10 JAN 2003

166166

SEMICONDUCTIVE CERAMIC COMPOSITION AND SEMICONDUCTIVE CERAMIC ELEMENT USING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a semiconductive ceramic composition, more specifically to a semiconductive ceramic composition having negative resistance-temperature characteristics. The present invention also relates to a semiconductive ceramic element making use of the semiconductive ceramic composition (a Negative Temperature Coefficient "NTC" thermistor). The element is used, for example, for the prevention of rush current and the realization of "soft-starting" of a motor.

Background Art

The word "thermistor" is derived from "thermally sensitive resistor" and refers to an element whose resistance varies depending on temperature. An NTC thermistor is a kind of semiconductive ceramic element and has characteristics by which resistance decreases with increase of temperature. B constant is defined by the following equation, wherein $\rho(T)$ is the resistivity at temperature T, $\rho(T_0)$ is the resistivity at temperature T_0, and ln is natural logarithm.

$$B \text{ constant} = [\ln\rho(T_0) - \ln\rho(T)] / (1/T_0 - 1/T)$$

The greater the value of B constant, the greater the variation of resistance of an NTC thermistor per unit

G00002

temperature change.

An NTC thermistor is incorporated into, for example, a rectification circuit for a power source in an electronic apparatus. The rectification circuit for a power source has a smoothing capacitor having large capacitance. The NTC thermistor suppresses strong rush current flowing into the capacitor upon switching-on of power. Thereafter, the thermistor comes to have lowered resistance through self-heating, so that the circuit operates in a steady state. The NTC thermistor is useful for achieving soft-starting of the circuit and for protecting the rectifier and the capacitor having large capacitance.

As a material for NTC thermistors, there has been used spinel composite oxide containing a transition metal element.

One requirement for an ideal NTC thermistor to prevent rush current is sufficiently low resistance of the thermistor at high temperature (140-200°C). As resistance of thermistors decreases, power is conserved during operation of the circuit in a steady state.

In order to decrease the resistance of a thermistor at high temperature, B constant at high temperature is increased. Conventional NTC thermistors have a B constant value of 3250 K at most.

Another requirement is that the resistance of the thermistor at low temperature (in the range between -10 and +60°C) must not be very high. Considerable increase of the

resistance is observed for conventional NTC thermistors, especially at a low temperature below 0°C. Consequently, a voltage drop occurs at low temperature to sometimes hamper normal starting-up of electronic apparatus. In order to prevent an increase of the resistance at low temperature, B constant at low temperature is reduced.

The B constant of a lanthanum cobalt oxide is reported to be temperature-dependent (see, for example, V. G. Bhide and D. S. Rajoria, Phys. Rev. B6, [3], 1072, 1972, etc.).

The present inventors previously obtained an NTC thermistor satisfying the two above requirements, i.e., having a B constant of 3000 K or less near room temperature and a B constant of 4000 K or more at high temperature, by incorporating at least one element selected from the group consisting of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, and Ce into a primary component formed of lanthanum cobalt oxide (Japanese Patent Application Laid-Open (*kokai*) No. 7-176406). Resistivity and B constant of the obtained NTC thermistors are in proportion to the amount of the additive(s). This is because the additive functions as a donor within the lanthanum cobalt oxide to compensate charge of impurities (acceptors such as Ni, Ca, etc.) contained in the oxide. Therefore, if additives are incorporated in excessive amounts, the resistivity and B constant come to decrease at room temperature.

The peak values of the resistivity and B constant of

10 JAN 2003

lanthanum cobalt oxide at room temperature (25°C-140°C) are approximately 20 Ω·cm and approximately 4700 K. Conventionally, there have been obtained no NTC thermistors having a resistivity equal to or higher than the above value.

Depending on use of an NTC thermistor, a resistance equal to or higher than the above value may be required. Although higher resistivity may be obtained by increasing the volume of the NTC thermistor, the increase of the volume is contradictory to demands for smaller elements. The modification of the volume thereof in accordance with the type of thermistor invites increase of manufacturing costs.

In the meantime, lanthanum cobalt oxide has extremely poor sinterability, and sintered density thereof sometimes fails to reach 90% or more of the theoretical density. Heretofore customary sintering aids such as SiO_2 have not been usable, since the balance between the donors and the acceptors——which exist in very small amounts——affects the resistance-temperature characteristics.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a semiconductive ceramic composition having a resistivity higher than that of the conventional compositions in the room temperature region.

