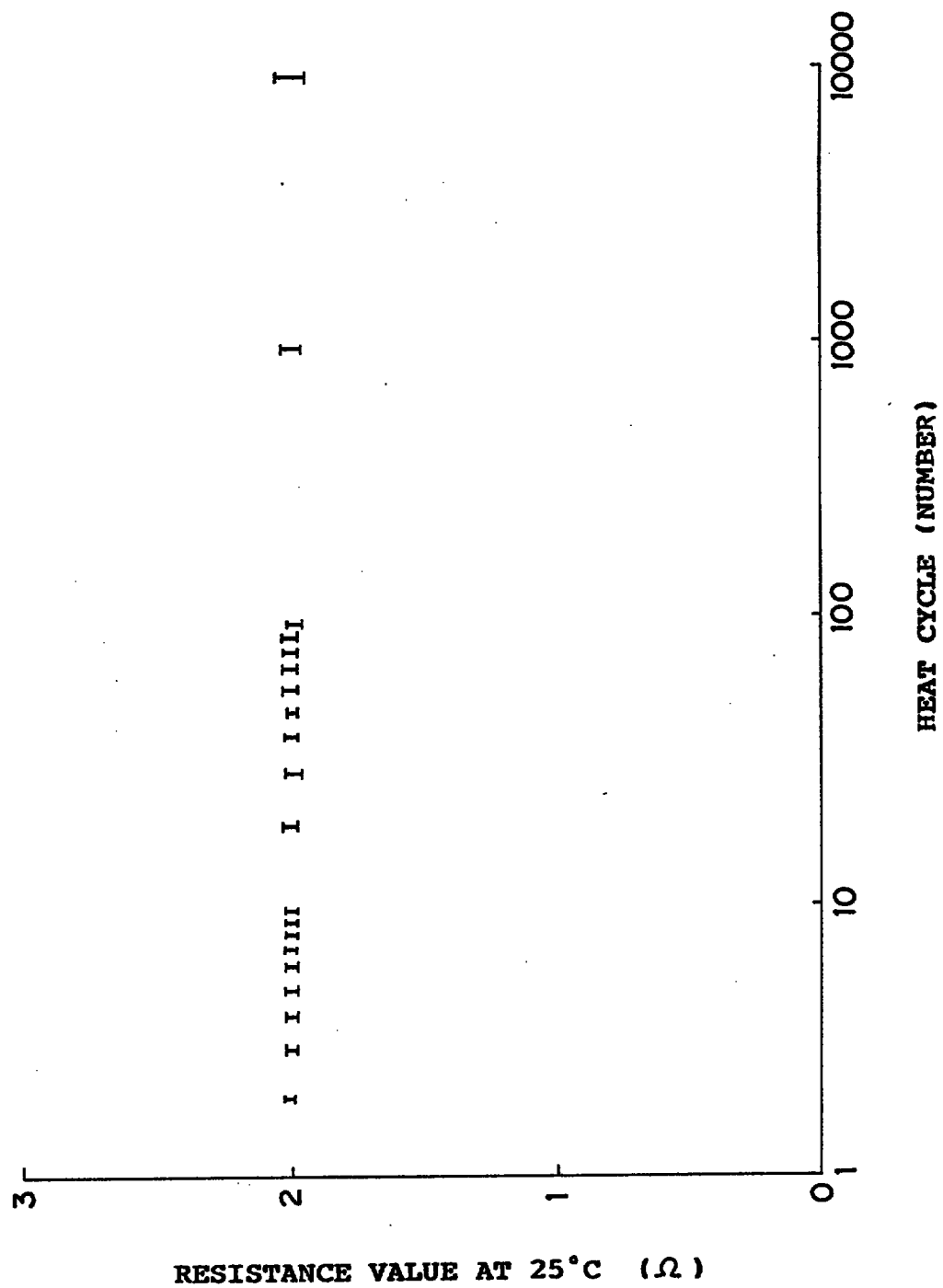


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FIG. 2



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TITLE OF THE INVENTION

Semiconductive Ceramics Having Negative Temperature
Coefficient of Resistance

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to semiconductive ceramics having negative temperature coefficient of resistance.

Description of the Background Art

In general, an element for preventing an inrush current is prepared from an element (NTC element) having negative temperature coefficient of resistance, whose electric resistance value decreases with a rise in temperature. This NTC element suppresses an inrush current due to a high resistance value at the room temperature, and thereafter increases in temperature and decreases in resistance by self heating, to reduce power consumption in a stationary state.

In a switching power source, for example, an inrush current flows at the instant when a switch is turned on, and hence the so-called NTC element is employed for absorbing such an initial rush current. When the switch is turned on, therefore, the NTC element suppresses the inrush current. The NTC element thereafter increases in temperature and decreases in resistance by self heating, to reduce power consumption in a stationary state.

When a toothed wheel of a gear which is so formed that

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supply of lubricating oil is started upon starting of a motor is immediately rotated at a high speed by the motor, the lubricating oil is so insufficiently supplied that the toothed wheel may be damaged. When a lapping machine which is employed for grinding a surface of ceramics by rotating a grindstone is rotated at a high speed immediately upon starting of a driving motor, on the other hand, the ceramics may be cracked.

In order to solve each of the aforementioned problems, it is necessary to delay the starting of the motor for a constant period. The NTC element is employed as an element for delaying the starting of the motor in such a manner.

The NTC element reduces a terminal voltage of the motor in starting, whereby it is possible to delay the starting of the motor. Thereafter the NTC element increases in temperature and decreases in resistance by self heating, so that the motor is normally rotated in a stationary state.

The aforementioned element for preventing an inrush current or delaying motor starting is generally formed by an NTC element which is prepared from a transition metal oxide having a spinel structure.

However, the conventional NTC element has such a disadvantage that the rate of reduction in resistance (constant B) caused by a temperature rise cannot be more than 3200K. Therefore, the resistance value of the NTC element cannot be sufficiently reduced in a high-temperature state, and hence

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power consumption inevitably increases in a stationary state. When the NTC element is in the form of a disk, for example, the resistance value in a high-temperature can be sufficiently reduced by enlarging its diameter or making its thickness thinner. However, such a countermeasure is contradictory to requirement for miniaturization of an electronic component. Further, there are limits to thinning to satisfy the strength.

In relation to an improvement in this point, known is a multilayer NTC element which is prepared by stacking a plurality of ceramics layers with interposition of a plurality of internal electrodes and forming a pair of external electrodes on side surfaces of the laminate for alternately electrically connecting the internal electrodes with the pair of external electrodes.

However, the internal electrodes which are opposed to each other are so close to each other that the multilayer NTC element may be broken by a current exceeding several amperes.

The inventors have made various composition experiments and practical tests to deeply study materials showing negative temperature coefficient of resistance, and noted oxides of rare earth transition elements. The rare earth transition element oxides have such characteristics that B constants increase and specific resistance decrease with temperature rises. Such characteristics are described in literature (Phys. Rev. B6, [3] 1021 (1972)) by V. G. Bhide and D. S. Rajoria.

