(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 723 276 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.07.1996 Bulletin 1996/30

(51) Int. Cl.[6]: **H01C 7/04**

(21) Application number: **96100708.5**

(22) Date of filing: **18.01.1996**

(84) Designated Contracting States:
DE FR GB IT NL

(30) Priority: **18.01.1995 JP 5870/95**

(71) Applicant: **MURATA MANUFACTURING CO., LTD.**
Nagaokakyo-shi Kyoto-fu 226 (JP)

(72) Inventors:
- **Mihara, Kenjiro,**
c/o Murata Manufact. Co., Ltd.
Nagaokakyo-shi, Kyoto-fu (JP)
- **Niimi, Hideaki,**
c/o Murata Manufact. Co., Ltd.
Nagaokakyo-shi, Kyoto-fu (JP)
- **Ishikawa, Terunobu,**
c/o Murata Manufact. Co., Ltd.
Nagaokakyo-shi, Kyoto-fu (JP)

(74) Representative: **Laufhütte, Dieter, Dr.-Ing. et al**
Lorenz-Seidler-Gossel
Widenmayerstrasse 23
80538 München (DE)

(54) Semiconductor ceramic having negative resistance/temperature characteristics and semiconductor ceramic component utilizing the same

(57) There is provided a semiconductor ceramic having negative resistance/temperature characteristics constituted by a YCaMn type oxide ceramic expressed by the formula $Y_{1-x}Ca_xMnO_3$ (x = 0.2 to 0.6). Further, there is provided a semiconductor ceramic component including a ceramic body having negative resistance/temperature characteristics and electrodes formed on the ceramic body. The ceramic body is made of a YCaMn type oxide ceramic expressed by the formula $Y_{1-x}Ca_xMnO_3$ (x = 0.2 to 0.6).

EP 0 723 276 A2

Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a semiconductor ceramic having negative resistance/temperature characteristics and a semiconductor ceramic component utilizing the same.

Description of the Related Art

Fig. 1 illustrates the appearance of a conventional semiconductor ceramic having negative resistance/temperature characteristics (hereinafter referred to as a negative characteristics thermistor). In the negative characteristics thermistor, electrodes (not shown) are formed on both principal surfaces of a semiconductor ceramic (not shown) having negative resistance/temperature characteristics made of a spinel type oxide; terminals 3a and 3b are connected to the electrodes by solder (not shown); and the external surface of the oxide is coated with resin 4.

For example, a switching power supply is subjected to an overcurrent, i.e., an initial rush current, when it is turned on. The so-called negative characteristics thermistor is used to absorb such a rush current. The negative characteristics thermistor exhibits high resistance at room temperature, and the resistance decreases as the temperature rises. Therefore, the rush current is suppressed immediately after energization, and the thermistor exhibits low resistance during steady state operation where the thermistor temperature has risen as a result of self-heating, which reduces power consumption. Spinel oxide type ceramics have been used for such negative characteristics thermistors.

Recently, there is an increased demand for electronic components which can be configured as a chip and which are compatible with a surface mounting device (hereinafter referred to as SMD). Thus, electronic devices are required to be more compact, lighter, and smaller in height. However, as shown in Fig. 1, a conventional negative characteristics thermistor is difficult to configure with a small height because it has terminals. Further, a spinel oxide type semiconductor ceramic which exhibits high specific resistance at room temperature must be geometrically large in order to keep the resistance thereof low. Therefore, it has not been possible to fabricate compact devices of this type, unlike general chip components such as ceramic capacitors.

When a negative characteristics thermistor is processed using an SMD, the self-heating of the negative characteristics thermistor causes a temperature rise of the circuit board to which it is connected. Since a conventional spinel oxide type negative characteristics thermistor has a B constant which is as small as 3000, and the resistance thereof at elevated temperatures is not sufficiently low which results in a more significant degree of self-heating during operation. As a result, it has been difficult to suppress the temperature rise at the circuit board.

A negative characteristics thermistor having low specific resistance made of a VO_2 type ceramic is excellent in preventing a rush current because it exhibits the characteristic of the specific resistance being abruptly decreased to 10 to 0.01 $\Omega \cdot$cm at 80°C. However, the shape of a VO_2 type ceramic is limited to a bead-like shape because such a ceramic is unstable and is manufactured using reduction firing followed by quenching. Further, since the allowable current value of such a ceramic is as small as several tens mA, it has not been possible to use it in a switching power supply through which a large current flows.