Another object of the present invention is to enhance sinterability of the above composition.

According to the present invention, there is provided a semiconductive ceramic composition having negative resistance-temperature characteristics, wherein the composition comprises lanthanum cobalt oxide as a primary component, and, as secondary components, at least one oxide of an element selected from among Fe and Al and at least one oxide of an element selected from among Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P.

Preferably, the at least one oxide of an element selected from among Fe and Al is contained in a total amount of 0.001-30 mol% as reduced to the element and the at least one oxide of an element selected from Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P is contained in a total amount of 0.001-10 mol% as reduced to the element.

Alternatively and preferably, the at least one oxide of an element selected from Fe and Al is contained in a total amount of 0.1-10 mol% as reduced to the element and the at least one oxide of an element selected from Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P is contained in a total amount of 0.1-5 mol% as reduced to the element.

The aforementioned lanthanum cobalt oxide may be in the form of La_xCoO_3 ($0.60 \leq x \leq 0.99$).

La of the aforementioned La_xCoO_3 may be partially substituted with any of Pr, Nd, and Sm.

An oxide of B may be added in a ceramic having negative

10 JAN 2003

resistance-temperature characteristics, comprising:

lanthanum cobalt oxide as a primary component;

at least one oxide of an element selected from among Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th and P as a secondary component.

Addition of an oxide of B enhances the sintered density.

These compositions are useful, among others, for the fabrication of an NTC thermistor which is used for preventing rush current or controlling a motor so as to achieve soft-starting.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partially-cut-away view of an NTC thermistor of the present invention.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

Next, embodiments of the present invention will be described by way of examples.

Example 1

This example is directed to an embodiment using $La_{0.94}CoO_3$ as a lanthanum cobalt oxide.

First, powders of La_xCoO_3 and Co_3O_4 were weighed and mixed so as to adjust the mole ratio of lanthanum to cobalt to 0.94. Subsequently, each of the additive elements shown in Tables 1 and 2 was weighed in a predetermined amount in the form of a compound such as an oxide, and was added to the weighed powder mixture. The amount of the added element shown in Tables 1 and 2 represents the amount reduced to the element.

Each of the thus-obtained powder was wet-mixed along with added pure water and nylon balls for 16 hours, followed by drying. The resultant mixture was calcined at 1000°C for two hours. The calcined material was ground, and vinyl acetate binder was added thereto in an amount of 3 wt.%, followed by additional wet-mixing along with added pure water and nylon balls for 16 hours. Thereafter, the mixture was subjected to drying, granulation, press-forming into a disk shape, and was calcined at 1350°C for two hours in air, to thereby obtain a semiconductive ceramic 1. Subsequently, platinum paste was screen-printed onto both surfaces of the semiconductive ceramic, and the semiconductive ceramic was baked at 1000°C for two hours in air to form external electrodes 2 and 3, to thereby obtain an NTC thermistor 4 (FIG. 1). Optionally, the surfaces of the semiconductive ceramic may be coated with a resin layer 5 for protection of the semiconductive ceramic. Also, there may be obtained an NTC thermistor having another structure, such as an NTC thermistor having layered electrodes contained therein.

The thus-obtained NTC thermistor was measured for the electric characteristics of resistivity ρ and B constant. The results are shown in Tables 1 and 2. In Tables 1 and 2, the Sample Nos. marked with "*" represent thermistors outside the scope of the present invention, and the others represent those within the scope of the present invention. resistivity ρ was measured at 25°C.

According to Equation (1), B constants, i.e., B(-10°C) and B(140°C), obtained herein are defined as follows:

$$B(-10°C) = [\ln\rho(-10°C) - \ln\rho(25°C)] / [1/(-10+273.15) - 1/(25+273.15)]$$

$$B(140°C) = [\ln\rho(140°C) - \ln\rho(25°C)] / [1/(140+273.15) - 1/(25+273.15)]$$

As B constant (-10°C) decreases, the fluctuation range of resistance induced by the change of outside temperature decreases, and the rise of resistance is suppressed at lower temperatures. Therefore, the above-mentioned problem of lowered voltage at low temperature is overcome.

