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PTC THERMISTOR OF $BaTiO_3$ AND OTHER OXIDES

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2 Sheets-Sheet 1

FIG. 1

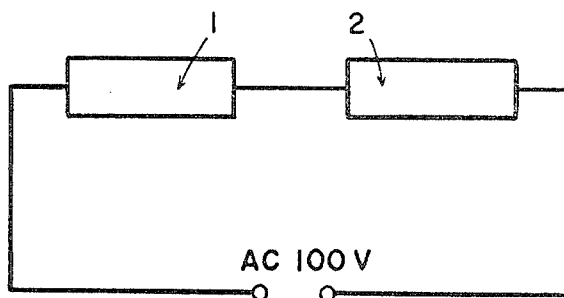
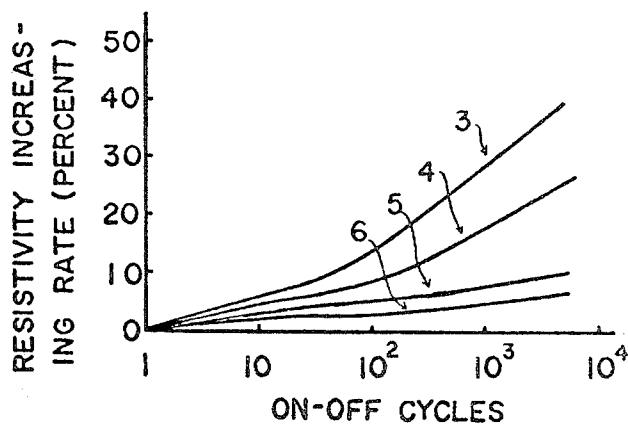


FIG. 2



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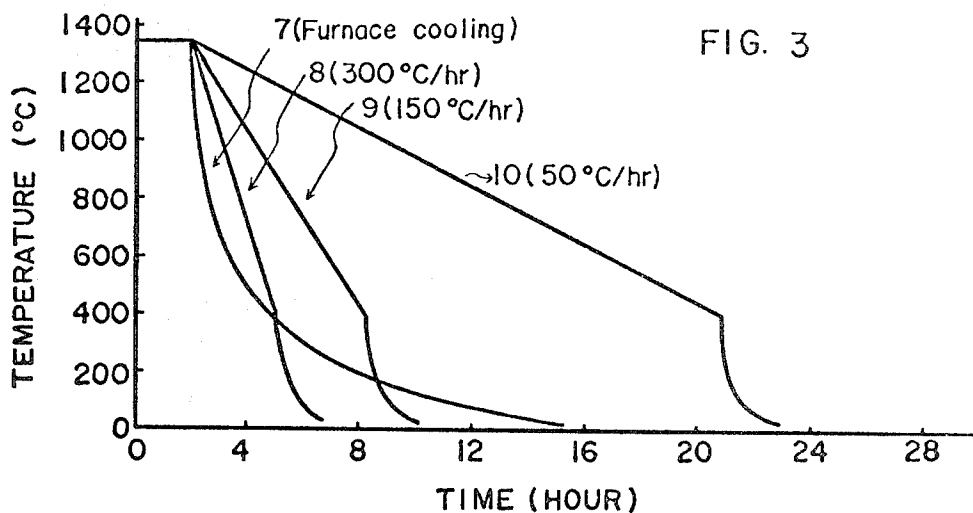
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PTC THERMISTOR OF BaTiO₃, AND OTHER OXIDES

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6 Claims

ABSTRACT OF THE DISCLOSURE

A PTC thermistor composition consisting of BaTiO₃, Al₂O₃, SiO₂, TiO₂, and one oxide selected from the group consisting of Nb₂O₅, Ta₂O₅, Sb₂O₃, Bi₂O₃, La₂O₃, CeO₂, Gd₂O₃, Sm₂O₃ and Y₂O₃, and a method of producing ceramic body for said PTC thermistor comprising mixing the constituents, calcining, pressing the calcined mixture into disks, firing the disks at 1240 to 1400° C. for 0.5 to 5 hours, and cooling the fired disks at a rate lower than 150° C. per hour.

This invention relates to a method of producing a ceramic thermistor having a positive temperature coefficient of electrical resistance, which will be hereinafter designated as PTC thermistor for convenience.