Although these rare earth transition element oxides exhibit

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small resistance value at a high temperature as compared with the conventional transitional metal oxides having a spinel structure, the same exhibit small B constant, with no provision of practical and meritorious effects.

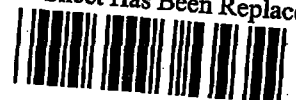
SUMMARY OF THE INVENTION

The present invention has been proposed in order to solve the aforementioned problems, and an object thereof is to provide semiconductive ceramics having negative temperature coefficient of resistance with low resistivity and a high B constant in a stationary state, to enable feeding of a heavy current.

Provided according to the present invention is semiconductive ceramics having negative temperature coefficient of resistance, which is mainly composed of an oxide of a rare earth transition element excluding Ce and including Y, with addition of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce.

The rare earth transition element oxide, such as LaCoO_3 or SmNiO_3 , is not restricted in particular. LaCoO_3 exhibits such practical characteristics that its B constant extremely increases with a temperature rise, with small resistivity at the room temperature. Among rare earth elements, Ce is excluded since it is difficult to obtain an oxide with a transition metal. On the other hand, Y is included in the group of rare earth elements in the present invention since this element can attain characteristics and effects which are similar to those of the

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rare earth elements.

According to the present invention, preferably 0.001 to 10 mole percent, more preferably 0.1 to 5 mole percent of the aforementioned additive is added to the main component.

It is possible to obtain a high B constant by adding at least 0.001 mole percent of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce to the main component of a rare earth transition element oxide, since the resistance value at a room temperature can be increased with maintaining low resistance value at a high temperature. If the content of the additive exceeds 10 mole percent, however, the B constant at a high temperature is reduced below that of an NTC element which is composed of a transition metal oxide having a spinel structure. Therefore, the content of the additive is preferably set in a range of 0.001 to 10 mole percent.

As to the rare earth transition element oxide, the mole ratio of a rare earth element to a transition element is not restricted to 1:1 but may be varied. Even if the mole ratio is varied within a range of 0.6 to 1.1, it is possible to obtain a B constant which is substantially identical to that obtained at the mole ratio of 1:1. If the mole ratio is less than 0.6 or in excess of 1.1, however, power consumption in a stationary state so increases that the semiconductive ceramics cannot be applied to a circuit which is supplied with a heavy current, since the resistance value will not decrease upon a temperature rise.

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As hereinabove described, the inventive semiconductive ceramics having negative temperature coefficient of resistance is composed of a rare earth transition element oxide with addition of a prescribed element, whereby it is possible to obtain an element having a high B constant at a high temperature, since the resistance value at a room temperature can be increased with maintaining low resistance value at a high temperature. Therefore, it is possible to sufficiently reduce a resistance value in a temperature rise state for reducing power consumption in a stationary state, so that the element can be applied to a circuit which is supplied with a heavy current.

Thus, the semiconductive ceramics according to the present invention is applicable to an NTC element for preventing an inrush current in a switching power source which is supplied with a heavy current, or that for delaying motor starting.

While the semiconductive ceramics having negative temperature coefficient of resistance according to the present invention is applied to an element for preventing a rush current or that for delaying motor starting, the present invention is not restricted to such application.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

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Fig. 1 is a characteristic diagram showing results of a test which was made by series-connecting an NTC element to a switching power source and measuring time change of a switching power source current upon power supply at a temperature of 25°C; and

Fig. 2 is a characteristic diagram showing relation between the number of times of a repetitive energization test and resistance values at a temperature of 25°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(Example 1)

This Example was carried out on a rare earth transition element oxide of LaCoO_3 .

First, LaCoO_3 powder materials were prepared in the following manner: Respective powder materials of Co_3O_4 and La_2O_3 were weighed so that La was at a mole ratio of 0.95 to Co. Prescribed amounts of additives shown in Tables 1, 2 and 3 were added to the powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours. Referring to Table 1, asterisked (*) amounts are out of the scope of the present invention.

Thus obtained calcined powder materials were pulverized by jet mills. Binders were added to the powder materials, which in turn were again wet-blended for 5 hours in ball mills employing nylon balls, filtered, dried and thereafter pressure-molded into the form of disks. The disks were fired in the atmosphere at

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1400°C for 2 hours, to obtain sintered bodies. Both major surfaces of the sintered bodies were coated with platinum paste by screen printing, and baked at 1000°C for 2 hours, to be provided with electrodes. NTC elements were thus obtained.

The NTC elements were subjected to measurement of electric characteristics of specific resistance values and B constants. Tables 1 to 3 as well as Tables 4 to 10 described later show resistivity values which were measured at a temperature of 25°C. Assuming that $\rho(T)$ and $\rho(T_0)$ represent resistivity values at temperatures T and T_0 respectively and $\ln$ represents a natural logarithm, each B constant, which is a constant showing resistance change caused by temperature change, is defined as follows:

$$B(T) = [\ln \rho(T_0) - \ln \rho(T)] / (1/T_0 - 1/T)$$

Temperature change caused by the temperature increases with this value.

Referring to Tables 1, 2 and 3, the B constants at -10°C and 140°C are defined as follows:

$$B \text{ constant } (-10^\circ\text{C}) = [\ln \rho(-10^\circ\text{C}) - \ln \rho(25^\circ\text{C})] / [1/(-10 + 273.15) - 1/(25 + 273.5)]$$

$$B \text{ constant } (140^\circ\text{C}) = [\ln \rho(25^\circ\text{C}) - \ln \rho(140^\circ\text{C})] / [1/(25 + 273.15) - 1/(140 + 273.5)]$$

Figs. 1 and 2 show results of a repetitive energization test which was made on a sample according to Example 1, containing 1 mole percent of Zr. Fig. 1 shows the results of the test which

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was made by series-connecting an NTC element to a switching power source and measuring time change of a switching power source current upon power supply at a temperature of 25°C. Fig. 2 is a characteristic diagram showing relation between the number of times of the repetitive energization test and resistance values at a temperature of 25°C. In this repetitive energization test, the NTC element was energized with a current for 1 minute and thereafter the power source was turned off for 30 minutes to cool the element to 25°C every cycle. As clearly understood from Figs. 1 and 2, no characteristic change was recognized even after 10000 cycles. Further, no NTC element was broken when currents of 200 A were continuously applied to 100 NTC elements. Thus, it was confirmed that the inventive NTC element is applicable to a heavy current.