As B constant (140°C) increases, resistivity decreases drastically with increase of temperature. Consequently, a heavy current is suppressed immediately after start-up of a circuit equipped with the NTC thermistor, and thereafter, in steady state operation, the power consumption of the circuit is suppressed to a low level. An NTC thermistor having such characteristics is particularly useful as an element for suppression of rush current in a circuit, such as that present during a power switching-on operation, or as a like component through which a heavy current flows.

Table 1

1) Sample No.

2) Added element

3) Resistivity

4) B constant

5) Species

6) Amount

Table 2

1) Sample No.

2) Added element

3) Resistivity

4) B constant

5) Species

6) Amount

As shown in Tables 1 and 2, in the semiconductive ceramic compositions containing $La_{0.94}CoO_3$ as the primary component and, as the secondary components, at least one oxide of an element selected from the group consisting of Fe and Al and at least one oxide of an element selected from the group consisting of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, and Ce, there is obtained negative resistance-temperature characteristics with a wide range of resistivity ρ at room temperature, while the fluctuations of B constant at -10°C and 140°C are restricted within a certain range.

Specifically, if the content of the at least one oxide of an element selected from the group consisting of Fe and Al is 0.001 mol% or more as reduced to the element, significant effects of the added element are obtained,

resulting in an increased resistivity at room temperature. Also, if the content is 30 mol% or less, resistivity at room temperature falls below 100 Ω·cm and B constant is maintained high at high temperature, preferably resulting in a sufficient reduction of resistance at high temperature.

Especially, if the total content of the at least one oxide of an element selected from the group consisting of Fe and Al is 0.001-30 mol% as reduced to the element and the total content of the at least one oxide of an element selected from the group consisting of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, and Ce is 0.001-10 mol% as reduced to the element, there can be obtained excellent results: B(-10°C) of 1820-2850 K, B(140°C) of 4120-4730 K, and ρ(25°C) of 15.4-99.4 Ω·cm.

Further, if the total content of the at least one oxide of an element selected from the group consisting of Fe and Al is 0.01-10 mol% as reduced to the element and the total content of the at least one oxide of an element selected from the group consisting of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, and Ce is 0.1-5 mol% as reduced to the element, B(-10°C) is 1970-2810 K, B(140°C) is 4310-4730 K, and ρ(25°C) is 18.9-50.3 Ω·cm. Thus, there is obtained a semiconductive ceramic composition in which the change of B constant is further suppressed, although the fluctuation range of resistivity ρ is narrowed.

Also, the same effects as obtained in this Example may

10 JAN 2003

be obtained by use of a composition represented by La_xCoO_3 as a lanthanum cobalt oxide.

Specifically, when the La_xCoO_3 wherein $0.60 \leq x \leq 0.99$ is used, B constant at high temperature increases to 3000 K or more, to thereby sufficiently reduce resistance at an elevated temperature.

Moreover, the same effects may also be obtained by use of Nb, Mn, Th, or P instead of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, or Ce employed in the above Example.

Example 2

$La_{0.85}Pr_{0.09}CoO_3$ may be use as a lanthanum cobalt oxide.

First, powders of La_2O_3, Pr_6O_{11}, and Co_3O_4 were weighed and mixed so as to adjust the mole ratios of La:Co and Pr:Co to 0.85 and 0.09, respectively. Subsequently, each of the additive elements shown in Table 3 was weighed in a predetermined amount in the form a compound such as an oxide, and was incorporated into the weighed powder mixture. The amount of the added element shown in Table 3 represents the amount reduced to the element.

Each of the thus-obtained powder was wet-mixed along with added pure water and nylon balls for 16 hours, followed by drying. The resultant mixture was calcined at 1000°C for two hours. The calcined material was treated in the same manner as in Example 1, to thereby obtain an NTC thermistor.

In the same manner as in Example 1, resistivity ρ and B constant were determined of the thus-obtained NTC thermistor.

The results are shown in Table 3.

Table 3

1) Sample No.

2) Added element

3) Resistivity

4) B constant

5) Species

6) Amount

As is apparent from Table 3, in the semiconductive ceramic compositions containing $La_{0.85}Pr_{0.09}CoO_3$ as a lanthanum cobalt oxide, as in the case of $La_{0.94}CoO_3$ shown in Example 1, there are obtained negative resistance-temperature characteristics with a broad range of resistivity ρ at room temperature, while the fluctuations of B constant at -10°C and 140°C are restricted.