It is well known that the BaTiO₃ ceramic shows a semiconductivity when being incorporated with a small amount of metal oxide such as oxide of a rare earth element: Y, Bi, Sb, Nb or Ta. The fired semiconductive ceramic body shows an anomalous PTC behavior in a specific temperature range, which will be hereinafter called PTC range. In both temperature sides lower and higher than said PTC range, the PTC thermistor has a negative temperature coefficient of resistivity. The PTC range coincides with the temperature range where the dielectric constant of ferroelectric BaTiO₃ varies with temperature in accordance with the Curie-Weiss law. The temperature at which the PTC behavior starts to appear coincides with the ferroelectric Curie-point at which the crystal structure transforms from tetragonal to cubic symmetry. The temperature at which the PTC behavior starts to appear will be hereinafter designated as PTC onset temperature. Therefore, a PTC onset temperature of the PTC thermistors can be shifted by a substitution of the constituents of the thermistor material compositions as well as in the case of ferroelectric BaTiO₃ solid solutions.

The PTC thermistors have been recognized as promising components for electric devices. Possible applications thereof are for use as an element of a heating device with a self-current regulating action, over-heat protector, temperature controller, etc.

The conventional PTC thermistors tend to show an increase in the electrical resistance thereof with aging and the increase is accelerated by a high electric power loading. Such increase in the electrical resistance is most seriously observed in the lower temperature side than in the PTC range. Since the electrical resistance of the

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PTC thermistor in the lower temperature range determines the limit of electric current to be regulated, an increase in the electrical resistance is undesirable for practical application in a high electric power situation.

For these reasons, PTC thermistors have not served as heating device elements for regulating high electric power.

It is, therefore, an object of the present invention to provide a PTC thermistor characterized by high stability during the working thereof under high electric power.

It is another object of the present invention to provide a method of producing a PTC thermistor characterized by high stability under a high electric power test.

These objects of the present invention and the manner of their attainment will be apparent to the art-skilled upon consideration of the following description taken together with the accompanying drawings in which:

FIG. 1 is a block diagram showing an electrical circuit for high power aging tests.

FIG. 2 is a graph showing comparison of the stability of PTC thermistors according to prior art and according to the present invention.

FIG. 3 is a graph showing cooling curves of the ceramic elements for PTC thermistors.

The novel PTC thermistor according to the present invention is of a composition consisting essentially of 89.5 to 99.955 weight percent BaTiO₃, 0.014 to 2.8 weight percent of Al₂O₃, 0.026 to 7.8 weight percent of SiO₂, and 0.01 to 3.0 weight percent of TiO₂, said Al₂O₃, SiO₂ and TiO₂ being totally less than 10 weight percent, and 0.005 to 0.5 weight percent of an oxide selected from the group consisting of Nb₂O₅, Ta₂O₅, Sb₂O₃, Bi₂O₃, La₂O₃, CeO₂, Gd₂O₃, Sm₂O₃ and Y₂O₃.

The conventional PTC thermistor is of a composition consisting of, for example, 99.8 weight percent of BaTiO₃ and 0.2 weight percent of rare earth oxide or other dopant such as Bi₂O₃ and Sb₂O₃. It has been known that the conventional PTC thermistor with a single addition of La₂O₃ is impaired in semiconductivity and PTC behavior when incorporated with a minor amount of Al₂O₃. However, the novel compositions according to the present invention include Al₂O₃ and show a good semiconductivity and a marked PTC behavior.

The fact that the compositions according to the present invention are not badly affected by an incorporation of Al₂O₃ is advantageous for PTC thermistor manufacturing. Mixing and crushing steps in the usual ceramic manufacturing process employ a ball mill which is made of ceramic material including Al₂O₃. The use of such ball mill results in a contamination by Al₂O₃, which impairs the semiconductivity of the conventional PTC thermistor. However, the novel compositions according to the present invention are not impaired by the use of ball mill made of ceramic material including Al₂O₃.

A PTC thermistor according to the present invention has a high stability while working under high electric power. On the contrary, the conventional PTC thermistor is stable during working under an electric current less than 50 ma. per cm.² but is not sufficiently stable with an electric current as high as 500 ma. per cm.².

The PTC thermistors according to the present invention are prepared in a manner similar to that of prior ceramic technique. The starting materials of a given composition

are well mixed in a ball mill made of ceramic material and are pressed into disks at a pressure of 500 to 1000 kg. per cm.² (kilograms per square centimeter). The pressed disks are fired in air at 1240 to 1400° C. for 0.5 to 5 hours. The fired disks are cooled to room temperature (15 to 30° C.) The ceramic disks are provided on both surfaces with ohmic aluminum electrodes prepared by the molten Al spraying method. Solders having a melting point higher than 350° C. are superposed on the aluminum electrodes by a metallizing method. Lead wires are attached to the electrode by soldering.