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Table 1

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-1	Zr	0 *	4.9	520	1590
1-2	Zr	0.0005*	8.4	890	2510
1-3	Zr	0.001	11.1	1220	3020
1-4	Zr	0.01	14.8	1650	3780
1-5	Zr	0.1	18.7	2150	4480
1-6	Zr	1	19.8	2620	4730
1-7	Zr	10	13.6	1600	3290
1-8	Zr	20*	4.7	790	1790

Table 2

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-9	Si	0.05	17.4	2010	4290
1-10	Mo	0.05	16.7	1820	4580
1-11	Sn	0.5	20.5	2400	4680
1-12	Sb	1	17.3	1970	4450
1-13	Te	1	20.2	2630	4530
1-14	Hf	5	18.4	2260	4310
1-15	Ta	5	17.5	2100	4570
1-16	W	10	16.4	1990	4320
1-17	Ce	10	17.0	2090	4480

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Table 3

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-18	Zr	0.05	19.6	2280	4230
	Mo	0.05			
1-19	Zr	1	18.3	2570	4550
	Sn	0.5			
1-20	Zr	0.05	17.8	2130	4510
	Sn	0.05			
	W	0.05			
1-21	Zr	1	16.2	2460	4290
	Mo	0.5			
	Ce	0.5			

(Example 2)

This Example was carried out on a rare earth transition element oxide of LaCrO_3 .

First, LaCrO_3 powder materials were prepared in the following manner: Respective powder materials of La_2O_3 and Cr_2O_3 were weighed so that Co was at a mole ratio of 0.95 to Cr. Additives shown in Table 4 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly

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to Example 1, to obtain NTC elements.

Table 4 also shows results of respective electric characteristics of the as-obtained NTC elements, which were measured similarly to Example 1.

Table 4

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
2-1	Zr	1	19.1	2670	4060
2-2	Mo	1	20.0	2710	4320
2-3	Sb	1	18.9	2430	4070
2-4	Hf	0.5	16.8	2610	4150
2-5	Ta	0.5	18.3	2420	4270
2-6	Ce	0.5	20.0	2590	4010
2-7	Sb	1	18.2	2530	3970
	Hf	1			
2-8	Zr	0.05	17.0	2680	4190
	Ta	0.1			
2-9	Sn	0.5	16.1	2420	3870
	Ce	0.5			
2-10	Si	0.05	17.3	2700	4260
	Mo	0.05			
	W	0.1			

(Example 3)

This Example was carried out on a rare earth transition

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element oxide of SmNiO_3 .

First, SmNiO_3 powder materials were prepared in the following manner: Respective powder materials of Sm_2O_3 and NiO were weighed so that Sm was at a mole ratio of 0.95 to Ni. Additives shown in Tables 5 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 5 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

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Table 5

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
3-1	Zr	0.05	14.8	2240	3920
3-2	Mo	0.05	14.0	2340	3870
3-3	Sb	1	13.8	2290	3790
3-4	Hf	1	12.1	2150	3740
3-5	Ta	0.5	14.3	2230	3800
3-6	W	0.5	15.0	2090	3750
3-7	Sb	0.5	12.9	2410	3930
	Ce	0.5			
3-8	Zr	0.05	14.3	2060	3620
	Ta	0.05			
3-9	Sn	1	12.0	2220	3890
	W	1			
3-10	Si	0.1	13.7	2390	3990
	Mo	0.1			
	W	0.1			

(Example 4)

This Example was carried out on a rare earth transition element oxide of NdNiO_3 .

First, NdNiO_3 powder materials were prepared in the following manner: Respective powder materials of Nd_2O_3 and NiO were weighed so that Nd was at a mole ratio of 0.95 to Ni.

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Additives shown in Tables 6 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 6 also shows results of respective electric characteristics of the obtained NTC elements, which were measured similarly to Example 1.

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Table 6

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
4-1	Si	0.5	24.3	2030	3860
4-2	Zr	0.5	24.0	2170	3790
4-3	Mo	5	25.8	2100	3910
4-4	Sn	5	24.1	2090	3730
4-5	Sb	1	23.6	2160	3850
4-6	Ce	1	22.6	2240	3930
4-7	Si	1	25.9	2120	3710
	Sn	1			
4-8	Zr	0.5	25.4	1990	3790
	W	0.5			
4-9	Mo	0.5	24.3	1970	3860
	Ta	0.5			
4-10	Zr	0.1	24.6	2080	3900
	Sn	0.1			
	Ta	0.1			

(Example 5)

This Example was carried out on a rare earth transition element oxide of PrNiO_3 .

First, PrNiO_3 powder materials were prepared in the following manner: Respective powder materials of Pr_6P_{11} and NiO were weighed so that Pr was at a mole ratio of 0.95 to Ni.

Additives shown in Tables 7 were added to the weighed powder



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materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 7 also shows results of respective electric characteristics of the obtained NTC elements, which were measured similarly to Example 1.

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Table 7

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
5-1	Zr	1	10.6	1960	3650
5-2	Mo	1	9.8	2100	3590
5-3	Sb	0.5	11.6	2060	3710
5-4	Te	0.5	8.9	1980	3690
5-5	Ta	0.05	10.3	2030	3740
5-6	W	0.05	12.0	2210	3820
5-7	Zr	1	9.7	2120	3640
	Hf	1			
5-8	Zr	0.5	9.6	1990	3630
	W	0.1			
5-9	Mo	0.1	11.3	1970	3670
	Sb	0.1			
5-10	Sb	0.5	10.2	2090	3710
	Hf	0.5			
	W	0.5			

(Example 6)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$.

First, respective powder materials of La_2O_3 , Nd_2O_3 and Co_3O_4 were weighed to obtain $\text{La}_{0.2}\text{Nd}_{0.1}\text{CoO}_3$ semiconductive ceramic materials. Additives shown in Tables 8 were added to the weighed powder materials, which in turn were wet-blended for 16

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hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 8 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 8

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
6-1	Zr	0.5	26.1	1870	3630
6-2	Sb	1	25.7	1720	3690
6-3	W	5	26.4	1910	3590
6-4	Si	1	24.0	1860	3540
	Hf	1			
6-5	Zr	0.5	25.6	1790	3680
	Mo	0.5			
	Ta	0.5			

(Example 7)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$.

First, respective powder materials of La_2O_3 , Gd_2O_3 and



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Co_3O_4 were weighed to obtain $\text{La}_{0.2}\text{Gd}_{0.1}\text{CoO}_3$ semiconductive ceramic materials. Additives shown in Tables 8 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 9 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 9

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
7-1	Sn	0.01	22.0	2010	3750
7-2	Ta	0.5	21.9	1960	3710
7-3	Ce	1	23.7	1840	3860
7-4	Zr	0.1	22.4	2020	3650
	Mo	0.1			
7-5	Zr	0.5	23.7	1970	3700
	Te	0.5			
	Hf	0.5			

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(Example 8)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.99}\text{Y}_{0.01}\text{MnO}_3$.

First, respective powder materials of La_2O_3 , Y_2O_3 and MnO were weighed to obtain $\text{La}_{0.99}\text{Y}_{0.01}\text{MnO}_3$ semiconductive ceramic materials. Additives shown in Tables 8 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 10 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

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Table 10

No.	Additional Element	Content (mol%)	Resistivity ($\Omega \cdot \text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
8-1	Sn	5	20.6	2190	3970
8-2	Mo	1	21.5	2290	3860
8-3	W	0.5	19.7	2200	3900
8-4	Sb	0.5	20.1	2260	3840
	Ta	0.5			
8-5	Zr	1	20.6	2270	3820
	Sb	1			
	Mo	1			

Although the aforementioned Examples were carried out on oxides of LaCoO_3 , LaCrO_3 , SmNiO_3 , NdNiO_3 and PrNiO_3 respectively, the present invention is also applicable to other rare earth transition element oxides, to attain similar effects.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

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WHAT IS CLAIMED IS:

1. Semiconductive ceramics having negative temperature coefficient of resistance, being mainly composed of an oxide of a rare earth transition element excluding Ce and including Y, with addition of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce.

2. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1, wherein 0.001 to 10 mole percent of said additive is added to said main component.

3. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1, wherein 0.1 to 5 mole percent of said additive is added to said main component.

4. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1, wherein said rare earth transition element oxide is an oxide being selected from a group of respective oxides of LaCoO_3 , LaCrO_3 , LaMnO_3 , SmNiO_3 , NdNiO_3 and PrNiO_3 .

5. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 4, wherein

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said rare earth transition element oxide of LaCoO_3 is
 $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$.

6. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 4, wherein said rare earth transition element oxide of LaCoO_3 is
 $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$.

7. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 4, wherein said rare earth transition element oxide of LaCoO_3 is
 $\text{La}_{0.99}\text{Y}_{0.01}\text{CoO}_3$.

8. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1, being applied to an element for preventing a rush current.

9. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1, being applied to an element for delaying motor starting.

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SEMICONDUCTIVE CERAMICS HAVING NEGATIVE
TEMPERATURE COEFFICIENT OF RESISTANCE

ABSTRACT OF THE DISCLOSURE

Semiconductive ceramics having negative temperature coefficient of resistance, which is mainly composed of an oxide of a rare earth transition element excluding Ce and including Y, with addition of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce.

FIGURE 1

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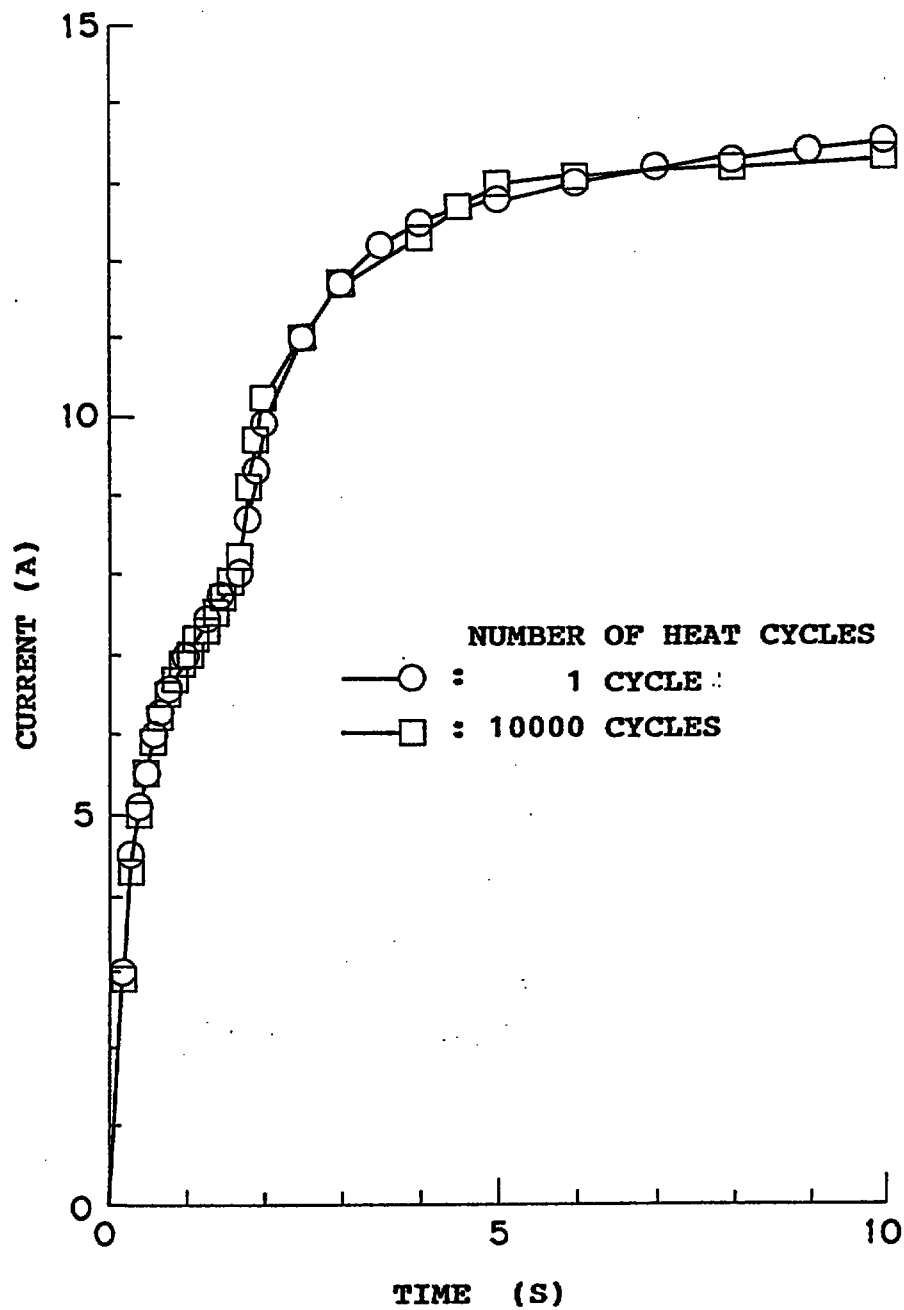
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FIG. 1



