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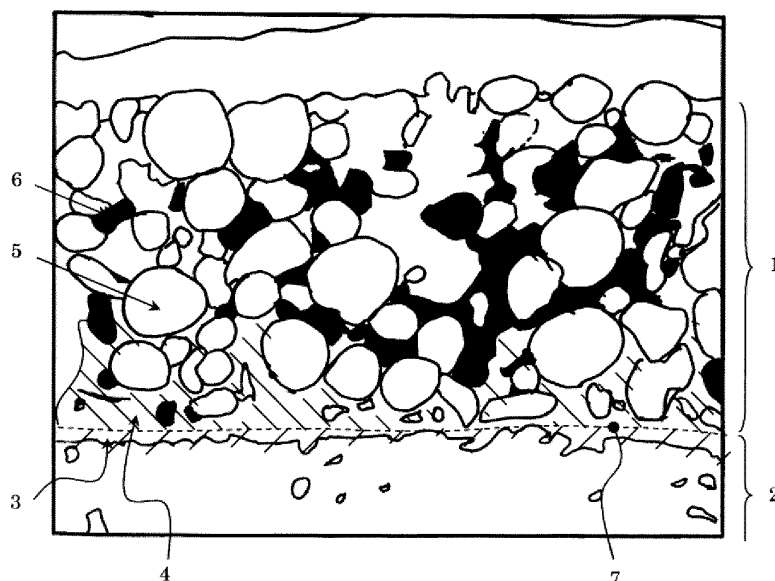
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(54) **PTC ELEMENT AND HEAT-GENERATING MODULE**

(57) Provided is a PTC element formed by baking a base metal-based electrode onto a semiconductor ceramic composition, wherein the semiconductor ceramic composition has a perovskite structure consisting of a BaTiO₃ type oxide, the base metal-based electrode contains, as a primary component, at least one of Al and Ni

as a metal component and also contains at least B, and a low resistance layer, which has a lower resistance than the parent phase of the semiconductor ceramic composition, is formed on the base metal-based electrode side of the semiconductor ceramic composition.

FIG. 2



Description

Technical Field

5 **[0001]** The present invention relates to: a PTC element in which an electrode is formed on a semiconductor ceramic composition having a positive temperature coefficient of resistivity; and a heat generating module.

Background Art

10 **[0002]** Conventionally, as materials showing a PTC characteristic (Positive Temperature Coefficient of resistivity), there have been proposed semiconductor ceramic compositions in which various semiconductor-forming elements are added to perovskite type compositions represented by BaTiO_3 . The PTC characteristic is a characteristic that a resistance value sharply increases at a high temperature of the Curie point or higher. Semiconductor ceramic compositions having the PTC characteristic are used as PTC elements after electrodes are formed thereon.

15 **[0003]** Patent Document 1 describes, with respect to a PTC element using a non-lead semiconductor ceramic composition and an electrode, that a composition containing 50 to 80% of BaTiO_3 , 3 to 15% of CaTiO_3 , up to 50% of SrTiO_3 and 1 to 2% of SiO_2 is preferred as a semiconductor ceramic composition (see paragraph 0006). Moreover, as a method of forming the electrode, the electrode or a partial layer of the electrode is preferably manufactured by a metal deposition method. Examples of the metal deposition method include sputtering, vapor deposition, electrolytic deposition and a chemical deposition. However, it is described that the electrode may be made by baking of a metal paste (see paragraph 0007).

20 **[0004]** Patent Document 2 describes a semiconductor ceramic wherein the ceramic has a Ba_mTiO_3 -based composition having a perovskite type structure represented by the general formula A_mBO_3 as a main component, a part of Ba constituting the A site is substituted by at least an alkali metal element, Bi and a rare earth element and also the molar ratio m of the A site to the B site is $0.990 \leq m \leq 0.999$, and the ceramic has a good rise characteristic (see paragraph 0026). Also, there is a description of forming an external electrode by plating, sputtering, electrode baking, or the like to thereby obtain a PTC thermistor (see paragraph 0069). In Examples, dry plating is performed to form an external electrode having a three-layer structure of NiCr/NiCu/Ag (see paragraph 0079).

25 **[0005]** As for a PTC element, in the whole production costs thereof, a material cost of electrodes and a cost of the production process for forming the electrode occupy a very large proportion.

30 **[0006]** The metal deposition method which is one of methods for forming electrodes has an advantage that the adhesion between the semiconductor ceramic composition and the electrode can be easily enhanced and thus the resistance at the interface between both (hereinafter referred to as "interfacial resistance") can be easily reduced. Smaller interfacial resistance also reduces the resistance of the PTC element (hereinafter referred to as "element resistance") and hence it is possible to improve the current efficiency of the PTC element. However, on the other hand, the metal deposition method has a problem that the production costs are high.

35 **[0007]** As a means for forming an electrode inexpensively, a method of baking is adopted in some cases. The baking is a method of manufacturing an electrode paste in which a metal powder is dispersed in a glass component or an organic component, applying the paste to a semiconductor ceramic composition by printing or the like, and heating the electrode paste to evaporate the glass component or the organic component from it to leave the metal component, thereby forming an electrode.

40 **[0008]** Patent Document 3 discloses a PTC element having at least two ohmic electrodes and a semiconductor ceramic composition in which a part of Ba of BaTiO_3 disposed between the electrodes is substituted by Bi-Na, wherein the semiconductor ceramic composition is represented by a composition formula of $[(\text{Bi-Na})_x(\text{Ba}_{1-y-\theta}\text{R}_y\text{A}_\theta)_{1-x}]\text{Ti}_{1-z}\text{M}_z\text{O}_3$ (where R is at least one kind of rare earth elements, A is at least one kind of Ca and Sr, M is at least one kind of Nb, Ta and Sb), wherein x , y , z , and θ satisfy $0 < x \leq 0.30$, $0 \leq y \leq 0.020$, $0 \leq z \leq 0.010$ and $0 \leq \theta \leq 0.20$, and the ratio of the area where the ohmic component of the electrodes and the semiconductor ceramic composition are not in contact therewith at the interface between the electrodes and the semiconductor ceramic composition is 25% or less. In Examples, it is described that the electrodes contains Ag as a main metal component.

45 **[0009]** Meanwhile, as metal elements, there are those using a noble metal-based electrode paste whose main component is an element such as Ag, Au or Pt and those using a base metal-based electrode paste whose main component is an element such as Al or Ni. When the noble metal-based electrode paste is used, it is possible to bake the electrode in the air since the paste is difficult to oxidize. However, since a noble metal element is expensive, it hinders cost reduction of the PTC element.

50 **[0010]** In contrast, since a base metal-based electrode paste contains Al, Ni or the like as a main metal component, the paste is very inexpensive. However, it prevents a decrease in resistance since it is easily oxidized.

55 **[0011]** Patent Document 4 discloses an electronic component electrode composed of a metal aluminum and 0.1 to 10 weight % of boron nitride and 0.01 to 5 weight % of glass frit (lead borosilicate glass). It is described that the electrode

material can be converted into an electrode having an ohmic property with respect to an ceramic element by firing at 850 to 900°C in the air.

Prior Art Documents

Patent Documents

[0012]

Patent Document 1: JP-T-2010-501988 (the term "JP-T" as used herein means a published Japanese translation of a PCT patent application)
 Patent Document 2: WO2010/067866
 Patent Document 3: JP-A-2012-169515
 Patent Document 4: JP-A-3-233805

Summary of the Invention

Problems that the Invention is to Solve

[0013] However, when a base metal-based electrode using Al or Ni is baked onto a BaTiO₃-based semiconductor ceramic composition (hereinafter sometimes simply referred to as an "electrode"), a gap is formed at the interface between the semiconductor ceramic composition and the electrode, so that the both do not come into ohmic contact. Therefore, there arises a problem that the interface resistance per unit area (1 cm²) at the interface between the semiconductor ceramic composition and the electrode increases, for example, beyond 10 Ω. When the interface resistance increases, the current efficiency of the PTC element is lowered. Hereinafter, the description of the "per unit area (1 cm²)" is omitted and the resistance is simply referred to as "interface resistance".

[0014] An object of the present invention is to provide: a PTC element having sufficiently small interface resistance when a base metal-based electrode is formed on a semiconductor ceramic composition having a perovskite structure composed of a BaTiO₃ type oxide by baking; and a heat generating module.

Means for Solving the Problems

[0015] The present invention is directed to a PTC element in which a base metal-based electrode is formed on a semiconductor ceramic composition by baking, wherein the semiconductor ceramic composition has a perovskite structure composed of a BaTiO₃ type oxide, the base metal-based electrode contains, as a main component, at least one kind of Al and Ni as a metal component and also contains at least B, and a low resistance layer having a resistance smaller than that of a matrix phase of the semiconductor ceramic composition is formed on a base metal-based electrode side of the semiconductor ceramic composition.

[0016] In the PTC element of the present invention, a thickness of the low resistance layer is preferably 0.1 μm or more.

[0017] In the present invention, in the PTC element, a thickness of the low resistance layer can be 0.4 μm or more and an interface resistance of the element per unit area (1 cm²) can be 5 Ω or less.

[0018] In the present invention, in the PTC element, an element resistance of the element per unit area (1 cm²) can be 10 Ω or less.

[0019] In the present invention, in the PTC element, a surface resistance thereof can be 10 mΩcm or less.

[0020] In the PTC element of the present invention, a reaction phase mainly including a Ba oxide is preferably present on a semiconductor ceramic composition side of the base metal-based electrode.

[0021] The base metal-based electrode in the present invention can have a composition containing B in an amount of 3 mass % or more and 25 mass % or less when a total of Al, Ni and B is 100 mass %.

[0022] The base metal-based electrode in the present invention can contain Si as a metal component and contain B in an amount of 3 mass % or more and 25 mass % or less and Si in an amount of more than 0 mass % and 26 mass % or less when a total of Al, Ni, B and Si is 100 mass %.

[0023] The base metal-based electrode in the present invention can contain Al in an amount of 50 mass % or more when a total of Al, Ni, B and Si is 100 mass %.

[0024] The base metal-based electrode in the present invention can contain Ni in an amount of 5 mass % or more and 40 mass % or less when a total of Al, Ni, B and Si is 100 mass %.

[0025] In the base metal-based electrode in the present invention, an Al particle having an average particle diameter of 1.2 μm or more and 10 μm or less can be dispersed in the base metal-based electrode.