Example 3

$La_{0.85}Nd_{0.09}CoO_3$ may be used as a lanthanum cobalt oxide.

First, powders of La_2O_3, Nd_2O_3, and Co_3O_4 were weighed and mixed so as to adjust the mole ratios of La:Co and Nd:Co to 0.85 and 0.09, respectively. Subsequently, each of the elements shown in Table 4 was weighed in a predetermined amount in the form of a compound such as an oxide, and was incorporated into the weighed powder mixture. The amount of the added element shown in Table 4 represents the amount as

reduced to the element.

Each of the thus-obtained powder was wet-mixed along with added pure water and nylon balls for 16 hours, followed by drying. The resultant mixture was calcined at 1000°C for two hours. The calcined material was treated in the same manner as in Example 1, to thereby obtain an NTC thermistor.

In the same manner as in Example 1, resistivity ρ and B constant were determined of the thus-obtained NTC thermistor. The results are shown in Table 4.

Table 4

1) Sample No.

2) Added element

3) Resistivity

4) B constant

5) Species

6) Amount

As is apparent from Table 4, in the semiconductive ceramic compositions containing $La_{0.85}Nd_{0.09}CoO_3$ as a lanthanum cobalt oxide, as in the case of $La_{0.94}CoO_3$ shown in Example 1, there are obtained negative resistance-temperature characteristics with a broad range of resistivity ρ at room temperature, while the fluctuations of B constant at -10°C and 140°C are restricted.

Example 4

10 JAN 2003

$La_{0.85}Sm_{0.09}CoO_3$ may be used as a lanthanum cobalt oxide.

First, powders of La_2O_3, Sm_2O_3, and Co_3O_4 were weighed and mixed so as to adjust the mole ratios of La:Co and Sm:Co to 0.85 and 0.09, respectively. Subsequently, each of the elements shown in Table 5 was weighed in a predetermined amount in the form of a compound such as an oxide, and was incorporated into the weighed powder mixture. The amount of the added element shown in Table 5 represents the amount as reduced to the element.

Each of the thus-obtained powder was wet-mixed along with added pure water and nylon balls for 16 hours, followed by drying. The resultant mixture was calcined at 1000°C for two hours. The calcined material was treated in the same manner as in Example 1, to thereby obtain an NTC thermistor.

In the same manner as in Example 1, resistivity ρ and B constant were determined of the thus-obtained NTC thermistor. The results are shown in Table 5.

Table 5

1) Sample No.

2) Added element

3) Resistivity

4) B constant

5) Species

6) Amount

As is apparent from Table 5, in the semiconductive ceramic compositions containing $La_{0.85}Sm_{0.09}CoO_3$ as a lanthanum cobalt oxide, as in the case of $La_{0.94}CoO_3$ shown in Example 1, there are obtained negative resistance-temperature characteristics with a broad range of resistance ρ at room temperature, while the fluctuations of B constant at -10°C and 140°C are restricted.

In the above Examples 1-4 are used, as lanthanum cobalt oxides, $La_{0.94}CoO_3$, $La_{0.85}Pr_{0.09}CoO_3$, $La_{0.85}Nd_{0.09}CoO_3$, and $La_{0.85}Sm_{0.09}CoO_3$, respectively; however, the present invention is not limited thereto. The amount of La to be substituted is not limited to 0.09. The same effects are obtainable in the case of a lanthanum cobalt oxide in which La is partially substituted with Eu, Y, or a like element.

As the above description clearly indicates, through incorporation of a lanthanum cobalt oxide as the primary component, and as the secondary components, at least one oxide of an element selected from the group consisting of Fe and Al and at least one oxide of an element selected from the group consisting of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P, there is obtained a semiconductive ceramic composition which has negative resistance-temperature characteristics with an arbitrary room-temperature resistivity from apoproximately 10 Ω·cm to 100 Ω·cm while B constant is maintained at a constant level.

Consequently, use of the semiconductive ceramic

composition enables the manufacture of a semiconductive ceramic element having negative resistance-temperature characteristics (NTC thermistor element) which is applicable to a circuit suffering a strong rush current or a circuit requiring intensive current suppression.