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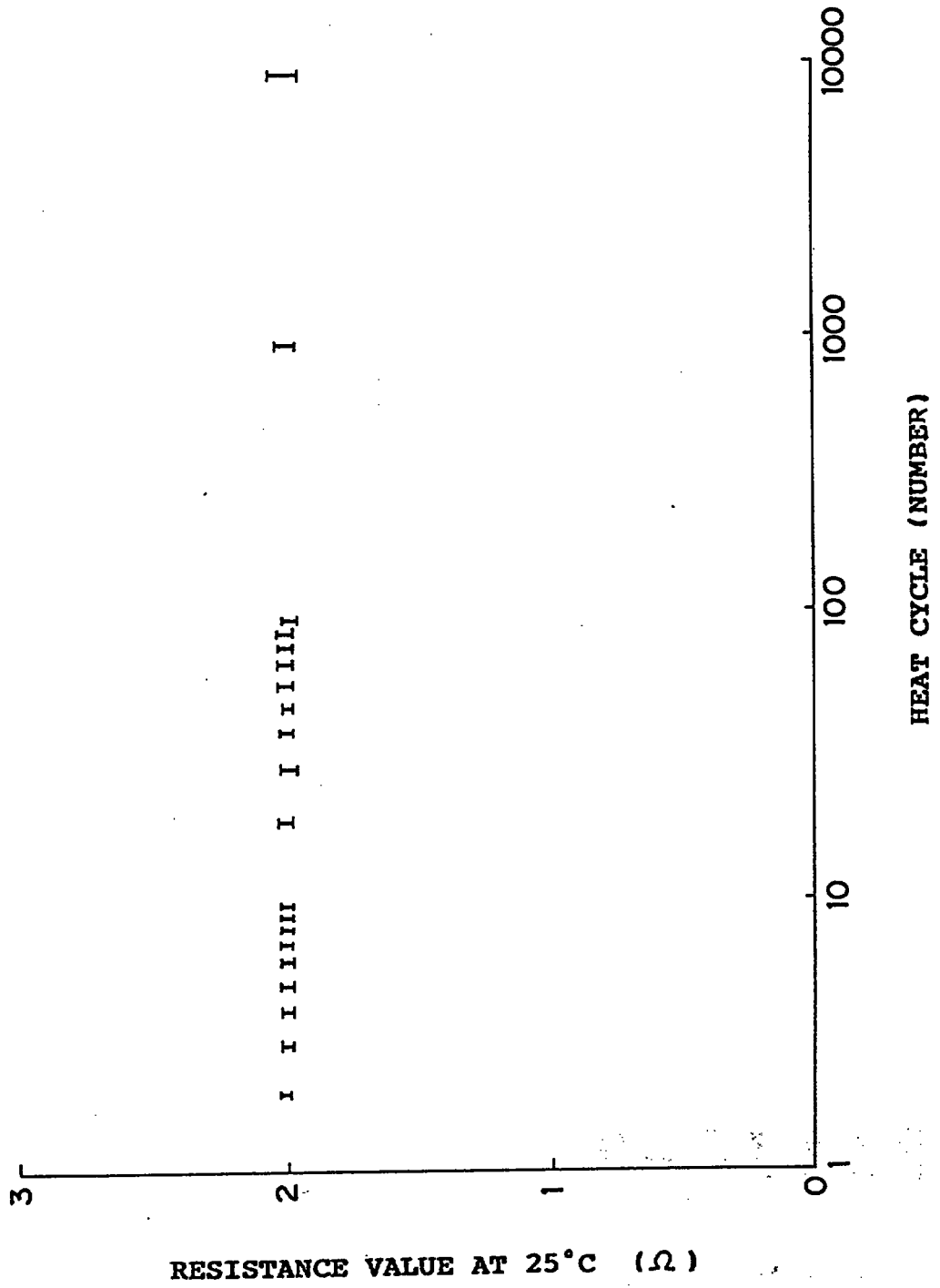


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FIG. 2





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CLAIMS:

1. Semiconductive ceramics having negative temperature coefficient of resistance, being mainly composed of an oxide which contains as main ingredients a rare earth material of the group IIIa excluding Ce and including Y and a transition element excluding Cr, with addition of at least one of Si, Zr, Hf, Ta and Ce in a range of 0.001 to 5 mole percent.
2. Semiconductive ceramics having negative temperature coefficient of resistance, being mainly composed of an oxide which contains as main ingredients a rare earth material of the group IIIa excluding Ce and including Y and a transition element excluding Cr, with addition of at least one of Sn, Sb, W, Mo or Te in a range of 0.001 to 5 mole percent.
3. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, wherein said oxide is at least one selected from LaCoO_3 , LaMnO_3 , SmNiO_3 , NdNiO_3 and PrNiO_3 .
4. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, wherein 0.1 to 5 mole percent of said additive is added to said main component.
5. Semiconductive ceramics having negative temperature coefficient resistance in accordance with claim 3, wherein said oxide of LaCoO_3 is $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$.
6. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 3, wherein said oxide of LaCoO_3 is $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$.
7. Semiconductive ceramics having negative temperature

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coefficient of resistance in accordance with claim 3, wherein
said oxide of LaCoO_3 is $\text{La}_{0.99}\text{Y}_{0.01}\text{CoO}_3$.

8. Semiconductive ceramics having negative temperature
coefficient of resistance in accordance with claim 1 or 2,
being applied to an element for preventing a rush current.

9. Semiconductive ceramics having negative temperature
coefficient of resistance in accordance with claim 1 or 2,
being applied to an element for delaying motor starting.

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SEMICONDUCTIVE CERAMICS HAVING NEGATIVE TEMPERATURE COEFFICIENT OF RESISTANCE

Description

The present invention relates to semiconductive ceramics having negative temperature coefficient of resistance.

In general, an element for preventing an inrush current is prepared from an element (NTC element) having negative temperature coefficient of resistance, whose electric resistance value decreases with a rise in temperature. This NTC element suppresses an inrush current due to a high resistance value at the room temperature, and thereafter increases in temperature and decreases in resistance by self heating, to reduce power consumption in a stationary state.

In a switching power source, for example, an inrush current flows at the instant when a switch is turned on, and hence the so-called NTC element is employed for absorbing such an initial rush current. When the switch is turned on, therefore, the NTC element suppresses the inrush current. The NTC element thereafter increases in temperature and decreases in resistance by self heating, to reduce power consumption in a stationary state.

When a toothed wheel of a gear which is so formed that supply of lubricating oil is started upon starting of a motor is immediately rotated at a high speed by the motor, the lubricating oil is so insufficiently supplied that the toothed wheel may be damaged. When a lapping machine which is employed for grinding a surface of ceramics by rotating a grindstone is rotated at a high speed immediately upon starting of a driving motor, on the other hand, the ceramics may be cracked.

In order to solve each of the aforementioned problems, it is necessary to delay the starting of the motor for a constant period. The NTC element is employed as an element for delaying the starting of the motor in such a manner.

The NTC element reduces a terminal voltage of the motor in starting, whereby it is possible to delay the starting of the motor. Thereafter the NTC element increases in temperature and decreases in resistance by self heating, so that the motor is normally rotated in a stationary state.

The aforementioned element for preventing an inrush current or delaying motor starting is generally formed by an NTC element which is prepared from a transition metal oxide having a spinel structure.

However, the conventional NTC element has such a disadvantage that the rate of reduction in resistance (constant B) caused by a temperature rise cannot be more than 3200K. Therefore, the resistance value of the NTC element cannot be sufficiently reduced in a high-temperature state, and hence power consumption inevitably increases in a stationary state. When the NTC element is in the form of a disk, for example, the resistance value in a high-temperature can be sufficiently reduced by enlarging its diameter or making its thickness thinner. However, such a countermeasure is contradictory to requirement for miniaturization of an electronic component. Further, there are limits to thinning to satisfy the strength.

In relation to an improvement in this point, known is a multilayer NTC element which is prepared by stacking a plurality of ceramics layers with interposition of a plurality of internal electrodes and forming a pair of external electrodes on side surfaces of the laminate for alternately electrically connecting the internal electrodes with the pair of external electrodes.

However, the internal electrodes which are opposed to each other are so close to each other that the multilayer NTC element may be broken by a current exceeding several amperes.