[0026] The semiconductor ceramic composition in the present invention can have a composition represented by a

composition formula of $[(\text{BiA})_x(\text{Ba}_{1-y}\text{R}_y)_{1-x}][\text{Ti}_{1-2}\text{M}_z]\text{O}_3$ (A is at least one kind of Na, Li and K, R is at least one kind of rare earth elements including Y, M is at least one kind of Nb, Ta and Sb), wherein x, y and z satisfy the ranges of $0 < x \leq 0.25$, $0 < y \leq 0.052$ and $0 \leq z \leq 0.01$ (where $y+z > 0$).

[0027] The base metal-based electrode in the present invention can be baked at a temperature of 720°C or higher and 850°C or lower in an air atmosphere.

[0028] In the present invention, a heat generating module includes the PTC element according to any one of the above ones, and the semiconductor ceramic composition generates heat.

Advantage of the Invention

[0029] According to the present invention, even when a base metal-based electrode is formed by baking, a PTC element having small interface resistance can be provided. In addition, the PTC element can become a PTC element also having small element resistance. Furthermore, it is possible to provide a heat generating module having excellent current efficiency using the PTC element.

Brief Description of the Drawings

[0030]

FIG. 1 is an SEM observation photograph of a cross-section of the PTC element according to one embodiment of the present invention.

FIG. 2 is a schematic view of FIG. 1.

FIG. 3 is an A1 mapping picture by EDX analysis in the same visual field as that of FIG. 1.

FIG. 4 is a schematic view of FIG. 3.

FIG. 5 is a Ba mapping picture by EDX analysis in the same visual field as that of FIG. 1.

FIG. 6 is a schematic view of FIG. 5.

FIG. 7 is an SSRM observation photograph of a cross-section of the PTC element according to another embodiment of the present invention.

FIG. 8 is a schematic view of FIG. 7.

FIG. 9 is a schematic view showing one example of the heat generating module according to one embodiment of the present invention.

FIG. 10 is a view for explaining the measuring method of interface resistance.

Modes for Carrying Out the Invention

[0031] The present inventors have found that, by incorporating a resistance-decreasing auxiliary agent such as B (boron) as a metal component of a base metal-based electrode using A1 or Ni, a low resistance layer having small resistance with respect to the matrix phase is formed on a base metal-based electrode side of the semiconductor ceramic composition, the layer improves ohmic contact, and accordingly, the interface resistance and the like can be reduced. The following will describe a decrease in resistance of the PTC element of the present invention.

[0032] FIG. 1 is an SEM observation photograph of a cross-section of the PTC element showing one example of the present invention and FIG. 2 is a schematic view thereof. FIG. 7 is also an observation photograph of the PTC element cross-section by a scanning spread resistance microscope (SSRM) and FIG. 8 is a schematic view thereof.

[0033] In FIGs. 1 and 2, 1 is a base metal-based electrode, 2 is a semiconductor ceramic composition having a perovskite structure composed of a BaTiO_3 type oxide. The interface between the base metal-based electrode 1 and the semiconductor ceramic composition 2 is a broken line part 7 drawn horizontally in the figure, and it is found that a low resistance layer 3 is formed on the base metal-based electrode side of the semiconductor ceramic composition 2. According to the resistance value distribution in FIGs. 7 and 8, the color tone of the low resistance layer 3 has become darker than the other and thus it is found that the layer has low resistance than the matrix phase. That is, in the present description, the low resistance layer means a layer that forms a portion having small resistance as compared with the matrix phase of the semiconductor ceramic composition and its resistance value is, for example, $1 \Omega \cdot \text{cm}$ or less. Details thereof will be described later.

[0034] Since the low resistance layer 3 has low electric resistance and has many carriers as a semiconductor, the Schottky barrier between the low resistance layer 3 and the base metal-based electrode 1 becomes low and the interface resistance is decreased due to ohmic contact. The low resistance layer 3 need not necessarily be a continuous layer but it is preferable that the layer is formed with being spread throughout the interface and the thickness is suitably $0.1 \mu\text{m}$ or more. When the thickness is $0.2 \mu\text{m}$ or more, the decrease in the resistance is promoted, so that the case is more preferred. The thickness is further preferably $0.4 \mu\text{m}$ or more and most preferably $0.5 \mu\text{m}$ or more. The upper limit of

the thickness is affected by the B content or baking temperature but the effect of reducing the interface resistance may not be expected so much even when the thickness is beyond 3 μm . This is because, since the resistance-decreasing auxiliary agent such as B itself has high resistance, there are rather inconveniences such as insulation resistance and a decrease in thermal conductivity when the added amount is excessive.

[0035] In the case where the low resistance layer 3 is formed, a reaction phase 4 to be formed resulting from the diffusion of Ba to the electrode side is formed thicker as before in the base metal-based electrode 1. The reaction phase 4 includes of an oxide containing Ba as a main component. Moreover, since the reaction phase 4 is formed so as to fill the gap at the interface between the low resistance layer 3 and the electrode 1 or the gap between A1 particles, the contact area therebetween is increased and thus the phase contributes to a decrease in the interface resistance. When the reaction phase 4 is further thickened, there is also an effect that the adhesion strength between the semiconductor ceramic composition and the electrode becomes high. Although the presence or absence of the reaction phase can be determined from the SEM observation photograph, the shape is irregular and the size is difficult to be identified, so that the phase is not defined in a quantitative manner. However, if the low resistance layer is formed, the reaction phase is also formed. With the thickening of the low resistance layer, the reaction phase also tends to become thicker.

[0036] The mechanism of the formation of the low resistance layer is not clear, but is considered as follows. When a readily oxidizable element such as B is introduced into the base metal-based electrode, B or the like deprives oxygen from the semiconductor ceramic composition during baking to make oxygen defects in the crystal structure. Emitted electrons are generated around the interface and it is considered that the low resistance layer is formed based on them. Also, all the oxygen defects made at this time not necessarily emit electrons and a part of them move from the semiconductor ceramic composition to the electrode side together with cations such as Ba and intend to keep electrical neutrality. It is considered that Ba which has moved at this time reacts with the electrode side to form the reaction phase. As the resistance-decreasing auxiliary agent having such an action, B is most preferred but the agent may be an element which expresses the above mechanism and, for example, at least one kind of Zn, Ca, Sb and Sn may be used together with B or solely.

[0037] In the present invention, the base metal-based electrode contains at least one kind of Al and Ni as a main component, as a whole metal component. The term "containing at least one kind of Al and Ni as a main component" means one in which the content of Al or Ni is 50 mass % or more or one in which the sum of the contents of Al and Ni is 50 mass % or more. However, since Al is cheaper in cost than Ni, it is preferable to form an electrode which contains Al more in amount than Ni. Also, since the vicinity of the metal surface is covered with an oxide layer, Al is chemically stable and excellent in reliability and, since oxidation hardly proceeds toward the inside, baking in the air atmosphere is easily conducted. Also in this respect, it is possible to reduce costs.

[0038] B to be incorporated in the base metal-based electrode may be contained in an amount of 3 mass % or more and 25 mass % or less based on 100 mass % of the total of Al, Ni and B. The incorporation of B enables the formation of a low resistance layer having a thickness of 0.1 μm or more. Furthermore, when the amount is controlled to 3 mass % or more, the thickness of the low resistance layer can be 0.4 μm or more and the low resistance layer and the reaction phase can be sufficiently formed, so that it is possible to obtain a PTC element having an interface resistance of 5 Ω or less. The electrode may contain Si as described below.

[0039] When B is contained in an amount of more than 25 mass %, B is exuded to the surface layer of the electrode and an oxide layer begins to be generated on the surface, so that there is a tendency that the surface resistance of the electrode increases. Since there is a tendency that the element resistance also increases, the upper limit is preferably 25 mass % or less. More preferred is 5 mass % or more and 17 mass % or less, and at this time, a PTC element having an interface resistance of 1.5 Ω or less, an element resistance of about 5 Ω or less and a surface resistance of 10 m Ωcm or less can be obtained. Furthermore, when the amount is 5 mass % or more and less than 10 mass %, a PTC element also having a surface resistance of 2 m Ωcm or less can be obtained. Here, the surface resistance is a measured value of the resistance of the base metal-based electrode itself. When the surface resistance is decreased, there is an effect that an electric field can be uniformly applied to the PTC element.

[0040] Moreover, the base metal-based electrode may contain Si as a metal component and contain B in an amount of 3 mass % or more and 25 mass % or less and Si in an amount of more than 0 mass % and 26 mass % or less based on 100 mass % of the total of Al, Ni, B and Si. When Si is incorporated in the above range, it is possible to improve moisture resistance and a change in element resistance with time, particularly a change of the PTC element with time under a high temperature and high humidity environment can be decreased. When Si is contained, Al particles that are difficult to melt can be easily melted and the ratio of the contact area at the interface between the A1 particles are increased and thus Si also acts on the reduction of the interface resistance. The content of Si is preferably 5.0 mass % or more and 20.0 mass % or less, and more preferably 5.0 mass % or more and 15.0 mass % or less.

[0041] It is preferred to add B in the form of not an oxide but a simple metal. When B is added as a stable compound such as an oxide or a nitride thereof, an ability to deprive oxygen from the semiconductor ceramic composition cannot be exhibited or a force to deprive oxygen is weak, so that it becomes difficult to form the low resistance layer. Moreover, when the low resistance layer is not formed, Ba in the semiconductor ceramic composition becomes difficult to move to

the electrode side, so that the reaction phase is also hardly formed.

[0042] Furthermore, the base metal-based electrode preferably one contains Si and contains A1 in an amount of 50 mass % or more based on 100 mass % of the total of Al, Ni, B and Si. The costs of the electrode can be further reduced.

[0043] Moreover, the base metal-based electrode may contain Ni in an amount of 5 mass % or more and 40 mass % or less based on 100 mass % of the total of Al, Ni, B and Si. Preferably, when it contains A1 in an amount of 50 mass % or more and Ni in the above range, Ni particles remove the oxide layer on the surface of A1 particles at low temperature to facilitate the alloying of the Al particles and the Ni particles, so that it is possible to lower electrode baking temperature. However, it is desirable to adjust the baking time to the extent that an excessive sintering reaction does not occur. When the amount of Ni is 5 mass % or more, the above effect can be sufficiently obtained. Moreover, when the amount of Ni is controlled so as not to exceed 40 mass %, an increase in the resistance of the electrode itself is easily avoided and further, an increase in the material cost of the electrode can be suppressed. When the amount of Ni is 20 mass % or more, the baking temperature can be further lowered and specifically, it becomes possible to perform baking at 700°C.