Although a device having a large B constant made of $BaTiO_3$ containing 20 mol % Li_2O_3 has been disclosed in Japanese examined patent publication No. 48-6352, such a device can not be fabricated in a chip type configuration because of its high specific resistance.

SUMMARY OF THE INVENTION

According to the present invention a chip type thermistor for current control that satisfies recent demands for more compact and lower profile devices is provided. The thermistor of the present invention has low resistance at elevated temperatures to suppress its heat generation. A large current can be applied to the thermistor.

In order to achieve the above-described object, the inventors made an active study to find a device made of a material having negative resistance/temperature characteristics which had a specific resistance sufficiently low to fabricate the device in a chip-size, which had a B constant large enough to suppress the self-heating of the device, and which was suitable for current control. As a result, it has been found that compositions based on YCaMn type oxides have specific resistance of 1 $\Omega \cdot$cm or less and a B constant of 4000 or more, and can provide satisfactory results in tests to examine practicality for the purpose of current control.

Such compositions are the type of materials described by Taguchi, Shimada et al. in Journal of Solid State Chemistry, Vol. 63, p.290 (1986). Those materials were studied as potential materials for the electrodes of fuel batteries, and the study was focused on their conductivity at high temperatures. Therefore, the study was intended for an application which is quite different from the intended application of the present invention wherein such materials are used for current control devices.

After various tests to see whether or not YCaMn type oxide materials can be actually used for current control devices, the inventors discovered the fact that certain of these oxides exhibit excellent characteristics which are not affected even by repeated energization tests and on that basis the present invention was conceived.

According to one aspect of the present invention, there is provided a negative characteristics thermistor made of a YCaMn type oxide ceramic.

According to another aspect of the present invention, there is provided a negative characteristics thermistor made of a YCaMn type oxide ceramic which is expressed by a general formula $Y_{1-x}Ca_xMnO_3$ in which x is about 0.2 to 0.6.

According to another aspect of the present invention, there is provided a semiconductor ceramic component constituted by a ceramic body and electrodes formed on the ceramic body, the ceramic body being made of a YCaMn type oxide ceramic.

According to still another aspect of the present invention, there is provided a semiconductor ceramic component made of a YCaMn type oxide ceramic which is expressed by a general formula $Y_{1-x}Ca_xMnO_3$ (x = about 0.2 to 0.6).

A negative characteristics thermistor according to the present invention is made of a YCaMn type oxide and has low specific resistance and a big B constant. Especially, a negative characteristics thermistor expressed by a general formula $Y_{1-x}Ca_xMnO_3$ (x = about 0.2 to 0.6) has specific resistance of 1 $\Omega \cdot$cm or less and a B constant of 4000 or more.

The use of the composition of a YCaMn type oxide allows a semiconductor ceramic component according to the present invention to have small specific resistance and a large B constant. Especially, a semiconductor ceramic component utilizing a ceramic body expressed by a general formula $Y_{1-x}Ca_xMnO_3$ (x = 0.2 to 0.6) exhibits excellent characteristics in that the specific resistance is 1 $\Omega \cdot$cm; the B constant is 4000 or more; and these characteristics are not affected by tests of practicality for the purpose of current control, e.g., repeated energization tests.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the appearance of a conventional negative characteristics thermistor.

Fig. 2 is a perspective view of a semiconductor ceramic component according to the present invention.

Fig. 3 illustrates temperature rises caused by energization observed on a semiconductor ceramic component according to the present invention and a conventional semiconductor ceramic component.

Fig. 4 illustrates changes in the specific resistance of a semiconductor ceramic component according to the present invention caused by intermittent energization of the same.

DETAILED DESCRIPTION OF THE INVENTION

In Fig.2, electrodes 2a and 2b are formed on both ends of a semiconductor ceramic body 1 having negative resistance/temperature characteristics.

First, the materials Y_2O_3, $CaCO_3$, and Mn_2O_3 are prepared and weighed to provide the compositions shown on Table 1. The resultant powders are subjected to wet mixing with purified water and zirconia balls for seven hours in a pot made of polyethylene. Thereafter, they are dried and are sintered for two hours at 1000°C. The resultant sintered powders are combined with an organic binder, a solvent, a dispersant, and polystyrene particles and are subjected to wet mixing for five hours in a polyethylene pot again to obtain a slurry. A ceramic green sheet having a thickness of 50µm is formed from the slurry. The green sheet is cut into predetermined dimensions, stacked and laminated, and contact-bonded to be finally formed in a size such that it has resistance of 8 1/2.