The inventors have made various composition experiments and practical tests to deeply study materials showing negative temperature coefficient of resistance, and noted oxides of rare earth transition elements. The rare earth transition element oxides have such characteristics that B constants increase and specific resistance decrease with temperature rises. Such characteristics are described in literature (Phys. Rev. B6, [3] 1021 (1972)) by V. G. Bhide and D. S. Rajoria.

Although these rare earth transition element oxides exhibit small resistance value at a high temperature as compared with the conventional transitional metal oxides having a spinel structure, the same exhibit small B constant, with no provision of practical and meritorious effects.

US-A-4,013,592 relates to a high temperature thermistor composition which comprises a spinel-type $MgAl_2O_4$ and perovskite-type $LaCrO_3$ or $(La,Sr)CrO_3$. The composition is usable for the temperature range from 400°C to 600°C. Further, a high temperature thermistor composition is disclosed which comprises spinel-type solid solution $Mg(Al,Cr)_2O_4$ and perovskite-type solid solution $(La,Sr)CrO_3$ or $LaCrO_3$. Such a composition is usable for a higher temperature range of up to 1000°C.

EP-A-0623569 relates to a ceramic composition for a thermistor element. The composition is used for a thermistor exhibiting a stable resistance value over a wide temperature range and is capable of being used for a prolonged time. The composition is represented by the formula $(M^1M^2O_2)_{1-x} \cdot M^1AlO_3)_x$ wherein M^1 is an element selected from the elements of the group 3A excluding La and M^2 is an element of the groups 4A, 5A, 6A, 7A and 8. The composition may be $YCrO_3$ to which 1 weight percent SiO_2 is added.

EP-A-0626356 concerns a ceramic composition of the formula $(M^1_{1-x} \cdot N^1_x)(P^2_{1-y-x} \cdot N^2_y \cdot Al_2)O_3$ where M^1 is one or more selected from the group 3A elements of the periodic table excluding La, N^1 is one or more selected from the group 2A elements of the periodic table, P^2 is one or more selected from the elements from the groups 4A, 5A, 6A, 7A and 8 of the periodic table whose oxides exhibit p-characteristics, and N^2 is one or more selected from the elements

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of the groups 4A, 5A, 6A, 7A and 8 whose oxides exhibit n-characteristics. The composition may be $Y(Cr_{0.8}Fe_{0.2}Al_{0.2})O_3$ to which SiO_2 is added.

JP-A-56125803 concerns a thermistor having a ceramic resistance body consisting of $LaCo_{1-x}V_xO_3$ in which x is 0.05-0.4. The ceramic contains an oxide of a rare earth element (La_2O_3) and oxides of transition elements (CoO and V_2O_5).

JP-A-1290549 concerns an oxide semiconductor composition for a negative temperature coefficient thermistor. This composition mainly contains an oxide of a rare earth element (La) and oxides for transition elements (Co, Mn).

It is the object of the present invention to provide semiconductive ceramics having negative temperature coefficients of resistance with low resistivity and a high B constant in a stationary state, to enable feeding of a heavy current.

This object is achieved by semiconductive ceramics according to claim 1 and claim 2.

The rare earth transition element oxide, such as $LaCoO_3$ or $SmNiO_3$, is not restricted in particular. $LaCoO_3$ exhibits such practical characteristics that its B constant extremely increases with a temperature rise, with high resistivity at the room temperature. Among rare earth elements, Ce is excluded since it is difficult to obtain an oxide with a transition metal. On the other hand, Y is included in the group of rare earth elements in the present invention since this element can attain characteristics and effects which are similar to those of the rare earth elements.

According to the present invention, 0.001 to 5 mole percent of the aforementioned additive is added to the main component.

It is possible to obtain a high B constant by adding at least 0.001 mole percent of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce to the main component of a rare earth transition element oxide, since the resistance value at a room temperature can be increased with maintaining low resistance value at a high temperature. If the content of the additive exceeds 10 mole percent, however, the B constant at a high temperature is reduced below that of an NTC element which is composed of a transition metal oxide having a spinel structure. The content of the additive is set in a range of 0.001 to 5 mole percent.

As to the rare earth transition element oxide, the mole ratio of the rare earth element to the transition element is not restricted to 1:1 but may be varied. Even if the mole ratio is varied within a range of 0.6 to 1.1, it is possible to obtain a B constant which is substantially identical to that obtained at the mole ratio of 1:1. If the mole ratio is less than 0.6 or in excess of 1.1, however, power consumption in a stationary state so increases that the semiconductive ceramics cannot be applied to a circuit which is supplied with a heavy current, since the resistance value will not decrease upon a temperature rise.

As hereinabove described, the inventive semiconductive ceramics having negative temperature coefficient of resistance is composed of a rare earth transition element oxide with addition of a prescribed element, whereby it is possible to obtain an element having a high B constant at a high temperature, since the resistance value at room temperature can be increased with maintaining low resistance value at a high temperature. Therefore, it is possible to sufficiently reduce the resistance value in a temperature rise state for reducing power consumption in a stationary state, so that the element can be applied to a circuit which is supplied with a heavy current.

Thus, the semiconductive ceramics according to the present invention is applicable to an NTC element for preventing an inrush current in a switching power source which is supplied with a heavy current, or that for delaying motor starting.

While the semiconductive ceramics having negative temperature coefficient of resistance according to the present invention is applied to an element for preventing a rush current or that for delaying motor starting, the present invention is not restricted to such application.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

Fig. 1 is a characteristic diagram showing results of a test which was made by series-connecting an NTC element to a switching power source and measuring time change of a switching power source current upon power supply at a temperature of 25°C; and

Fig. 2 is a characteristic diagram showing relation between the number of times of a repetitive energization test and resistance values at a temperature of 25°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(Example 1)

This Example was carried out on a rare earth transition element oxide of $LaCoO_3$.

First, $LaCoO_3$ powder materials were prepared in the following manner: Respective powder materials of Co_3O_4 and La_2O_3 were weighed so that La was at a mole ratio of 0.95 to Co. Prescribed amounts of additives shown in Tables

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1, 2 and 3 were added to the powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours. Referring to Table 1, asterisked (*) amounts are out of the scope of the present invention.

Thus obtained calcined powder materials were pulverized by jet mills. Binders were added to the powder materials, which in turn were again wet-blended for 5 hours in ball mills employing nylon balls, filtered, dried and thereafter pressure-molded into the form of disks. The disks were fired in the atmosphere at 1400°C for 2 hours, to obtain sintered bodies. Both major surfaces of the sintered bodies were coated with platinum paste by screen printing, and baked at 1000°C for 2 hours, to be provided with electrodes. NTC elements were thus obtained.

The NTC elements were subjected to measurement of electric characteristics of specific resistance values and B constants. Tables 1 to 3 as well as Tables 4 to 9 described later show resistivity values which were measured at a temperature of 25°C. Assuming that $\rho(T)$ and $\rho(T_0)$ represent resistivity values at temperatures T and T_0 respectively and $\ln$ represents a natural logarithm, each B constant, which is a constant showing resistance change caused by temperature change, is defined as follows:

$$B(T) = [\ln \rho(T_0) - \ln \rho(T)] / (1/T_0 - 1/T)$$

Temperature change caused by the temperature increases with this value.