[0044] When a base metal-based electrode containing Ni in an amount of 20 mass % or less, B in an amount of 5 mass % or more and 10 mass % or less, and Si in an amount of 5.0 mass % and 15.0 mass % or more, the balance being Al, is used, it is possible to obtain a PTC element having an interface resistance of 1.5 Ω or less, an element resistance of 10 Ω or less, and a surface resistance of 2.0 m Ω cm or less.

[0045] As the A1 powder to be used in the base metal-based electrode, one having an average particle diameter of 1.2 μm or more and 10 μm or less can be suitably used. Furthermore, it is more preferable to use the powder having a particle size distribution that a particle diameter of median diameter d30 is 0.1 μm or more and less than 1.2 μm .

[0046] The A1 particles in the base metal-based electrode is less likely to melt since an oxide film is present on the surface and, as shown in FIG. 2, remain at about the same size as the size at the time when the particles are contained in the electrode paste before baking. Therefore, a gap 6 is easily generated between the A1 particles and thus the contact area between the semiconductor ceramic composition and the electrode decreases, so that the interface resistance is likely to increase. For the reason, it is appropriate to use A1 particles having an average particle diameter of 1.2 μm or more and 10 μm or less, and further, by adopting an electrode structure of a particle size distribution containing about 20 to 40% of small particles having an average particle diameter of less than 1.2 μm , there is obtained a form that small A1 particles having an average particle diameter of 0.1 μm or more and less than 1.2 μm are filled between Al particles of 1.2 μm or more and 10 μm or less, so that the gap at the interface decrease. Moreover, since the ratio of the contact area between the semiconductor ceramic composition and the electrode is increased by the presence of the reaction phase 4 to be formed in a relatively thick state, even when there is formed an electrode in which relatively large A1 particles are dispersed, it is easy to reduce the interface resistance of the PTC element. In addition, the adhesion strength of the electrode becomes high.

[0047] In the case where Al particles and Ni particles are both dispersed in the base metal-based electrode, it is preferable to use Ni particles having an average particle diameter smaller than that of A1 particles. It is easy to achieve a state that the Ni particles are filled into the gap between the A1 particles and the semiconductor ceramic composition and thus the state contributes to the reduction of the interface resistance. For example, when the average particle size of the A1 particles is 1.2 μm or more and 10 μm or less, the average particle diameter of the Ni particles is preferably 0.1 μm or more and 5 μm or less.

[0048] A1 particles increase a risk of dust explosion and become difficult to handle as the particle diameter decreases. On the other hand, when the particle diameter exceeds 10 μm , the ratio of the contact area tends to decrease and it tends to be difficult to reduce the interface resistance.

[0049] Next, a preferred method for obtaining the PTC element of the present invention will be described.

[0050] A production method, in which a semiconductor ceramic composition having a perovskite structure composed of a BaTiO₃ type oxide is first prepared, a base metal-based electrode paste containing, as a metal component, at least one kind of Al and Ni as a main component and containing at least B is applied to the semiconductor ceramic composition in a desired thickness by printing or the like, and the paste is heated in the air atmosphere at a temperature of 720°C or higher and 850°C or lower to bake a base metal-based electrode, can be adopted.

[0051] As for the base metal-based electrode, even when the baking temperature is as low as about 720°C, the bonding of the semiconductor ceramic composition and the electrode is less likely to be insufficient and an increase in the interface resistance is easily suppressed.

[0052] Since B has an effect as an oxidation inhibitor, the oxidation of the semiconductor ceramic composition and base metal-based electrode can be suppressed by using a base metal-based electrode paste to which B has been added, even when the baking temperature is as high as about 850°C. Thereby, it becomes easy to obtain a PTC element having small element resistance.

[0053] The baking temperature is preferably 750°C or higher and 830°C or lower and thus a PTC element having an interface resistance of 5 Ω or less and an element resistance of 10 Ω or less can be obtained. By decreasing the element resistance, it is possible to obtain a PTC element excellent in current efficiency. More preferably, the temperature is 750°C or higher and 800°C or lower.

[0054] As for the baking time of the base metal-based electrode, the time for exposure to a temperature of 720°C or higher and 850°C or lower is suitably 10 minutes or more and 5 hours or less. When the baking time is longer than 10 minutes, an increase in the interface resistance resulting from insufficient bonding of the semiconductor ceramic composition and the electrode can be easily suppressed. The oxidation suppression effect tends to fade when the baking time exceeds 5 hours, and therefore, when the baking time is shorter than the above time, it becomes easy to obtain a PTC element having small element resistance with suppressing the oxidation of the semiconductor ceramic composition. The baking time is preferably 15 minutes or more and 1 hour or less, and more preferably 20 minutes or more and 50 minutes or less.

[0055] The thickness of the electrode is suitably 5 μm or more and 50 μm or less. When the thickness is 5 μm or more, it becomes easy to suppress uneven application and peeling of the electrode. When the thickness is controlled to 50 μm or less, the costs of the electrode can be reduced. The thickness is preferably 10 μm or more and 35 μm or less, and more preferably 12 μm or more and 30 μm or less.

[0056] As for the base metal-based electrode paste, the baking temperature can be lowered to 700°C by controlling Ni to 20 mass % or more.

[0057] For the purpose of preventing oxidation of the base metal-based electrode and improving wettability of a solder, a noble metal electrode such as Ag-based one can be also formed as a second-layer electrode on the base metal-based electrode. Furthermore, an electrode structure of three layers or more is also possible, in which other electrode(s) is formed on the noble metal-based electrode.

[0058] Next, a preferred embodiment of the semiconductor ceramic composition will be described.

[0059] The semiconductor ceramic composition may have a perovskite structure composed of a BaTiO₃ type oxide but, in particular, is preferably a lead-free semiconductor ceramic composition. For example, it preferably has a composition represented by the composition formula of $[(\text{BiA})_x(\text{Ba}_{1-y}\text{R}_y)_{1-x}][\text{Ti}_{1-z}\text{M}_z]\text{O}_3$ (A is at least one kind of Na, Li and K, R is at least one kind of rare earth elements including Y, M is at least one kind of Nb, Ta, and Sb) wherein x, y and z satisfy the ranges of $0 < x \leq 0.25$, $0 \leq y \leq 0.052$, and $0 \leq z \leq 0.01$ (where $y+z > 0$).

[0060] By using the above-described semiconductor ceramic composition, a PTC element having a high temperature coefficient of resistivity α can be easily obtained as compared with the case of the use of a semiconductor ceramic composition containing Pb as a dopant. Specifically, even in the case of a PTC element having small element resistance (10 Ω or less), a PTC element having a temperature coefficient of resistivity α of 2.5%/°C or more, preferably 3.5%/°C or more is obtained.

[0061] The semiconductor ceramic composition containing Pb as a dopant tends to have a small temperature coefficient of resistivity α . It is presumed that this is because the base metal-based electrode paste deprives the oxygen in the grain boundary layer in the semiconductor ceramic composition during baking, the Schottky barrier formed inside the composition is thereby easily lost, and thus the temperature coefficient of resistivity α is likely to decrease. In contrast, in the semiconductor ceramic composition having the above composition, only the oxygen in the surface layer in contact with the electrode in the semiconductor ceramic composition is deprived and the oxygen in the grain boundary phase inside the composition that expresses a jump characteristic is hardly deprived, and as a result, it is possible to maintain a high temperature coefficient of resistivity α . For such a reason, it is more preferable to use the semiconductor ceramic composition having the above composition and this point is one of new findings obtained in the course of the studies of the present invention.

[0062] The following will describe limitation reasons for each element in the composition formula of the above semiconductor ceramic composition.

[0063] The added amount x of Bi and A is more than 0 and 0.25 or less. In the case where x is more than 0, the Curie temperature can be increased to 130°C or higher.

[0064] In the case where x is more than 0.25, the element resistance becomes large. Moreover, since the elements Bi and A are prone to evaporate during sintering, the number of moles of elements in the Ba site is decreased as compared with the Ti site. As a result, the semiconductor ceramic composition becomes Ti-rich, and the Ti-rich phase would precipitate as a different phase. Since a part of the Ti-rich phase melts during sintering, the yield may be deteriorated or a semiconductor ceramic composition having a desired shape may not be obtained.

[0065] At least one of the added amount y of R and the added amount z of M is essential, that is, $y+z > 0$. The addition of the R element and the M element can increase the temperature coefficient of resistivity α . However, it is not necessary that both R and M are essential and it is sufficient to use at least one of them.

[0066] The range of the added amount y of R is 0 or more and 0.052 or less (where $y+z > 0$). When y is more than 0.052, the temperature coefficient of resistivity that is the PTC characteristic is small and a semiconductor ceramic composition having good heat resistance is not obtained. In addition, the temperature necessary for sintering increases, and there is a possibility that the temperature exceeds heat resistance of a sintering furnace, so that the case is not preferred on production. R is at least one or more elements selected from rare earth metals (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) including Y and particularly, Y and La are preferable since an excellent PTC characteristic is obtained.

[0067] The range of the added amount z of M is 0 or more and 0.01 or less (where $y+z>0$). When z is more than 0.01, the element resistance increases. Also, mechanical strength of the semiconductor ceramic composition decreases, and breakage is prone to occur when the composition has been formed into a PTC element, so that the case is not preferred on production. Particularly, M is preferably Nb since an excellent PTC characteristic is obtained.

[0068] The ratio of Bi to A may be 1:1 but there is included the case where the ratio is 1:1 at material formulation but fluctuation may be caused in the ratio of Bi to A owing to evaporation of Bi during the calcination or sintering steps and the ratio is not 1:1 in a sintered body. That is, a range of Bi:A=0.78 to 1.55:1 is acceptable and, since an increase of the different phase can be suppressed when the ratio falls within this range, it is possible to suppress an increase in room temperature resistivity and a change with time. Still more preferable range is Bi:A=0.90 to 1.2:1. When the ratio is controlled to this range, an effect of improving the Curie temperature is achieved.

[0069] In this description, evaluation methods of the individual property values are as follows.

(Element Resistance per Unit Area)

[0070] Base metal-based electrodes were formed on both main surfaces of a semiconductor ceramic composition to form a PTC element, probes of a current meter and a voltage meter were brought into contact with the base metal-based electrodes at both sides, and element resistance was measured at room temperature (25°C) by 4 terminal method.