The resultant PTC thermistors are subjected to aging test under an electrical loading. The PTC thermistors for testing have a diameter of 30 mm. and a thickness of 3 mm. The PTC thermistor is connected in series with an Ni-Cr alloy resistor and the series circuit is supplied with AC 100 v. as shown in FIG. 1, where said PTC thermistor and alloy resistor are respectively designated as 1 and 2. The aging test is carried out by repeating the cycle of supplying the voltage on and off for 5 minutes and 3 minutes, respectively. Said Ni-Cr alloy resistor is adjusted in the resistance to limit the maximum current flowing through the PTC thermistor. The high electric power tests are carried out at a condition of maximum current density of 500 ma. per cm.². This current density corresponds to approximately 7 amps with a disk type thermistor of 30 mm. in diameter. Such high current density is taken in view of the practical application of the PTC thermistor to a heating device.

Since the PTC thermistor has a low resistance in the lower temperature side than the PTC range, a large current, i.e. a rush current, flows through the circuit for a moment immediately after the AC 100 voltage is supplied. Accordingly, the PTC thermistor is self-heated by the rush current and reaches a temperature at which a thermal equilibrium is attained between the PTC thermistor and the ambient. Since the resistance of the PTC thermistor in the PTC range is much larger than that of an alloy resistor, the larger part of the supplying voltage is supplied to the PTC thermistor. Within the 3 minutes off-time, the PTC thermistor is cooled to room temperature. Before and after the aging test, the resistivity is measured and resistivity increasing rate is calculated. It is desirable to lower the increasing rate of resistivity as low as possible.

One aging test run has 5000 on-off cycles of electric loadings.

In FIG. 2, the curve 3 is for the conventional PTC thermistor of a composition of BaTiO₃ with 0.2 weight percent of Nb₂O₅ and curve 4 is for the novel PTC thermistor of a composition of BaTiO₃ with 0.225 weight percent of Al₂O₃, 1.9 weight percent of SiO₂, 0.375 weight percent of TiO₂, and 0.05 weight percent Nb₂O₅. Both thermistors are prepared in a manner similar to that set forth above. They are fired at 1350° C. for 2 hours in air and cooled to room temperature at a cooling rate defined by curve 7 of FIG. 3. It is clear from FIG. 2 that the novel composition is superior to the conventional composition in respect of stability in the high electric power test.

According to the present invention, the cooling rate has a large effect on stability in the high electric power test. It is desirable that the fired ceramic body be cooled from the firing temperature to room temperature at a cooling rate less than 150° C. per hour. As a practical matter, an advantageous procedure is that the fired ceramic body is cooled at a cooling rate of 50 to 150° C. per hour in the temperature range from the firing temperature to approximately 400° C.

The following description will explain examples of the novel cooling rate. A PTC thermistor of a composition similar to that of curve 4 of FIG. 2 is fired at 1350° C. for 2 hours in air and cooled at a rate defined by curves 9 and 10 of FIG. 3. The results for the high power tests are shown in FIG. 2 as curves 5 and 6. It will be clear on

comparison of curve 4 with curves 5 and 6 that the novel cooling rate results in a high stability in high power tests.

A PTC thermistor is required to shift the PTC onset temperature depending on practical applications thereof.

Said PTC thermistor has a lower PTC onset temperature without impairing the semiconductivity thereof by a partial replacement of Ba with Sr. The larger the amount of replaced Ba, the lower the PTC onset temperature. Operable amount of replaced Ba is less than 40 atomic percent.

Said PTC thermistor composition has a higher PTC onset temperature without impairing the semiconductivity when the Ba atoms in an amount less than 30 atomic percent are partially replaced by an equivalent atomic percent of Pb. The higher the amount of the replaced Ba, the higher the PTC onset temperature.

The PTC onset temperature of said PTC thermistor is lowered without impairing the semiconductivity by substituting Sn, in an amount less than 30 atomic percent, for an equivalent atomic percent of Ti in said BaTiO₃.

The substitution of Zr in an amount less than 20 atomic percent for an equivalent amount of Ti in said BaTiO₃ also lowers the PTC onset temperature without impairing the semiconductivity.