Table 1

Sample No.	$Y_{1-x}Ca_xMnO_3$ x	Specific Resistance at 25°C Ω • cm	B Constant 25/50°C K
1 *	0	2800	5200
2 *	0.1	20	5000
3	0.2	1	4800
4	0.4	0.8	4400
5	0.6	0.4	4000
6 *	0.7	0.008	3000
7 *	1.0	less than 0.001	2700

Next, the elements thus formed are dispersed on a firing sheath so that they do not overlap with each other. After being degreased at 400°C, they are fired at 1400°C in an atmosphere with a partial pressure of oxygen of 0.5 MPa or more to obtain a ceramic body. The resultant ceramic body is chamfered by means of barrel polishing. An electrode paste containing a conductive powder mainly composed of Ag is applied to the ends of the ceramic body and is baked at 800°C to form the electrodes of the semiconductor ceramic component.

For the purpose of comparison, a conventional semiconductor ceramic component as shown in Fig. 1 was fabricated as follows.

CO_3O_4, Mn_3O_4, and $CuCO_3$ are weighed to achieve a weight ratio of 6:3:1. The product is combined with a binder and subjected to wet mixing and pulverization for seven hours in a polyethylene pot containing zirconia balls. After being dried, it is molded in the form of a disc so that it has resistance at room temperature of 8Ω and is fired for two hours at 1250°C in the air. Then, electrodes are baked on both principal surfaces of the resultant disc-shaped ceramic body; terminals are soldered to the electrodes; and the external surface of the body is coated with resin.

Fig. 3 is a graph showing the results of an energization test in which the surface temperature (°C) of the semiconductor ceramic components and the value of the energizing current (A) are plotted along the vertical and horizontal axles, respectively. The solid line and broken line indicate the results for the components according to the invention and the prior art, respectively. As apparent from Fig. 3, the self-heating of the semiconductor ceramic component according to the present invention is significantly less than that of the conventional component.

Fig. 4 is a graph showing the results of an intermittent energization test in which the percentages of change in resistance and the number of times when the energization is performed and stopped are plotted. Intermittent energization was performed by repeating 10000 cycles of the application of a current of 5 A to samples according to the present invention for one minute and the removal of the current for five minutes, and changes in the resistance over time were measured. The measurement was made on 20 samples according to the present invention at each point in time, and the average, maximum, and minimum values were obtained. The graph indicates sufficient applicability of the invention to current control devices because there is almost no fluctuation of the percentage of change in resistance during the 10000 cycles of intermittent energization.

Although electrodes made of Ag is used in the present invention, the same characteristics can be obtained using Pt, Pd, Rh, or alloys obtained from them.

Since a semiconductor ceramic component according to the present invention has a ceramic body made of a YCaMn type oxide, negative resistance/temperature characteristics can be achieved wherein the specific resistance is low and the B constant is large, and it is possible to provide a semiconductor ceramic component for current control which is compatible with an SMD. Further, it is possible to provide the effect of suppressing the self-heating of a device during normal energization of the circuit to suppress the temperature rise of the substrate. Especially, a $Y_{1-x}Ca_xMnO_3$ (x = 0.2 to 0.6) type ceramic exhibits significant negative characteristics wherein the specific resistance is as low as 1 Ω • cm or less and the B constant for the temperature rise is 4000 or more.

While a specific illustrated embodiment has been shown and described, it will be appreciated by those skilled in the art that various modifications, changes and additions can be made to the invention without departing from the spirit and scope thereof as set forth in the following claims.

Claims

1. A semiconductor ceramic comprising a YCaMn type oxide ceramic and having negative resistance/temperature characteristics.

2. The semiconductor ceramic according to Claim 1, wherein said YCaMn type oxide ceramic is expressed by the formula $Y_{1-x}Ca_xMnO_3$ in which x is about 0.2 to 0.6.

3. A semiconductor ceramic component comprising a ceramic body and at least one electrode in contact with said ceramic body, said ceramic body comprises a YCaMn type oxide ceramic.