Referring to Tables 1, 2 and 3, the B constants at -10°C and 140°C are defined as follows:

$$B \text{ constant } (-10^\circ\text{C}) = [\ln \rho(-10^\circ\text{C}) - \ln \rho(25^\circ\text{C})] / [1/(-10 + 273.15) - 1/(25 + 273.5)]$$

$$B \text{ constant } (140^\circ\text{C}) = [\ln \rho(25^\circ\text{C}) - \ln \rho(140^\circ\text{C})] / [1/(25 + 273.15) - 1/(140 + 273.5)]$$

Figs. 1 and 2 show results of a repetitive energization test which was made on a sample according to Example 1, containing 1 mole percent of Zr. Fig. 1 shows the results of the test which was made by series-connecting an NTC element to a switching power source and measuring the time change of the switching power source current upon power supply at a temperature of 25°C. Fig. 2 is a characteristic diagram showing relation between the number of times of the repetitive energization test and resistance values at a temperature of 25°C. In this repetitive energization test, the NTC element was energized with a current for 1 minute and thereafter the power source was turned off for 30 minutes to cool the element to 25°C every cycle. As clearly understood from Figs. 1 and 2, no characteristic change was recognized even after 10000 cycles. Further, no NTC element was broken when currents of 200 A were continuously applied to 100 NTC elements. Thus, it was confirmed that the inventive NTC element is applicable to a heavy current.

Table 1

No.	Additional Element	Content (mol%)	Resistivity ($\Omega\cdot\text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-1	Zr	0 *	4.9	520	1590
1-2	Zr	0.000*	8.4	890	2510
1-3	Zr	0.001	11.1	1220	3020
1-4	Zr	0.01	14.8	1650	3780
1-5	Zr	0.1	18.7	2150	4480
1-6	Zr	1	19.8	2620	4730
1-7	Zr	10*	13.6	1600	3290
1-8	Zr	20*	4.7	790	1790

Table 2

No.	Additional Element	Content (mol%)	Resistivity ($\Omega\cdot\text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-9	Si	0.05	17.4	2010	4290

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Table 2 (continued)

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-10	Mo	0.05	16.7	1820	4580
1-11	Sn	0.5	20.5	2400	4680
1-12	Sb	1	17.3	1970	4450
1-13	Te	1	20.2	2630	4530
1-14	Hf	5	18.4	2260	4310
1-15	Ta	5	17.5	2100	4570
1-16	W	10*	16.4	1990	4320
1-17	Ce	10*	17.0	2090	4480

Table 3

No.	Additional Element :	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-18	Zr	0.05	19.6	2280	4230
	Mo	0.05			
1-19	Zr	1	18.3	2570	4550
	Sn	0.5			
1-20	Zr	0.05	17.8	2130	4510
	Sn	0.05			
	W	0.05			
1-21	Zr	1	16.2	2460	4290
	Mo	0.5			
	Ce	0.5			

(Example 2)

This Example was carried out on a rare earth transition element oxide of SmNiO_3 .

First, SmNiO_3 powder materials were prepared in the following manner: Respective powdery materials of Sm_2O_3 and NiO were weighed so that Sm was at a mole ratio of 0.95 to Ni. Additives shown in Table 4 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 4 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 4

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (K)	B Constant (-10°C) (140°C) (K)
3-1	Zr	0.05	14.8	2240	3920
3-2	Mo	0.05	14.0	2340	3870
3-3	Sb	1	13.8	2290	3790
3-4	Hf	1	12.1	2150	3740

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Table 4 (continued)

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (K)	B Constant (-10°C) (140°C) (K)
3-5	Ta	0.5	14.3	2230	3800
3-6	W	0.5	15.0	2090	3750
3-7	Sb	0.5	12.9	2410	3930
	Ce	0.5			
3-8	Zr	0.05	14.3	2060	3620
	Ta	0.05			
3-9	Sn	1	12.0	2220	3890
	W	1			
3-10	Si	0.1	13.7	2390	3990
	Mo	0.1			
	W	0.1			

(Example 3)

This Example was carried out on a rare earth transition element oxide of NdNiO_3 .

First, NdNiO_3 powder materials were prepared in the following manner. Respective powder materials of Nd_2O_3 and NiO were weighed so that Nd was at a mole ratio of 0.95 to Ni. Additives shown in Table 5 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 5 also shows results of respective electric characteristics of the obtained NTC elements, which were measured similarly to Example 1.

Table 5

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
4-1	Si	0.5	24.3	2030	3860
4-2	Zr	0.5	24.0	2170	3790
4-3	Mo	5	25.8	2100	3910
4-4	Sn	5	24.1	2090	3730
4-5	Sb	1	23.6	2160	3850
4-6	Ce	1	22.6	2240	3930
4-7	Si	1	25.9	2120	3710
	Sn	1			
4-8	Zr	0.5	25.4	1990	3790
	W	0.5			
4-9	Mo	0.5	24.3	1970	3860
	Ta	0.5			
4-10	Zr	0.1	24.6	2080	3900
	Sn	0.1			
	Ta	0.1			

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(Example 4)

This Example was carried out on a rare earth transition element oxide of PrNiO_3 .

First, PrNiO_3 powder materials were prepared in the following manner: Respective powder materials of Pr_6P_{11} and NiO were weighed so that Pr was at a mole ratio of 0.95 to Ni. Additives shown in Table 6 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 6 also shows results of respective electric characteristics of the obtained NTC elements, which were measured similarly to Example 1.

Table 6

No.	Additional Element	Content (mol%)	Resistivity ($\Omega\text{-cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
5-1	Zr	1	10.6	1960	3650
5-2	Mo	1	9.8	2100	3590
5-3	Sb	0.5	11.6	2060	3710
5-4	Te	0.5	8.9	1980	3690
5-5	Ta	0.05	10.3	2030	3740
5-6	W	0.05	12.0	2210	3820
5-7	Zr	1	9.7	2120	3640
	Hf	1			
5-8	Zr	0.5	9.6	1990	3630
	W	0.1			
5-9	Mo	0.1	11.3	1970	3670
	Sb	0.1			
5-10	Sb	0.5	10.2	2090	3710
	Hf	0.5			
	W	0.5			

(Example 5)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$.

First, respective powder materials of La_2O_3 , Nd_2O_3 and Co_3O_4 were weighed to obtain $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$ semiconductive ceramic materials. Additives shown in Table 7 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 7 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 7

No.	Additional Element	Content (mol%)	Resistivity ($\Omega\text{-cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
6-1	Zr	0.5	26.1	1870	3630
6-2	Sb	1	25.7	1720	3690
6-3	W	5	26.4	1910	3590

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Table 7 (continued)

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
6-4	Si	1	24.0	1860	3540
	Hi	1			
6-5	Zr	0.5	25.6	1790	3680
	Mo	0.5			
	Ta	0.5			

(Example 6)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$.