[0071] The element resistance is an element resistance of the entire PTC element, and the element resistance per unit area (1 cm²) can be calculated by dividing the value by the area of the range covered by the electrode (cm²).

[0072] Since the element resistance is evaluated when the thickness of the semiconductor ceramic composition is 1 mm and the area is 1 cm², the element resistance can be converted into room temperature resistivity (Ωcm) by multiplying a numerical value of the element resistance by 10.

(Interface Resistance per Unit Area)

[0073] First, base metal-based electrodes are provided on a semiconductor ceramic composition and the element resistance is measured. Then, the electrodes are once peeled off, the thickness of the semiconductor ceramic composition is decreased to a thickness of 3/4 of the initial thickness, the base metal-based electrodes are again provided, and the element resistance is measured. Similarly, the thickness of the semiconductor ceramic composition is decreased to a thickness of 2/4 or 1/4 of the initial thickness and the element resistance is measured in each case. As shown in FIG. 10, data are taken by plotting the thickness of the semiconductor ceramic composition on the horizontal axis and the element resistance on the vertical axis. From the data, there is obtained an approximate straight line between the thickness of the semiconductor ceramic composition and the element resistance. In the case where this approximate straight line is expressed as $R=a\cdot\Delta t+R_0$ (Δt : thickness, R : element resistance, a : resistivity of semiconductor ceramic composition), the resistance value R_0 when the thickness Δt is 0 on the graph can be calculated for convenience. In the present invention, this resistance value R_0 was regarded to be interface resistance. The interface resistance is interface resistance of the entire PTC element, and the interface resistance per unit area (1 cm²) can be calculated by dividing the value by the area of the range covered by the electrode (cm²).

(Thickness of Low resistance layer)

[0074] The thickness of the low resistance layer was measured from the SEM observation photograph as shown in FIG. 1 (magnification: 3,000 times) and the mapping (Al) on EDX analysis in the same visual field as shown in FIG. 3. In the mapping (Al) on the EDX analysis, a site where Al was no longer detected was regarded as an interface between the semiconductor ceramic composition and the electrode (indicated by the dotted line 7 in FIG. 2). On the SEM observation photograph, a width having a different color tone was measured arbitrarily at 10 points on the matrix phase side of the semiconductor ceramic composition from the interface, and an average value thereof was taken as the thickness of the low resistance layer. In the SEM observation photograph, the low resistance layer is darker than the matrix phase and thus is different in color tone. Also, the reaction phase is pictured in similar different shades and can be discriminated by a difference in color tone. Since the low resistance layer and the reaction phase are almost simultaneously formed, the presence of both the low resistance layer and the reaction phase can be confirmed if a layer pictured darker than the matrix phase can be visually recognized on the electrode side of the semiconductor ceramic composition in the SEM observation photograph.

(Confirmation Means of Decrease in Resistance)

[0075] Furthermore, as a confirmation means for a decrease in resistance of the low resistance layer, evaluation was performed using a scanning spreading resistance microscopy (manufactured by Bruker AXS, Inc.: NanoScope IVa AFM

Dimension 3100). According to this method, by scanning the interface between the semiconductor ceramic composition and the electrode with a conductive probe, the distribution of resistance values can be two-dimensionally measured and the resistance can be visualized. Specifically, since there is obtained a mapping image in which the height of the electrical resistance values is represented by shades of color and a dark color part exhibits low resistance, it is possible to visually recognize the resistance by the difference in color tone (tint) between the matrix phase (a depth of at least about 5 μm from the surface when viewed in the thickness direction) and the low resistance layer.

(Surface Resistance)

[0076] The surface resistance is a value obtained by measuring the resistance of the base metal-based electrode itself. The resistance R_w in the planar direction of the formed electrode was measured by 4 terminal method and was converted to resistivity ($=R_w \times (W \times T)/L$) based on length L , electrode width W , and electrode thickness T measured on SEM observation. In the present Examples, W was 1 cm, L was 1 cm and T was aimed at 0.0025 cm. However, since it is difficult to control the thickness T of the electrode to a constant value, the thickness was measured in each case. The first m of $\text{m}\Omega\text{cm}$ of a unit indicates milli (10^{-3}).

(Curie Temperature)

[0077] The temperature at which resistance twice the room-temperature resistivity at room temperature was shown was taken as the Curie temperature.

(Temperature Coefficient of Resistivity α)

[0078] The temperature coefficient of resistivity α was calculated by measuring a resistance-temperature characteristic while raising temperature up to 260°C.

[0079] The temperature coefficient of resistivity α is defined by the following equation.

$$\alpha = (\ln R_1 - \ln R_c) \times 100 / (T_1 - T_c)$$

R_1 is room temperature resistivity at 260°C, T_1 is temperature at which R_1 is shown, T_c is the Curie temperature, and R_c is room temperature resistivity at T_c .

[0080] A change with time is preferably 15% or less, and further preferably 10% or less.

(Change with Time)

[0081] It was evaluated by a high-temperature high-humidity test as a reliability test of the electrode. A change in element resistance was measured before and after standing for 1,000 hours under conditions of 80°C and 95%RH.

(Metal Component Ratio of Electrode)

[0082] The ratio of each element was determined while the total of Al, Ni, B and Si is regarded as 100 mass %. For the measurement, an electron beam microanalyzer (manufactured by Shimadzu Corporation: EPMA1610) was used. As measurement conditions, accelerating voltage was 15 kV, current was 100 nA, and the beam diameter was 10 μm , and an average value of five points was determined.

Examples

[0083] The following will describe the present invention in further detail by way of Examples. However, the present invention should not be construed as being limited by the following Examples.

(Example 1: No. 1-1)

[0084] A base metal-based electrode paste was formed by using 100 mass parts of spherical A1 particles having an average particle diameter of 5 μm , adding 10 mass parts of glass frit and 10 mass parts of B thereto, and further adding an organic binder and an organic solvent.

[0085] As B, not an oxide but simple metal B particles were used. As the B particles, those having an average particle

diameter of 1 μm or less were used.

[0086] The A1 ratio and the B ratio in the base metal-based electrode paste are as shown in No. 1-1 in Table 1.

[0087] As a semiconductor ceramic composition to be a substrate, one processed into a plate of 10 mm $\times$ 10 mm (plane dimensions) $\times$ 1.00 mm (thickness dimension) was used.

[0088] The above base metal-based electrode paste was applied to both sides of the semiconductor ceramic composition by screen printing. After drying of the applied electrode paste at 150°C, in the air, temperature was raised at 30°C/minute, held at 775°C for 10 minutes, and lowered at 30°C/minute to obtain a PTC element on which a baked electrodes were formed. The area of the range covered by the electrodes was 1 cm² and the thickness of the electrodes was about 25 μm .

[0089] The semiconductor ceramic composition used in Example was produced as follows.

[0090] Raw material powders of BaCO₃, TiO₂ and La₂O₃ were prepared and then blended so as to be (Ba_{0.994}La_{0.006})TiO₃, followed by mixing in pure water. The resulting mixed raw material powder was calcined in the air at 900°C for 4 hours to prepare a first calcined powder.

[0091] Raw material powders of Na₂CO₃, Bi₂O₃ and TiO₂ were prepared and then weighed and blended so as to be Bi_{0.5}Na_{0.5}TiO₃, followed by mixing in ethanol. The resulting mixed raw material powder was calcined in the air at 800°C for 2 hours to prepare a second calcined powder.

[0092] The prepared first calcined powder (Ba_{0.994}La_{0.006})TiO₃ and second calcined powder Bi_{0.5}Na_{0.5}TiO₃ were blended so that the molar ratio became 73:7, thereby obtaining a composition of [(Bi_{0.5}Na_{0.5})_{0.0875}(Ba_{0.994}La_{0.006})_{0.9125}]TiO₃. Mixing and pulverization were performed by a pot mill using pure water as a medium until the average particle diameter of the mixed calcined powder became from 1.0 to 2.0 μm , followed by drying. Then, the resulting one was subjected to a heat treatment at 1,150°C for 4 hours to obtain a third calcined powder. Y₂O₃ was added in an amount of 1.0 mol % to the calcined powder obtained, and mixing and pulverization were performed by a pot mill using pure water as a medium until the average particle diameter of the mixed calcined powder became from 1.0 to 2.0 μm , followed by drying to obtain a mixed calcined powder. PVA was added in an amount of 10 mass % to the pulverized powder of the mixed calcined powder and, after mixing, the resulting powder was granulated by means of a granulating apparatus. The resulting granulated powder was formed on a monoaxial pressing apparatus to make a formed body. After subjected to binder removal at 700°C, the formed body was kept in a nitrogen atmosphere having an oxygen concentration of 0.01% (100 ppm) at 1,400°C for 4 hours and then gradually cooled to obtain a sintered body having a size of 50 mm $\times$ 25 mm $\times$ 4 mm.

[0093] The above production method is merely an example and is optional. For example, the raw material powders may be mixed in a batch, ground, dried, and then subjected to a heat treatment to obtain a calcined powder (corresponding to the above third calcined powder) without obtaining the first and second calcined powders, Y₂O₃ may be added thereto, and thereafter, manufacturing may be conducted in the same manner as described above.

[0094] Moreover, in order to measure interface resistance, the above sintered body was processed to prepare sintered bodies of the semiconductor ceramic composition, which were processed into plates having plane dimensions of 10 mm $\times$ 10 mm and a thickness dimension of 1.00 mm, 0.75 mm, 0.50 mm, or 0.25 mm, respectively. They were then processed in the same manner to manufacture PTC elements, respectively.

[0095] FIG. 1 shows the results of observation, by SEM, of the boundary part between the semiconductor ceramic composition and the electrode of the PTC element. FIG. 2 is a schematic view thereof. FIG. 3 is a mapping image of A1 by EDX (energy dispersive X-ray spectroscopy) in the same visual field as that of FIG. 1, FIG. 4 is a schematic view of FIG. 3, FIG. 5 is a EDX mapping image of Ba in the same visual field as that of FIG. 1, and FIG. 6 is a schematic view of FIG. 5.

[0096] A site at which A1 is no longer detected is regarded as an interface between the base metal electrode 1 and the semiconductor ceramic composition 2 (shown by a dotted line 7 in FIG. 2 and FIG. 4). It is found that a low resistance layer 3 having a different color tone is formed on the semiconductor ceramic composition 2 side from the interface and an irregular reaction phase 4 having a different color tone into which Ba is infiltrated is formed also on the base metal electrode 1 side. A degree of infiltration of Ba is not clear but the infiltration is considered to occur to the extent indicated by dots in FIG. 6.