That is, the thus-obtained semiconductive ceramic element can be widely used as an element for retarding of starting of a motor, protection of the drum of a laser printer, protection of bulbs such as halogen lamps, and elimination of rush current occurring in an apparatus or machine in which an excess current flows at the initial stage of voltage application as well as rush current occurring in a power switching-on operation, and also can be used as a temperature-compensated crystal oscillator or for temperature compensation. However, the present invention is not limited only to these applications.

Example 5

Through incorporation of B, the sintered density of the semiconductive ceramic composition may be increased. $La_{0.94}CoO_3$ was used as a lanthanum cobalt oxide through utilization of sintering performance.

First, powders of La_2O_3 and Co_3O_4 were weighed and mixed so as to adjust the mole ratio of La to Co to 0.94. Subsequently, each of the elements shown in Table 6 was weighed in a predetermined amount in the form of a compound such as an oxide, and was incorporated into the weighed

powder mixture. The amount of the added element shown in Table 6 represents the amount as reduced to the element.

Each of the thus-obtained powder was wet-mixed along with added pure water and nylon balls for 16 hours, followed by drying. The resultant mixture was calcined at 1000°C for two hours. The calcined material was ground, and a vinyl acetate binder was added thereto in an amount of 3 wt.%, followed by additional wet-mixing along with added pure water and nylon balls for 16 hours. Thereafter, the mixture was subjected to drying, granulation, press-forming into a disk shape, and was calcined at 1350°C for two hours in air, to thereby obtain a semiconductive ceramic. Subsequently, platinum paste was screen-printed onto both surfaces of the semiconductive ceramic, and the semiconductive ceramic was baked at 1000°C for two hours in air to form external electrodes, to thereby obtain an NTC thermistor.

The thus-obtained NTC thermistor was measured for the electric characteristics of resistivity ρ and B constant. The results are shown in Table 6. In Table 6, the Sample Nos. marked with "*" represent thermistors outside the scope of the present invention, and the others represent those within the scope of the present invention.

Table 6

1) Sample No.

2) Added element

3) Resistivity ρ

4) B constant

5) Sintered density

6) Species

7) Amount

As shown in Table 6, in the semiconductive ceramic compositions containing $La_{0.94}CoO_3$ as the primary component, and at least one oxide of an element selected from the group consisting of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, and Ce and an oxide of B, negative resistance-temperature characteristics provide a high sintered-density material, while the fluctuations of resistivity at room temperature and B constant at 140°C are restricted.

If the content of B is 0.0001 mol% or more as reduced to B, significant effects of the added element are obtained, resulting in an increased sintered density. Also, if the content is 5 mol% or less, resistance is sufficiently reduced at high temperature, while B constant is maintained high at high temperature.

Specifically, if the total content of the at least one oxide of an element selected from the group consisting of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, and Ce is 0.001-10 mol% as reduced to the element, and the content of an oxide of B is 0.0001-5 mol%, sintered density is advantageously increased to 6.9 or more, while the fluctuation of resistivity ρ (25°

10 JAN 2003

C) is restricted to 9.2-12.6 and that of B constant (140°C) is restricted to 4520-4740.

Also, the same effects as in this Example may be obtained by use of a composition represented by La_xCoO_3 as a lanthanum cobalt oxide. Specifically, when the La_xCoO_3 wherein $0.60 \leq x \leq 0.99$ is used, B constant increases to 3000 K or more at a high temperature, to thereby sufficiently reduce resistance at an elevated temperature.

Further, the same effects can be obtained in the case of a lanthanum cobalt oxide in which La is partially substituted with Pr, Nd, Sm, Eu, Y, or a like element.

Moreover, the same effects as obtained in this Example may be obtained by use of oxides of Nb, Mn, Th, or P instead of oxides of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, or Ce.