Both substitutions of Pb for Ba and of Sn for Ti in the novel compositions of the present invention produce a PTC thermistor having a higher stability in the high electric power test. Advantageous substitution amounts are 1 to 30 atomic percent of Sn for Ti and 1 to 20 atomic percent of Pb for Ba in said BaTiO₃, respectively. Both substitutions cause the PTC onset temperature of the resultant PTC thermistor to shift to the lower temperature side when the Sn substitution amount in atomic percent is larger than 0.4 times the Pb substitution amount in atomic percent. On the contrary, the PTC onset temperature of the both-substituted PTC thermistors shifts to the higher temperature side when the Sn substitution amount in atomic percent is smaller than 0.4 times the Pb substitution amount in atomic percent. When the Sn substitution amount in atomic percent is 0.4 times of the Pb substitution amount in atomic percent, the resultant PTC thermistor shows no shift of the PTC onset temperature.

In all cases of both substitutions, the resultant PTC thermistors show a higher stability in the high electric power test in accordance with the present invention.

EXAMPLE

For the preparation of the PTC thermistor compositions listed in Table I, mixtures of BaCO₃, TiO₂, Al₂O₃, SiO₂ and one oxide selected from the group consisting of Nb₂O₅, Ta₂O₅, Bi₂O₃, Sb₂O₃, La₂O₃, CeO₂, Gd₂O₃, Sm₂O₃ and Y₂O₃ were well mixed by a wet ball mill, calcined, and pressed at a pressure of 700 kg. per cm.² into disks. The pressed disks were fired at various temperatures for various periods of time as shown in Table II. The fired disks were cooled from the firing temperature to 400° C. at a cooling rate defined by curve 7, 8, 9 or 10 of FIG. 3 and afterward the disks were allowed to cool to room temperature. The cooled disks were in a size of 30 mm. diameter and 3 mm. thickness and were provided, at both surfaces, with an ohmic Al electrode by the molten Al spraying method. Two lead wires were attached to the Al electrodes by using solder having a melting point of 350° C. The resultant disks were measured with respect to the PTC characteristics as shown in Table II and also subjected to the high electric power test in a manner hereinbefore described. Table II also shows the results of the high electric power tests.

It is clear from Table II that the PTC thermistors of compositions according to the present invention are superior to conventional PTC thermistors in stability in high power test. Table II also shows that the novel cooling rate according to the present invention has a marked effect to improve the stability in the high power test.

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TABLE I

Sample No.	Principal composition	Additives (weight percent)			
		Al ₂ O ₃	SiO ₂	TiO ₂	Nb ₂ O ₅
1	BaTiO ₃	0	0	0	0.2
2	Same as above	0	0	3	0.2
3	do	0.7	1.3	0.5	0.005
4	do	0.7	1.3	0.5	0.01
5	do	0.7	1.3	0.5	0.1
6	do	0.7	1.3	0.5	0.5
7	do	0.014	0.026	0.01	0.1
8	do	0.14	0.26	0.10	0.1
9	do	0.175	2.15	0.175	0.1
10	do	2.8	5.2	2.0	0.1
11	do	0.9	7.6	1.5	0.1
12	do	4.2	7.8	3.0	0.1
13	do	0.225	1.9	0.375	0.05
14	Ba _{0.5} Pb _{0.2} TiO ₃	0.225	1.9	0.375	0.1
15	Ba _{0.5} Sr _{0.1} TiO ₃	0.7	1.3	0.5	0.1
16	Ba _{0.5} Sr _{0.3} TiO ₃	0.7	1.3	0.5	0.1
17	BaTi _{0.35} Sn _{0.65} O ₃	0.7	1.3	0.5	0.1
18	BaTi _{0.3} Sn _{0.2} O ₃	0.7	1.3	0.5	0.1
19	BaTi _{0.2} Zr _{0.1} O ₃	0.7	1.3	0.5	0.1
20	Ba _{0.35} Pb _{0.35} Ti _{0.25} Sn _{0.05} O ₃	0.7	1.3	0.5	0.1
21	Ba _{0.35} Pb _{0.35} Ti _{0.25} Sn _{0.05} O ₃	0.7	1.3	0.5	0.1
22	Ba _{0.5} Pb _{0.1} Ti _{0.5} Sn _{0.2} O ₃	1.0	1.5	0.5	0.2
23	BaTiO ₃	0.7	1.3	0.5	0.005
					Sb ₂ O ₃
24	Same as above	0.7	1.3	0.5	0.5
					Bi ₂ O ₃