[0097] From the A1 mapping in FIG. 3, it is found that the site that looks primarily spherical in the base metal electrode 1 in FIG. 1 (portion 5 in FIG. 2) is Al. The Al particles substantially keep the shape at the time when it has been incorporated into the electrode paste in the electrode after baking, but relatively small particles enter between large particles and also particle pieces intervene in the vicinity of the interface. In FIG. 1, the site that looks black (portion 6 in FIG. 2) between the A1 particles is an inner void of the electrode.

[0098] FIG. 7 is a resistance mapping image of SSRM. It shows that a dark color portion is low in resistance and a light color portion is high in resistance. It is clearly found from FIG. 7 that a dark color layer is formed on the semiconductor ceramic composition 2 side from the interface 7 between the base metal electrode 1 and the semiconductor ceramic composition 2. That is, the layer has a darker color tone than the inner matrix phase and can be said to be a low resistance layer 3 in which the resistance has been decreased. The low resistance layer 3 was confirmed to be coincident with the

low resistance layer 3 appearing in the SEM observation image of FIG. 1.

[0099] Then, with respect to the obtained PTC elements, the A1 ratio (mass %), the Ni ratio (mass %), the B ratio (mass %), and the Si ratio (mass %) in the metal component of the electrode, thickness of the low resistance layer (μm), interface resistance (Ω), element resistance (Ω), surface resistance ($\text{m}\Omega\cdot\text{cm}$), the Curie temperature ($^{\circ}\text{C}$), the temperature coefficient of resistivity α ($\%/^{\circ}\text{C}$) and the change with time (%) were measured. The characteristics other than the interface resistance were measured using a semiconductor ceramic composition having a thickness of 1.00 mm. The obtained evaluation results are shown in Table 1.

[0100] In the present Example, the thickness of the low resistance layer was $0.5\ \mu\text{m}$, the reaction phase was also present, the interface resistance was $1.1\ \Omega$, the element resistance was $4.9\ \Omega$, the surface resistance was $0.9\ \text{m}\Omega\cdot\text{cm}$, the Curie temperature was 160°C , the temperature coefficient of resistivity α was $4.1\ \%/^{\circ}\text{C}$, and the change with time was 12.5% . Thus, the effect of a decrease in resistance was observed in both of the interface resistance and the element resistance, and the PTC characteristic was also satisfactory.

[0101] When the composition of the base metal-based electrode was measured by EPMA, the ratios (mass %) of Al, Ni, B and Si shown in Table 1 were observed. Also in the following Examples and Comparative Examples, the ratios of Al, Ni, B and Si in the table indicate values measured by EPMA. The values were the same as the respective content ratios in the electrode paste.

(Example 2: Nos. 1-2 to 1-9)

[0102] In No. 1-2 to 1-9, there were formed electrodes in which, with respect to No. 1-1, a portion of A1 was substituted by Si and the added amount of B was changed.

[0103] Spherical A1 particles having an average particle diameter of $5\ \mu\text{m}$ and Si particles having an average particle diameter of $5\ \mu\text{m}$ were mixed so as to be 92:8 by mass ratio and, a total value thereof being regarded as 100 mass parts, glass frit in an amount of 10 mass parts and B in an amount of 3 mass parts, 5 mass parts, 7.5 mass parts, 10 mass parts, 12.5 mass parts, 15 mass parts, 20 mass parts and 25 mass parts, respectively, were added thereto.

[0104] When the metal component after the formation of the base metal-based electrode was measured, the A1 ratio, the B ratio and the Si ratio are as shown in Nos. 1-2 to 1-9 of Table 1. As mentioned above, the A1 ratio, the B ratio and the Si ratio in the base metal-based electrode pastes were the same as the values shown in Table 1.

[0105] The other manufacturing methods and evaluation methods of PTC elements were conducted in the same methods as in Example 1. The evaluation results obtained are shown in Table 1.

[0106] In any of the PTC elements, it was able to confirm that there is a low resistance layer having small resistance than that of the matrix phase. Also, the presence of a reaction phase corresponding to the thickness of the low resistance layer was confirmed.

[0107] According to Table 1, in the PTC elements of Nos. 1-3 to 1-9 having a B ratio of 3 mass % or more, the low resistance layer had a thickness of $0.4\ \mu\text{m}$ or more and the interface resistance was $5\ \Omega$ or less.

[0108] Moreover, in the PTC elements of Nos. 1-4 to 1-8 having a B ratio of 5 mass % or more and 17 mass % or less, the interface resistance was $1.5\ \Omega$ or less and the element resistance was also about $5\ \Omega$ or less. In addition, the surface resistance of the PTC element was $10\ \text{m}\Omega\text{cm}$ or less. Furthermore, in the PTC element of Nos. 1-4 to 1-5 having a B ratio of 5 mass % or more and 10 mass % or less, the surface resistance was $2\ \text{m}\Omega\text{cm}$ or less.

(Comparative Example 1: No. 1-10)

[0109] There was formed a base metal-based electrode to which B was not added.

[0110] Si particles were added in a ratio of 8 mass parts to 92 mass parts of the same A1 particles as in Example 1 so that the total amount was 100 mass parts, and 10 mass parts of glass frit was added thereto, thereby forming a base metal-based electrode paste.

[0111] The other manufacturing methods and evaluation methods of a PTC element were conducted in the same methods as in Example 1. The evaluation results obtained are shown in Table 1.

[0112] In this example, it was not able to confirm any low resistance layer. A reaction phase was confirmed but the thickness of the reaction phase was as small as nearly about $1/5$ or less as compared with the case where B was added. Moreover, the interface resistance was so much large as $12\ \Omega$ and the element resistance was also as large as $15.5\ \Omega$.

(Comparative Example 2: Nos. 1-11 and 1-12)

[0113] There were formed base metal-based electrodes using B_2O_3 and H_3BO_3 as additives of B.

[0114] Si was added in a ratio of 8 mass parts to 92 mass parts of the same A1 particles as in Example 1 so that the total amount was 100 mass parts, and 10 mass parts of B_2O_3 or H_3BO_3 and 10 mass parts of glass frit was added thereto, thereby forming a paste.

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[0115] The other manufacturing methods and evaluation methods of PTC elements were conducted in the same methods as in Example 1. The results obtained are shown in Table 1.

[0116] In this example, it was not able to confirm any low resistance layer in both of No. 1-11 and No. 1-12. However, a reaction phase was confirmed but the interface resistance was so much large as 23.4 Ω and 13.7 Ω , respectively, and the element resistance was also so large as 26.2 Ω and 16.9 Ω , respectively.

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[Table 1]

No.	Al ratio (mass%)	Ni ratio (mass%)	B ratio (mass%)	Si ratio (mass%)	Baking temper- ature (°C)	Thickness of low resist- ance layer (μm)	Interface re- sistance (Ω)	Element re- sistance (Ω)	Surface re- sistance ($\text{m}\Omega\cdot\text{cm}$)	Curie tempera- ture (°C)	Temperature coefficient of re- sistivity ($\%/^{\circ}\text{C}$)	Change with time (%)
1-1	90.9	0	9.1	0	775	0.5	1.1	4.9	0.9	160	4.1	12.5
1-2	89.3	0	2.9	7.8	775	0.3	7.7	11.2	0.6	159	4.1	7.4
1-3	87.6	0	4.8	7.6	775	0.5	1.9	5.9	1.0	160	4.1	5.1
1-4	85.6	0	7.0	7.4	775	0.6	1.3	5.1	1.2	161	4.0	6.0
1-5	83.6	0	9.1	7.3	775	0.8	0.6	4.4	1.3	162	3.9	5.5
1-6	81.8	0	11.1	7.1	775	1.0	0.6	4.3	3.4	162	3.8	6.2
1-7	80.0	0	13.0	7.0	775	1.2	1.0	4.9	6.7	159	4.1	5.7
1-8	76.6	0	16.7	6.7	775	1.8	0.8	4.6	9.6	160	4.0	4.8
1-9	73.6	0	20.0	6.4	775	2.9	1.5	5.2	12.1	160	4.3	4.3
1-10*	92.0	0	0	8.0	775	0	12.0	15.5	0.1	162	4.4	8.0
1-11*	89.4	0	2.8	7.8	775	0	23.4	26.2	0.3	162	4.1	9.6
1-12*	89.0	0	3.2	7.8	775	0	13.7	16.9	0.4	160	4.3	8.9
(No. to which * is attached is Comparative Example)												

(Example 3: Nos. 2-1 to 2-5)

[0117] A base metal-based electrode was formed with changing the baking temperature.

[0118] Spherical A1 particles having an average particle diameter of 5 μm and Si particles having an average particle diameter of 5 μm were mixed so as to be 92:8 by mass ratio and, a total value thereof being regarded as 100 mass parts, glass frit in an amount of 10 mass parts and B in an amount of 10 mass parts were added thereto.

[0119] As a semiconductor ceramic composition, there was used one processed into a plate of 10 mm $\times$ 10 mm (plane dimensions) $\times$ 1.00 mm (thickness dimension). Moreover, in order to measure the interface resistance, there were also prepared semiconductor ceramic compositions processed into plates of 10 mm $\times$ 10 mm $\times$ 0.75 mm, 10 mm $\times$ 10 mm $\times$ 0.50 mm, and 10 mm $\times$ 10 mm $\times$ 0.25 mm.

[0120] The above base metal-based electrode paste was applied on both sides of the semiconductor ceramic composition by screen printing. After drying of the applied base metal-based electrode paste at 150°C, in the air, temperature was raised at 30°C/minute, holding temperature was changed to 725°C, 750°C, 775°C, 800°C, 825°C, or 850°C and was held for 10 minutes, and then temperature was lowered at 30°C/minute to obtain PTC elements on which baked electrodes were formed. The area of the range covered by the electrode was 1 cm² and the thickness of the electrode was about 25 μm . The semiconductor ceramic compositions having the above each thickness were similarly converted into PTC elements, respectively.

[0121] The other manufacturing methods and evaluation methods of PTC elements were conducted in the same methods as in Example 1. The evaluation results obtained are shown in Table 2.

[0122] In any of the PTC elements, it was able to confirm that there is a low resistance layer having small resistance than that of the matrix phase. Also, the presence of a reaction phase corresponding to the thickness of the low resistance layer was confirmed.