TABLE 1

(1)	(2)		(2)		(3)	B(4)	
	(5)	(6) (mol%)	(5)	(6) (mol%)	ρ 25℃ (Ω·cm)	B(-10℃) (K)	B(140℃) (K)
*1-1	Zr	1	Fe	0	19.8	2620	4730
1-2	Zr	1	Fe	0.0005	19.8	2630	4730
1-3	Zr	1	Fe	0.001	22.6	2610	4720
1-4	Zr	1	Fe	0.01	24.9	2680	4730
1-5	Zr	1	Fe	0.1	26.2	2650	4720
1-6	Zr	1	Fe	1	28.6	2630	4720
1-7	Zr	1	Fe	10	50.3	2670	4730
1-8	Zr	1	Fe	20	76.1	2650	4720
1-9	Zr	1	Fe	30	99.4	2640	4730
1-10	Zr	1	Fe	40	139.7	2970	4210
*1-11	Zr	0	Fe	5	9.4	520	1580
1-12	Zr	0.0005	Fe	5	13.1	900	2510
1-13	Si	0.001	Fe	5	19.8	1930	4250
1-14	Mo	0.05	Fe	5	19.8	1820	4580
1-15	Sn	0.5	Fe	5	22.6	2410	4680
1-16	Sb	1	Fe	5	24.9	1970	4460
1-17	Te	1	Fe	5	26.2	2630	4530
1-18	Hf	5	Fe	5	19.6	2260	4310
1-19	Ta	5	Fe	5	18.9	2100	4320
1-20	W	10	Fe	5	15.4	2000	4120
1-21	Ce	10	Fe	5	16.1	2090	4200
1-22	Zr	20	Fe	5	12.4	800	1790

TABLE 2

(1)	(2)		(2)		(3) ρ 25℃ (Ω·cm)	B (4)	
	(5)	(6) (mol%)	(5)	(6) (mol%)		B(-10℃) (K)	B(140℃) (K)
1-23	Zr	1	Fe Al	0.5 0.5	28.6	2630	4720
1-24	Si	1	Fe Al	1 5	27.3	2570	4550
1-25	Mo	0.5	Fe Al	5 5	50.3	2810	4430
1-26	W	0.5	Fe Al	5 10	62.4	2850	4410
1-27	Zr Ce	0.5 0.5	Fe Al	15 5	72.0	2730	4500
1-28	W Ce	0.05 1	Fe Al	10 5	67.9	2590	4620

TABLE 3

(1)	(2)		(2)		(3) ρ 25℃ (Ω·cm)	B(4)	
	(5)	(6) (mol%)	(5)	(6) (mol%)		B(-10℃) (K)	B(140℃) (K)
2-1	Zr	1	Fe	0.5	29.1	2550	4620
			Al	0.5			
2-2	Si	1	Fe	1	27.0	2590	4440
			Al	5			
2-3	Mo	0.5	Fe	5	48.7	2630	4460
			Al	5			
2-4	W	0.5	Fe	5	65.0	2790	4450
			Al	10			
2-5	Zr	0.5	Fe	15	72.3	2740	4510
	Ce	0.5	Al	5			
2-6	W	0.05	Fe	10	65.7	2580	4560
	Ce	1	Al	5			

TABLE 4

(1)	(2)		(2)		(3) ρ 25℃ ($\Omega \cdot cm$)	B(4)	
	(5)	(6) (mol%)	(5)	(6) (mol%)		B(-10℃) (K)	B(140℃) (K)
3-1	Zr	1	Fe	0.5	28.5	2650	4700
			Al	0.5			
3-2	Si	1	Fe	1	24.9	2690	4560
			Al	5			
3-3	Mo	0.5	Fe	5	55.1	2830	4490
			Al	5			
3-4	W	0.5	Fe	5	60.0	2810	4500
			Al	10			
3-5	Zr	0.5	Fe	15	76.4	2700	4510
	Ce	0.5	Al	5			
3-6	W	0.05	Fe	10	66.0	2620	4630
	Ce	1	Al	5			

TABLE 5

(1)	(2)		(2)		(3) ρ 25℃ (Ω·cm)	B(4)	
	(5)	(6) (mol%)	(5)	(6) (mol%)		B(-10℃) (K)	B(140℃) (K)
4-1	Zr	1	Fe Al	0.5 0.5	25.0	2700	4650
4-2	Si	1	Fe Al	1 5	24.3	2690	4690
4-3	Mo	0.5	Fe Al	5 5	48.3	2600	4570
4-4	W	0.5	Fe Al	5 10	58.0	2870	4510
4-5	Zr Ce	0.5 0.5	Fe Al	15 5	67.9	2620	4630
4-6	W Ce	0.05 1	Fe Al	10 5	65.1	2680	4540