4. The semiconductor ceramic component according to Claim 3, wherein said YCaMn type oxide ceramic is the formula $Y_{1-x}Ca_xMnO_3$ in which x is about 0.2 to 0.6.

5. In a current control device comprising a semiconductor ceramic the improvement which comprises said ceramic comprising a YCaMn type oxide ceramic and having negative resistance/temperature characteristics.

6. The device according to claim 5, wherein said YCaMn type oxide ceramic is expressed by the formula $Y_{1-x}Ca_xMnO_3$ in which x is about 0.2 to 0.6.

7. The device according to claim 6, wherein said device is a rush current protection device.

8. The device according to claim 5, wherein said device is a rush current protection device.

FIG.1

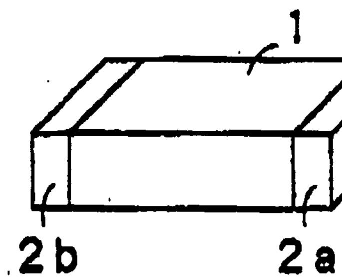

1
2b
2a

FIG.2

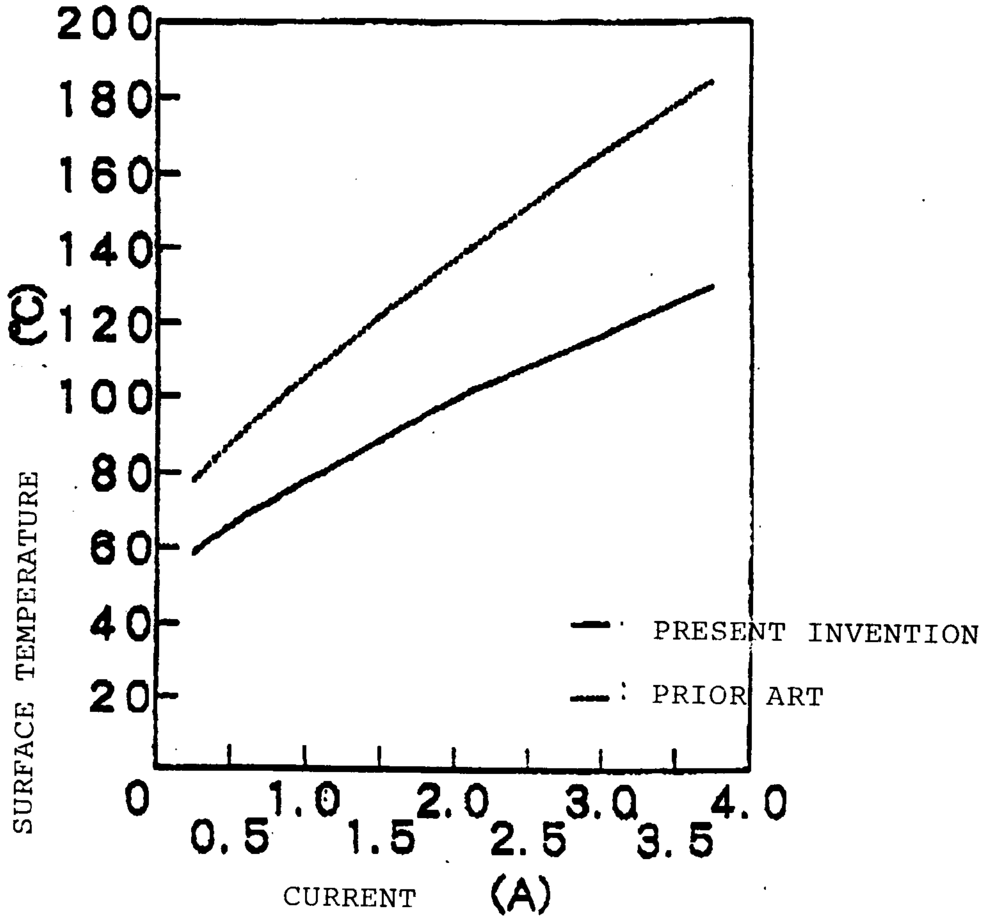

200
180
160
140
(℃) 120
100
80
60
40
20
0
SURFACE TEMPERATURE
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
CURRENT (A)
PRESENT INVENTION
PRIOR ART