[0123] According to Table 2, in No. 2-1 where the baking temperature was 725°C, the thickness of the low resistance layer was as thin as 0.2 μm and the interface resistance was 6.8 Ω . In Nos. 2-2 to 2-5 where the baking temperature was 750°C or higher, the thickness of the low resistance layer was 0.4 μm or more and the interface resistance was 5 Ω or less. In addition, in Nos. 2-2 to 2-4 where the baking temperature was 830°C or lower, the element resistance was 10 Ω or less.

[0124] From the above, it can be said that the baking temperature is preferably 750°C or higher and 830°C or lower. It has been found that, when the baking temperature is more than 850°C, the semiconductor ceramic composition itself is oxidized and has increased resistance and thus the case is not preferred.

[Table 2]

No.	Al ratio (mass%)	Ni ratio (mass%)	B ratio (mass%)	Si ratio (mass%)	Baking temper- ature (°C)	Thickness of low resist- ance layer (μm)	Interface re- sistance (Ω)	Element re- sistance (Ω)	Surface re- sistance ($\text{m}\Omega\cdot\text{cm}$)	Curie tempera- ture (°C)	Temperature coefficient of re- sistivity ($\%/^{\circ}\text{C}$)	Change with time (%)
2-1	83.6	0	9.1	7.3	725	0.2	6.8	10.5	0.9	162	3.9	75.7
2-2	83.6	0	9.1	7.3	750	0.6	3.6	7.1	1.1	163	4.0	14.9
2-3	83.6	0	9.1	7.3	800	0.9	0.5	4.6	1.5	163	3.8	4.5
2-4	83.6	0	9.1	7.3	825	1.1	0.4	6.5	1.8	162	4.1	5.0
2-5	83.6	0	9.1	7.3	850	1.5	0.4	10.1	1.3	163	3.9	9.5

(Example 4: Nos. 3-1 to 3-8)

[0125] As base metal-based electrodes, there were produced those in which the Si amount was changed.

[0126] Using the same A1 particles and Si particles as in the above Examples, they were mixed so as to be 98:2, 96:4, 94:6, 88:12, 84:16, 80:20, 76:24, or 72:28 by mass ratio. A total value thereof being regarded as 100 mass parts, glass frit in an amount of 10 mass parts and B in an amount of 10 mass parts were added thereto.

[0127] The other manufacturing methods and evaluation methods of PTC elements were conducted in the same methods as in Example 1. The evaluation results obtained are shown in Table 3.

[0128] In any of the PTC elements, it was able to confirm that there is a low resistance layer having small resistance than that of the matrix phase. Also, the presence of a reaction phase corresponding to the thickness of the low resistance layer was confirmed.

[0129] According to Table 3, in Nos. 3-1 to 3-7 having an Si ratio of 1.8 to 21.8 mass %, there were obtained those having an interface resistance of 5 Ω or less, an element resistance of 10 Ω or less, and a surface resistance of 10 m Ω cm or less. Moreover, in Nos. 3-3 to 3-7 having an Si ratio of 5.5 to 21.8 mass %, the change with time was 10% or less and an effect of reducing the change with time is observed even at a small Si amount.

[0130] In No. 3-8 having an Si ratio of 25.5 mass %, the surface resistance was more than 10 m Ω cm but a PTC element having small element resistance and interface resistance was obtained.

[0131] From the above, Si also has an effect of suppressing the change with time and, when a decrease in resistance is also considered, it can be said that the Si ratio is more preferably 5.0 mass % or more and 15.0 mass % or less.

[Table 3]

No.	Al ratio (mass%)	Ni ratio (mass%)	B ratio (mass%)	Si ratio (mass%)	Baking temper- ature (°C)	Thickness of low resist- ance layer (μm)	Interface re- sistance (Ω)	Element re- sistance (Ω)	Surface re- sistance ($\text{m}\Omega\cdot\text{cm}$)	Curie tempera- ture (°C)	Temperature coefficient of re- sistivity ($\%/^{\circ}\text{C}$)	Change with time (%)
3-1	89.1	0	9.1	1.8	775	0.5	1.8	5.5	1.3	160	4.1	13.8
3-2	87.3	0	9.1	3.6	775	0.6	1.6	5.3	1.1	159	4.1	11.5
3-3	85.5	0	9.1	5.5	775	0.7	1.2	4.9	1.4	157	4.2	8.2
3-4	80.0	0	9.1	10.9	775	1.0	1.0	4.7	2.0	161	4.0	6.1
3-5	76.4	0	9.1	14.5	775	0.9	1.5	5.1	1.9	161	4.1	7.6
3-6	72.7	0	9.1	18.2	775	0.7	2.2	5.9	2.6	162	3.9	9.3
3-7	69.1	0	9.1	21.8	775	0.7	3.0	6.4	9.8	160	4.1	9.9
3-8	65.5	0	9.1	25.5	775	0.9	3.9	7.8	34.1	162	3.8	11.8

(Example 5: Nos. 4-1 to 4-6)

[0132] As base metal-based electrodes, there were produced those to which Ni was added.

[0133] Spherical A1 particles having an average particle diameter of 5 μm , Si particles having an average particle diameter of 5 μm and Ni particles having an average particle diameter of 0.2 μm were mixed so as to be 82.8:7.2:10, 73.6:6.4:20, 64.4:5.6:30, 55.2:4.8:40, 27.6:2.4:70, or 9.2:0.8:90 by mass ratio and, a total value thereof being regarded as 100 mass parts, B in an amount of 10 mass parts was added thereto. Glass frit was 0 mass part.

[0134] The other manufacturing methods and evaluation methods of PTC elements were conducted in the same methods as in Example 1. The evaluation results obtained are shown in Table 4.

[0135] In any of the PTC elements, it was able to confirm that there is a low resistance layer having small resistance than that of the matrix phase. Also, the presence of a reaction phase corresponding to the thickness of the low resistance layer was confirmed.

[0136] According to Table 4, in all the PTC elements, the interface resistance was such a small value as 2.5 Ω or less. Moreover, in No. 4-1, the lowest resistance value was shown. Particularly, in Nos. 4-1 and 4-2 where an Ni ratio was 5 mass % or more and 20 mass % or less, there were obtained PTC elements having an interface resistance of 1 Ω or less, an element resistance of 5 Ω or less, and a surface resistance of 2.0 $\text{m}\Omega\text{cm}$ or less.

[0137] From the above, since an effect of a decrease in the interface resistance is enhanced by the addition of a small amount of Ni, it can be said that the Ni ratio is more preferably 20 mass % or less.

[0138] Also, from the present Examples, the addition of glass frit is not always necessary and it is considered that the addition is desired in the case where the baking temperature is more than 800°C.

(Nos. 4-7 to 4-9)

[0139] As base metal-based electrodes, there were produced those to which Ni was added and in which the B amount was changed.

[0140] For Nos. 4-7 to 4-12, spherical A1 particles having an average particle diameter of 5 μm , Si particles having an average particle diameter of 5 μm , and Ni particles having an average particle diameter of 0.2 μm were mixed so as to be 55.2:4.8:40 by mass ratio and, a total value thereof being regarded as 100 mass parts, B was added thereto in an amount of 5.0 mass parts, 7.5 mass parts and 12.5 mass parts, respectively. Glass frit was 0 mass part.

[0141] The other manufacturing methods and evaluation methods of PTC elements were conducted in the same methods as in Example 1. The evaluation results obtained are collectively shown in Table 4.

[0142] In any of the PTC elements, it was able to confirm that there is a low resistance layer having small resistance than that of the matrix phase. Also, the presence of a reaction phase corresponding to the thickness of the low resistance layer was confirmed.

[0143] According to Table 4, in all the PTC elements, there were obtained PTC elements having such small values as an interface resistance of 1.0 Ω or less and an element resistance of 5 Ω or less.

(Nos. 4-10 to 4-12)

[0144] Using the base metal-based electrode paste manufactured in No. 4-9, PTC elements were manufactured with changing the baking temperature. The evaluation results obtained are collectively shown in Table 4.

[0145] In any of the PTC elements, it was able to confirm that there is a low resistance layer having small resistance than that of the matrix phase. Also, the presence of a reaction phase corresponding to the thickness of the low resistance layer was confirmed.

[0146] According to Table 4, in all the PTC elements, there were obtained PTC elements having such small values as an interface resistance of 1.0 Ω or less and an element resistance of 5 Ω or less. Even in the PCT element of No. 4-12 in which the baking temperature was lowered to 700°C, the interface resistance and the element resistance on similar levels were observed.

[Table 4]

No.	Al ratio (mass%)	Ni ratio (mass%)	B ratio (mass%)	Si ratio (mass%)	Baking temper- ature (°C)	Thickness of low resist- ance layer (μm)	Interface re- sistance (Ω)	Element re- sistance (Ω)	Surface re- sistance ($\text{m}\Omega\cdot\text{cm}$)	Curie tempera- ture (°C)	Temperature coefficient of re- sistivity ($\%/^{\circ}\text{C}$)	Change with time (%)
4-1	75.2	9.1	9.1	6.6	775	1.1	0.2	4.0	1.0	160	4.0	8.0
4-2	66.9	18.2	9.1	5.8	775	0.9	0.6	4.3	1.6	159	4.3	11.4
4-3	58.5	27.3	9.1	5.1	775	0.8	0.7	4.5	2.2	165	3.7	11.3
4-4	50.2	36.4	9.1	4.4	775	0.9	0.6	4.4	2.5	163	3.8	13.7
4-5	25.1	63.6	9.1	2.2	775	1.2	1.5	5.3	5.7	161	4.0	7.9
4-6	8.4	81.8	9.1	0.7	775	1.4	2.3	6.1	9.8	159	4.1	8.1
4-7	52.6	38.1	4.8	4.5	775	0.4	0.2	4.0	1.6	160	4.3	14.8
4-8	51.3	37.2	7.0	4.5	775	0.7	0.5	4.3	2.0	159	4.3	14.2
4-9	49.1	35.6	11.1	4.2	775	1.1	0.6	4.4	3.7	162	4.5	8.3
4-10	49.1	35.6	11.1	4.2	750	0.9	0.5	4.3	3.5	163	4.3	10.6
4-11	49.1	35.6	11.1	4.2	725	0.6	0.5	4.3	3.3	165	4.1	12.2
4-12	49.1	35.6	11.1	4.2	700	0.4	0.4	4.2	3.3	167	4.0	13.1

(Example 6: Nos. 5-1 to 5-8)

[0147] With respect to the composition of the semiconductor ceramic composition, there were manufactured the compositions in which the ratios of x and y were changed.