First, respective powder materials of La_2O_3 , Gd_2O_3 and Co_3O_4 were weighed to obtain $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$ semiconductive ceramic materials. Additives shown in Table 8 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 8 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 8

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
7-1	Sn	0.01	22.0	2010	3750
7-2	Ta	0.5	21.9	1960	3710
7-3	Ce	1	23.7	1840	3860
7-4	Zr	0.1	22.4	2020	3650
	Mo	0.1			
7-5	Zr	0.5	23.7	1970	3700
	Te	0.5			
	Hi	0.5			

(Example 7)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.99}\text{Y}_{0.01}\text{NiO}_3$.

First, respective powder materials of La_2O_3 , Y_2O_3 and NiO were weighed to obtain $\text{La}_{0.99}\text{Y}_{0.01}\text{NiO}_3$ semiconductive ceramic materials. Additives shown in Table 9 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 9 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 9

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
8-1	Sn	5	20.6	2190	3970
8-2	Mo	1	21.5	2290	3860
8-3	W	0.5	19.7	2200	3900

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Table 9 (continued)

No.	Additional Element	Content (mol%)	Resistivity ($\Omega\cdot\text{cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
8-4	Sb	0.5	20.1	2260	3840
	Ta	0.5			
8-5	Zr	1	20.6	2270	3820
	Sb	1			
	Mo	1			

Although the aforementioned Examples were carried out on oxides of LaCoO_3 , SmNiO_3 , NdNiO_3 and PrNiO_3 respectively, the present invention is also applicable to other rare earth transition element oxides, to attain similar effects.



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Claims

1. Semiconductive ceramics having negative temperature coefficient of resistance, being mainly composed of an oxide which contains as main ingredients a rare earth material of the group IIIa excluding Ce and including Y and a transition element excluding Cr, with addition of at least one of Si, Zr, Hf, Ta and Ce in a range of 0.001 to 5 mole percent.
2. Semiconductive ceramics having negative temperature coefficient of resistance, being mainly composed of an oxide which contains as main ingredients a rare earth material of the group IIIa excluding Ce and including Y and a transition element excluding Cr, with addition of at least one of Sn, Sb, W, Mo or Te in a range of 0.001 to 5 mole percent.
3. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, wherein said oxide is at least one selected from LaCoO_3 , LaMnO_3 , SmNiO_3 , NdNiO_3 and PrNiO_3 .
4. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, wherein 0.1 to 5 mole percent of said additive is added to said main component.
5. Semiconductive ceramics having negative temperature coefficient resistance in accordance with claim 3, wherein said oxide of LaCoO_3 is $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$.
6. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 3, wherein said oxide of LaCoO_3 is $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$.
7. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 3, wherein said oxide of LaCoO_3 is $\text{La}_{0.99}\text{Y}_{0.01}\text{CoO}_3$.
8. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, being applied to an element for preventing a rush current.
9. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, being applied to an element for delaying motor starting.

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SEMICONDUCTIVE CERAMICS HAVING NEGATIVE
TEMPERATURE COEFFICIENT OF RESISTANCE

ABSTRACT OF THE DISCLOSURE

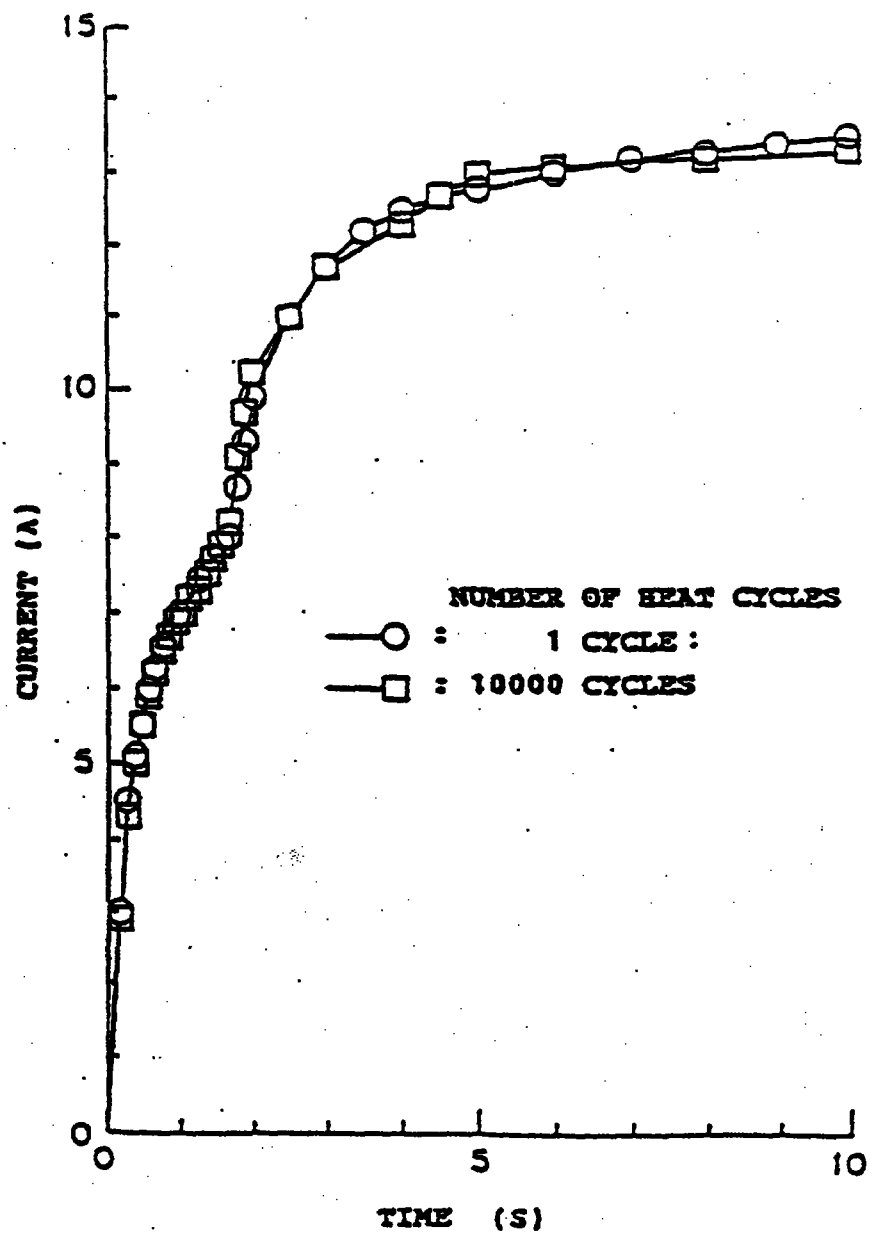
Semiconductive ceramics having negative temperature coefficient of resistance, which is mainly composed of an oxide of a rare earth transition element excluding Ce and including Y, with addition of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce.

FIGURE 1

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FIG. 1



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FIG. 2