TABLE 6

(1)	(2)		(2)		(3) ρ 25°C ($\Omega \cdot cm$)	B(4) B(140°C) (K)	(5) (g/cm^2)
	(6)	(7) (mol%)	(6)	(7) (mol%)			
*1-1	Zr	0.5	B	0	12.5	4730	6.2
1-2	Zr	0.5	B	0.00005	12.5	4720	6.2
1-3	Zr	0.5	B	0.0001	12.6	4720	6.9
1-4	Zr	0.5	B	0.001	12.4	4730	7.0
1-5	Zr	0.5	B	0.01	12.5	4720	7.0
1-6	Zr	0.5	B	0.1	12.5	4720	7.1
1-7	Zr	0.5	B	1	12.6	4730	7.1
1-8	Zr	0.5	B	5	12.6	4740	7.1
1-9	Zr	0.5	B	10	14.5	4330	7.1
1-10	Zr	0.5	B	20	17.6	4040	7.1
*1-11	Zr	0	B	0.1	2.3	1920	7.1
1-12	Zr	0.0005	B	0.1	5.3	3400	7.1
1-13	Si	0.001	B	0.1	9.2	4520	7.1
1-14	Mo	0.05	B	0.1	9.8	4570	7.1
1-15	Sn	0.5	B	0.1	10.1	4620	7.1
1-16	Sb	1	B	0.1	10.8	4650	7.1
1-17	Te	1	B	0.1	10.7	4650	7.1
1-18	Hf	5	B	0.1	12.1	4770	7.1
1-19	Ta	5	B	0.1	12.1	4740	7.1
1-20	W	10	B	0.1	11.1	4630	7.1
1-21	Ce	10	B	0.1	10.9	4610	7.1
1-22	Zr	20	B	0.1	5.7	3600	7.1

10 JAN 2003

WHAT IS CLAIMED IS:

1. A semiconductive ceramic composition having negative resistance-temperature characteristics, which composition comprises lanthanum cobalt oxide as a primary component, and, as secondary components, at least one oxide of an element selected from among Fe and Al and at least one oxide of an element selected from among Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P.

2. A semiconductive ceramic composition according to Claim 1, wherein said at least one oxide of an element selected from among Fe and Al is contained in a total amount of 0.001-30 mol% as reduced to the element and said at least one oxide of an element selected from Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P is contained in a total amount of 0.001-10 mol% as reduced to the element.

3. A semiconductive ceramic composition according to Claim 1, wherein said at least one oxide of an element selected from among Fe and Al is contained in a total amount of 0.1-10 mol% as reduced to the element and said at least one oxide of an element selected from Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P is contained in a total amount of 0.1-5 mol% as reduced to the element.

4. A semiconductive ceramic composition according to any one of Claims 1 though 3, wherein said lanthanum cobalt oxide is in the form of La_xCoO_3 ($0.60 \leq x \leq 0.99$).

5. A semiconductive ceramic composition according to

Claim 4, wherein La of said La_xCoO_3 is partially substituted with any of Pr, Nd, and Sm.

6. A semiconductive ceramic element including a semiconductive ceramic having negative resistance-temperature characteristics and at least one pair of electrodes connected to the semiconductive ceramic, wherein the ceramic comprises lanthanum cobalt oxide as a primary component, and, as secondary components, at least one oxide of an element selected from among Fe and Al and at least one oxide of an element selected from among Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P.

7. A semiconductive ceramic element according to Claim 6, wherein said at least one oxide of an element selected from among Fe and Al is contained in a total amount of 0.001-30 mol% as reduced to the element and said at least one oxide of an element selected from Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P is contained in a total amount of 0.001-10 mol% as reduced to the element.

8. A semiconductive ceramic element according to Claim 6, wherein said at least one oxide of an element selected from among Fe and Al is contained in a total amount of 0.1-10 mol% as reduced to the element and said at least one oxide of an element selected from Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te, Ce, Nb, Mn, Th, and P is contained in a total amount of 0.1-5 mol% as reduced to the element.

9. A semiconductive ceramic element according to any

10 JAN 2003

one of Claims 6 though 8, wherein said lanthanum cobalt oxide is in the form of La_xCoO_3 ($0.60 \leq x \leq 0.99$).

10. A semiconductive ceramic element according to Claim 9, wherein La of said La_xCoO_3 is partially substituted with any of Pr, Nd, and Sm.

11. A semiconductive ceramic element according to any one of claims 6 through 10, which is for the prevention of rush current or the retarding of starting of a motor.