[0148] There were manufactured semiconductor ceramic compositions where $y=0.006$ and $z=0$, and the value of x was 0.02, 0.14, 0.18, or 0.2 with respect to No. 1-5 in Nos. 5-1 to 5-4 and $x=0.0875$ and $z=0$, and the value of y was 0.003, 0.048, or 0.05 in Nos. 5-5 to 5-7. As the electrode, the same one as in No. 1-5 was formed. The same shall apply to the following example. The other manufacturing methods and evaluation methods of PTC elements were conducted in the same methods as in Example 1. The evaluation results obtained are shown in Table 5.

[0149] Moreover, in No. 5-8, any rare earth element was not used as a semiconductor-forming element ($y=0$), a part of the Ti site was substituted by Ta, and the value of z in the composition formula was controlled to 0.009, with respect to No. 1-5.

[0150] In this example, raw material powders of BaCO_3 , TiO_2 , and Ta_2O_5 were prepared and then blended so as to be $\text{Ba}(\text{Ti}_{0.991}\text{Ta}_{0.009})\text{O}_3$, followed by mixing in pure water. The resulting mixed raw material powder was calcined in the air at 900°C for 4 hours to prepare a first calcined powder.

[0151] The manufacture of a second calcined powder was conducted in the same manner as in Example 1. Moreover, the production of PTC elements by subsequent mixing of the first calcined powder and the second calcined powder, forming, sintering, and electrode formation and evaluation methods were conducted in the same methods as in Example 1. The evaluation results obtained are shown in Table 5.

[0152] In any of the PTC elements, it was able to confirm that there is a low resistance layer having small resistance than that of the matrix phase. Also, the presence of a reaction phase corresponding to the thickness of the low resistance layer was confirmed.

[0153] From the results in Table 5, in all the PTC elements, the interface resistance was $5\ \Omega$ or less. There are obtained PTC elements having a surface resistance of $2.0\ \text{m}\Omega\text{cm}$ or less and a temperature coefficient of resistivity α of $2.5\%/^\circ\text{C}$ or more.

[Table 5]

No.	Al ratio (mass%)	Ni ratio (mass%)	B ratio (mass%)	Si ratio (mass%)	Baking temper- ature (°C)	Thickness of low resist- ance layer (μm)	Interface re- sistance (Ω)	Element re- sistance (Ω)	Surface re- sistance ($\text{m}\Omega\cdot\text{cm}$)	Curie tempera- ture (°C)	Temperature coefficient of re- sistivity ($\%/^{\circ}\text{C}$)	Change with time (%)
5-1	83.6	0	9.1	7.3	775	0.8	0.7	5.2	1.3	133	5.5	5.7
5-2	83.6	0	9.1	7.3	775	0.9	0.5	8.8	1.2	184	4.6	9.9
5-3	83.6	0	9.1	7.3	775	0.9	0.9	9.8	1.3	190	4.2	11.3
5-4	83.6	0	9.1	7.3	775	1.0	1.5	13.8	1.1	193	4.4	7.7
5-5	83.6	0	9.1	7.3	775	0.7	0.9	8.4	1.3	171	4.0	7.9
5-6	83.6	0	9.1	7.3	775	0.8	0.3	3.1	1.4	150	3.5	8.1
5-7	83.6	0	9.1	7.3	775	0.9	0.2	2.8	1.2	145	2.9	5.4
5-8	83.6	0	9.1	7.3	775	0.8	0.8	9.3	1.3	155	4.9	9.3

(Example 7: Nos. 6-1 to 6-4)

[0154] There were manufactured those in which the particle diameter of the Al particles used in the base metal-based electrode.

[0155] A1 particles having an average particle diameter of 3.8 μm , A1 particles having an average particle diameter of 2.5 μm , and A1 particles having an average particle diameter of 1.5 μm were used in No. 6-1, in No. 6-2, and in Nos. 6-3 and 6-4, respectively. Each of these A1 particles and Si particles were mixed so as to be 92:8 by mass ratio and, a total value thereof being regarded as 100 mass parts, glass frit in an amount of 10 mass parts and B in an amount of 10 mass parts were added thereto. Moreover, in No. 6-4, the baking temperature was changed to 750°C.

[0156] The other manufacturing methods and evaluation methods of PTC elements were conducted in the same methods as in Example 1. The evaluation results obtained are shown in Table 6.

[0157] In any of the PTC elements, it was able to confirm that there is a low resistance layer having small resistance than that of the matrix phase. Also, the presence of a reaction phase corresponding to the thickness of the low resistance layer was confirmed.

[0158] According to Table 6, in both cases, there were obtained PTC elements having an interface resistance of 1 Ω or less, an element resistance of 5 Ω or less, and a surface resistance of 10.0 m Ωcm or less.

[0159] When the A1 particles are decreased in size, the surface resistance tends to increase.

[Table 6]

No.	Al ratio (mass%)	Ni ratio (mass%)	B ratio (mass%)	Si ratio (mass%)	Particle diameter of A1 par- ticles (μm)	Baking tem- perature ($^{\circ}\text{C}$)	Thickness of low re- sistance layer (μm)	Interface resistance (Ω)	Element re- sistance (Ω)	Surface re- sistance ($\text{m}\Omega\cdot\text{cm}$)	Curie temper- ature ($^{\circ}\text{C}$)	Temperature coefficient of resistivity ($\%/^{\circ}\text{C}$)	Change with time (%)
6-1	83.6	0	9.1	7.3	3.8	775	0.9	0.6	4.2	1.3	161	4.1	3.9
6-2	83.6	0	9.1	7.3	2.5	775	1.0	0.5	4.0	1.2	163	4.2	5.2
6-3	83.6	0	9.1	7.3	1.5	775	1.0	0.8	4.6	9.6	160	4.4	6.5
6-4	83.6	0	9.1	7.3	1.5	750	0.6	0.5	4.3	9.4	163	4.0	9.6

(Example 8: No. 7-1)

[0160] As a semiconductor ceramic composition, a semiconductor ceramic composition containing Pb was used.

[0161] As the semiconductor ceramic composition containing Pb, there was used one in which the composition formula was represented by $(\text{Ba}_{0.83}\text{Pb}_{0.17})\text{TiO}_3$. The other manufacturing methods and evaluation methods of PTC elements were conducted in the same methods as in No. 1-5. The evaluation results obtained are shown in Table 7.

[0162] It was able to confirm that there is a low resistance layer having small resistance than that of the matrix phase. Also, the presence of a reaction phase corresponding to the thickness of the low resistance layer was confirmed. Although there was a disadvantage of a small temperature coefficient of resistivity, the element resistance, interface resistance, and surface resistance were shown to be all low values.

[Table 7]

No.	A1 ratio (mass%)	Si ratio (mass%)	Ni ratio (mass%)	B ratio (mass%)	Baking temper- ature (°C)	Thickness of low resist- ance layer (μm)	Interface re- sistance (Ω)	Element re- sistance (Ω)	Surface re- sistance ($\text{m}\Omega\cdot\text{cm}$)	Curie tempera- ture (°C)	Temperature coefficient of re- sistivity ($\%/^{\circ}\text{C}$)	Change with time (%)
7-1	83.6	7.3	0	9.1	775	1.1	0.2	2.3	1.2	170	0.83	6.5

(Heat Generating Module)

[0163] FIG. 9 is a schematic view of the heat generating module (PTC heater) according to one embodiment of the present invention.

[0164] The PTC element described above is sandwiched and fixed between metal-made heat radiating fins 21a, 21b and 21c as shown in FIG. 9, and then, a heat generating module 20 can be configured. The PTC element 11 includes a base body 1a of a semiconductor ceramic composition and base metal-based electrodes 2a, 2b and 2c, the electrodes 2a and 2c are thermally and electrically closely attached to power supplying electrodes 20a and 20c at positive side, respectively, and the electrode 2b formed on another face is thermally and electrically closely attached to a power supplying electrode 20b at negative side. Moreover, the power supplying electrodes 20a, 20b and 20c are thermally connected to the heat radiating fins 21a, 21b and 21c, respectively. An insulating layer 2d is provided between the power supplying electrode 20a and the power supplying electrode 20c to electrically insulate both from each other. Heat generated at the PTC element 11 is transmitted to the electrodes 2a, 2b and 2c, the power supplying electrodes 20a, 20b and 20c and the heat radiating fins 21a, 21b and 21c in this order and is mainly radiated from the heat radiating fins 21a, 21b and 21c into the atmosphere.

[0165] In the case where a power source 30c is connected between the power supplying electrode 20a and the power supplying electrode 20b or between the power supplying electrode 20c and the power supplying electrode 20b, power consumption becomes small, and in the case where the source is connected between both of the power supplying electrodes 20a and 20c and the power supplying electrode 20b, the power consumption becomes large. That is, it is possible to change the power consumption in two stages. Thus, the heat generating module 20 can switch heating capacity depending on load situation of the power source 30c and the desired degree of requirement for rapid or slow heating. By connecting the heat generating module 20 capable of switching the heating capacity to the power source 30c, a heating apparatus 30 can be configured. The power source 30c is a direct-current power source. The power supplying electrode 20a and the power supplying electrode 20c of the heat generating module 20 are connected in parallel to one of the electrodes of the power source 30c through separate switches 30a and 30b and the power supplying electrode 20b is connected as a common terminal to the other electrode of the power source 30c. In the case where either of the switches 30a or 30b is only put on, the heating capacity is small and the load on the power source 30c can be lightened. When both are put on, the heating capacity can be enlarged.

[0166] According to the heating apparatus 30, the PTC element 11 can be maintained at a constant temperature without equipping the power source 30c with a particular mechanism. That is, when a base body 1a having a large temperature coefficient of resistivity is heated to around the Curie temperature, the resistance value of the base body 1a sharply increases and the flow of current through the PTC element 11 decreases, so that the material is no more heated automatically. Moreover, when the temperature of the PTC element 11 lowers from the vicinity of the Curie temperature, the current is again allowed to flow through the element and the PTC element 11 is heated. Since the temperature of the PTC element 11 and also the whole temperature of heat generating module 20 can be made constant through repetition of such a cycle, a circuit for regulating the phase and amplitude of the power source 30c and also a temperature detecting mechanism or a mechanism for comparison with a target temperature, a circuit for regulating power for heating and the like are also unnecessary.