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TABLE I.—Continued

	Sample No.	Principal composition	Additives (weight percent)			
			Al ₂ O ₃	SiO ₂	TiO ₂	Nb ₂ O ₅
5	25	BaTiO ₃	0.7	1.3	0.5	0.005
	26	BaTi _{0.9} Sn _{0.1} O ₃	0.5	1.5	0.5	0.1
10						La ₂ O ₃
	27	BaTiO ₃	0.7	1.3	0.5	0.5
	28	BaTi _{0.9} Sn _{0.1} O ₃	0.7	1.3	0.5	0.1
						CeO ₂
15	29	BaTiO ₃	0.7	1.3	0.5	0.05
						Gd ₂ O ₃
	30	BaTiO ₃	0.7	1.3	0.5	0.05
	31	Ba _{0.95} Pb _{0.05} Ti _{0.95} Sn _{0.02} O ₃	0.7	1.5	0.5	0.1
20						Sm ₂ O ₃
	32	BaTiO ₃	0.7	1.3	0.5	0.05
20						Y ₂ O ₃
	33	Ba _{0.95} Pb _{0.05} TiO ₃	0.7	2.0	0.5	0.5

TABLE II

[illegible]

TABLE II.—Continued

Column								
	1	2	3	4	5	6	7	
Sample No.	Firing condition		Resistivity at 25° C. (ohm-cm.)	PTC onset temp. (° C.)	Resistivity at PTC onset, temp. (ohm-cm.)	PTC of resistivity (ohm-cm.)	Cooling rate (° C.hr.)	Increasing rate of resistivity (after 5,000 on-off cycle aging test (percent)
	Temp. (° C.)	Time (hr.)						
21-----	1,260	0.75	150	90	140	12	FC 20 150 10 50 7	
22-----	1,260	0.75	750	10	200	8	FC 18 300 10 150 5	
23-----	1,320	2	100	110	95	15	FC 25 300 10 150 8	
24-----	1,320	2	2,000	110	1,800	16	FC 20 300 8 150 8	
25-----	1,320	2	850	110	800	13	FC 25 300 10 150 8	
26-----	1,340	2	30	20	25	10	FC 20 300 10 150 6	
27-----	1,340	2	80	115	70	15	FC 30 300 12 150 10	
28-----	1,360	2	120	50	110	10	FC 25 300 18 150 10	
29-----	1,320	2	90	115	80	14	FC 25 300 20 150 12	
30-----	1,320	2	90	110	90	15	FC 25 300 20 150 15	
31-----	1,280	1	80	115	70	12	FC 20 300 12 150 5	
32-----	1,320	2	85	120	70	13	FC 28 300 20 150 12	
33-----	1,280	1	80	145	70	12	FC 22 300 14 150 8	

NOTE.—FC=Furnace cooling.

What is claimed is:

1. A PTC thermistor composition consisting essentially of 89.5 to 99.955 percent by weight of BaTiO₃, 0.014 to 2.8 percent by weight of Al₂O₃, 0.026 to 7.8 percent by weight of SiO₂, and 0.01 to 3 percent by weight of TiO₂, said Al₂O₃, SiO₂, and TiO₂ being less than 10 percent by weight in all, and 0.005 to 0.5 percent by weight of one oxide selected from the group consisting of Nb₂O₅, Ta₂O₅, Sb₂O₃, Bi₂O₃, La₂O₃, CeO₂, Gd₂O₃, Sm₂O₃ and Y₂O₃.

2. A PTC thermistor composition according to claim 1, wherein Ba is replaced by an amount of Sr less than 40 atomic percent.

3. A PTC thermistor composition according to claim 1, wherein Ba is replaced by an amount of Pb less than 30 atomic percent.

4. A PTC thermistor composition according to claim 1, wherein Ti is replaced by an amount of Sn less than 30 atomic percent.

5. A PTC thermistor composition according to claim 1, wherein Ti is replaced by an amount of Zr less than 20 atomic percent.

6. A PTC thermistor composition according to claim 1, wherein Ba is replaced by an amount of 1 to 20 atomic percent of Pb and Ti is replaced by an amount of 1 to 30 atomic percent of Sn.

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U.S. Cl. X.R.

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