FIG. 3

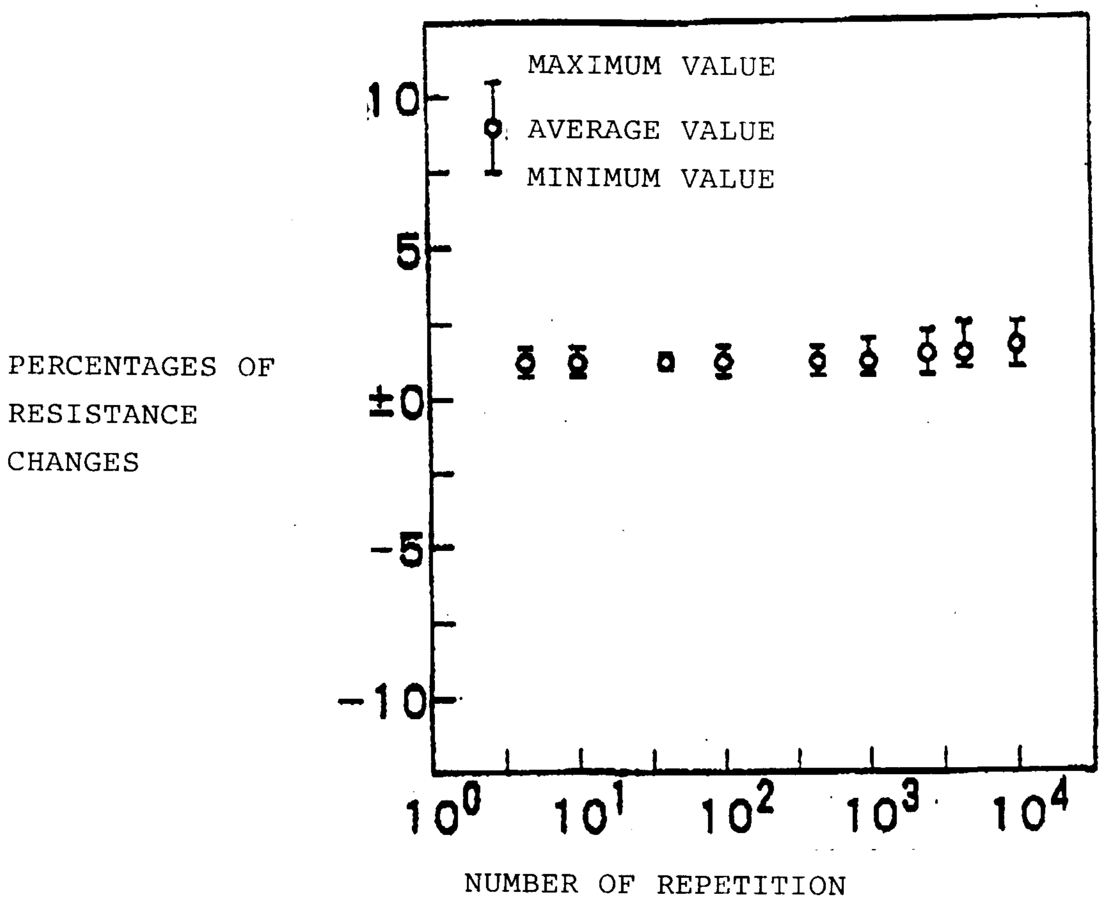
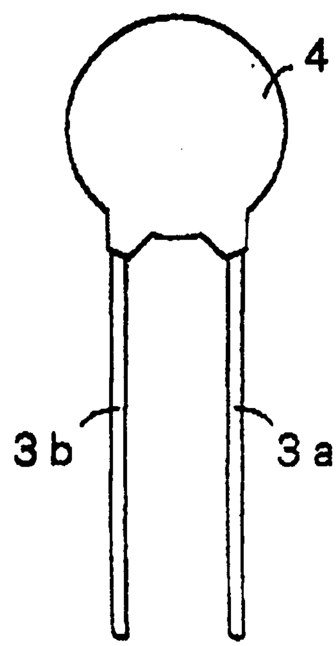

MAXIMUM VALUE
AVERAGE VALUE
MINIMUM VALUE
10
5
±0
-5
-10
PERCENTAGES OF RESISTANCE CHANGES
10^0
10^1
10^2
10^3
10^4
NUMBER OF REPETITION

FIG. 4


4
3b
3a