[0167] The heating apparatus 30 can heat air with introducing air between the heat radiating fins 21a to 21c or can heat a liquid such as water with connecting a metal tube for liquid flow among the heat radiating fins 21a to 21c. On this occasion, since the PTC element 11 is also kept at a constant temperature, a safe heating apparatus 30 can be configured.

[0168] Such a heat generating module is merely one example and changes and modifications such as simplification of the above electrodes into two electrodes can be added.

[0169] While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

[0170] The present application is based on Japanese Patent Application No. 2013-139001 filed on July 2, 2013, the contents of which are incorporated herein by reference. Also, all the references cited herein are incorporated as a whole.

Description of Reference Numerals and Signs

[0171]

- 1: Base metal-based electrode
- 2: Semiconductor ceramic composition
- 3: Low resistance layer
- 4: Reaction phase
- 5: Al particle

6:	Void
11:	PTC element
20:	Heat generating module
20a, 20b, 20c:	Power supplying electrodes
21a, 21b, 21c:	Heat radiating fins
30a, 30b:	Switches
30c:	Power source

Claims

1. A PTC element in which a base metal-based electrode is formed on a semiconductor ceramic composition by baking, wherein the semiconductor ceramic composition has a perovskite structure composed of a BaTiO_3 type oxide, the base metal-based electrode contains, as a main component, at least one kind of Al and Ni as a metal component and also contains at least B, and a low resistance layer having a resistance smaller than that of a matrix phase of the semiconductor ceramic composition is formed on a base metal-based electrode side of the semiconductor ceramic composition.
2. The PTC element according to claim 1, wherein a thickness of the low resistance layer is $0.1\text{ }\mu\text{m}$ or more.
3. The PTC element according to claim 1 or 2, wherein a thickness of the low resistance layer is $0.4\text{ }\mu\text{m}$ or more and an interface resistance of the element per unit area (1 cm^2) is $5\text{ }\Omega$ or less.
4. The PTC element according to any one of claims 1 to 3, wherein an element resistance of the element per unit area (1 cm^2) is $10\text{ }\Omega$ or less.
5. The PTC element according to any one of claims 1 to 4, wherein a surface resistance thereof is $10\text{ m}\Omega\text{cm}$ or less.
6. The PTC element according to any one of claims 1 to 5, wherein a reaction phase mainly including a Ba oxide is present on a semiconductor ceramic composition side of the base metal-based electrode.
7. The PTC element according to any one of claims 1 to 6, wherein the base metal-based electrode has a composition containing B in an amount of 3 mass % or more and 25 mass % or less when a total of Al, Ni and B is 100 mass %.
8. The PTC element according to claim 7, wherein the base metal-based electrode contains Si as a metal component and contains B in an amount of 3 mass % or more and 25 mass % or less and Si in an amount of more than 0 mass % and 26 mass % or less when a total of Al, Ni, B and Si is 100 mass %.
9. The PTC element according to claim 7 or 8, wherein the base metal-based electrode contains Al in an amount of 50 mass % or more when a total of Al, Ni, B and Si is 100 mass %.
10. The PTC element according to any one of claims 7 to 9, wherein the base metal-based electrode contains Ni in an amount of 5 mass % or more and 40 mass % or less when a total of Al, Ni, B and Si is 100 mass %.
11. The PTC element according to any one of claims 1 to 10, wherein an Al particle having an average particle diameter of $1.2\text{ }\mu\text{m}$ or more and $10\text{ }\mu\text{m}$ or less is dispersed in the base metal-based electrode.
12. The PTC element according to any one of claims 1 to 11, wherein the semiconductor ceramic composition has a composition represented by a composition formula of $[(\text{BiA})_x(\text{Ba}_{1-y}\text{R}_y)_{1-x}]\text{Ti}_{1-z}\text{M}_z\text{O}_3$ (A is at least one kind of Na, Li and K, R is at least one kind of rare earth elements including Y, M is at least one kind of Nb, Ta and Sb), wherein x, y and z satisfy the ranges of $0 < x \leq 0.25$, $0 \leq y \leq 0.052$ and $0 \leq z \leq 0.01$ (where $y+z > 0$).
13. The PTC element according to any one of claims 1 to 12, wherein the base metal-based electrode is baked at a temperature of 720°C or higher and 850°C or lower in an air atmosphere.
14. A heat generating module comprising the PTC element according to any one of claims 1 to 13, wherein the semiconductor ceramic composition generates heat.

FIG. 1

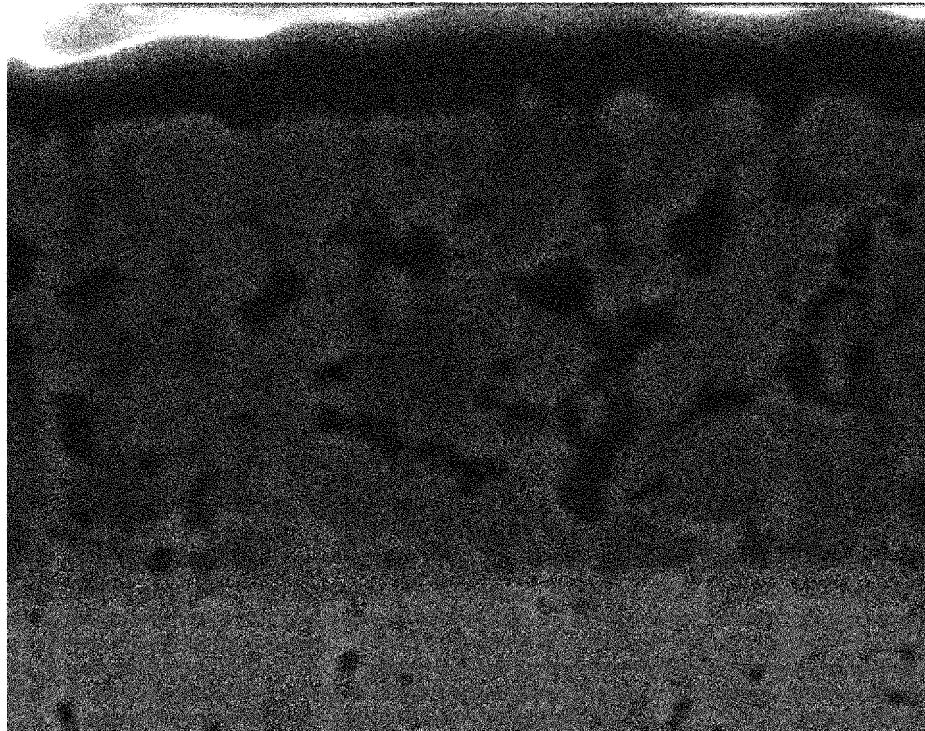


FIG. 2

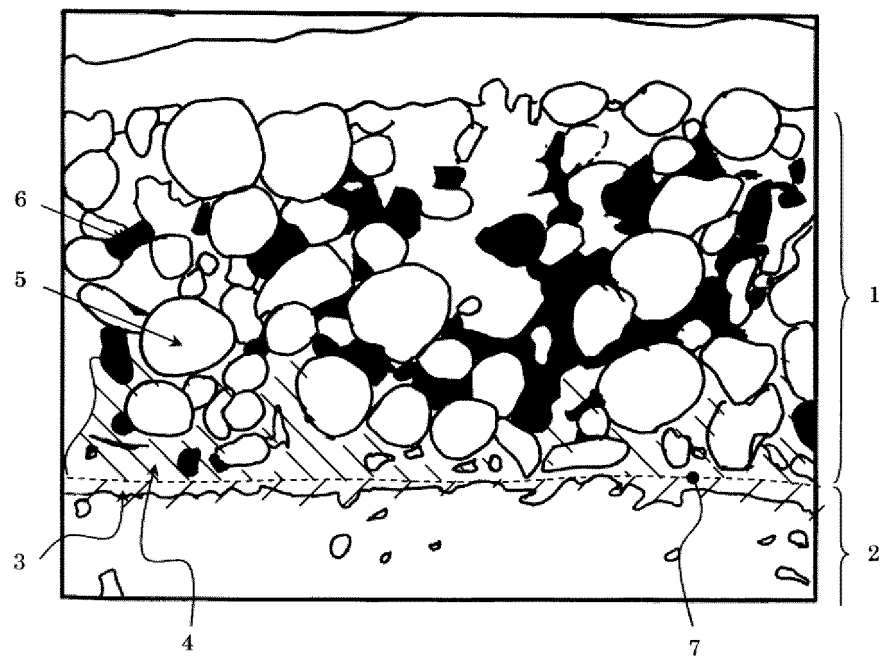


FIG. 3

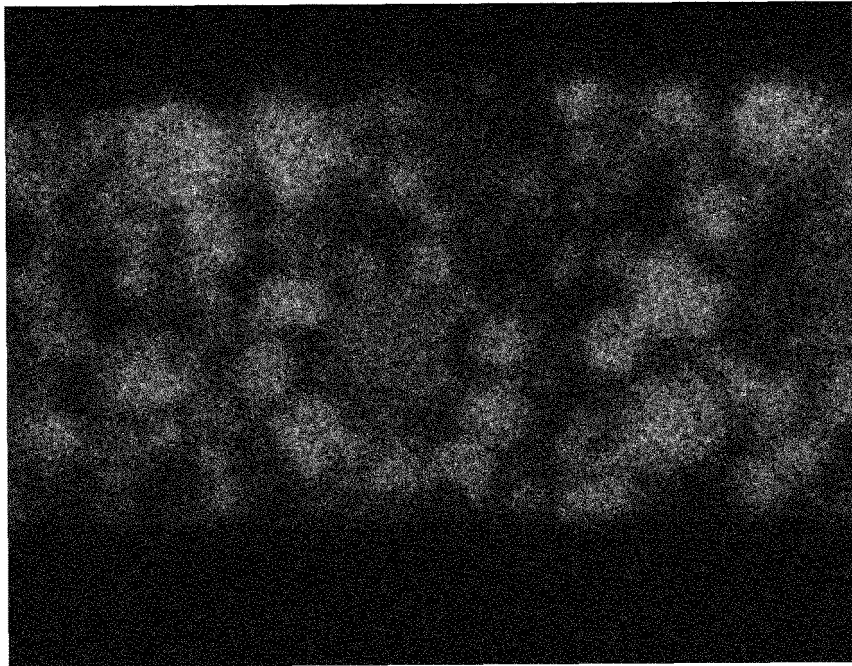


FIG. 4

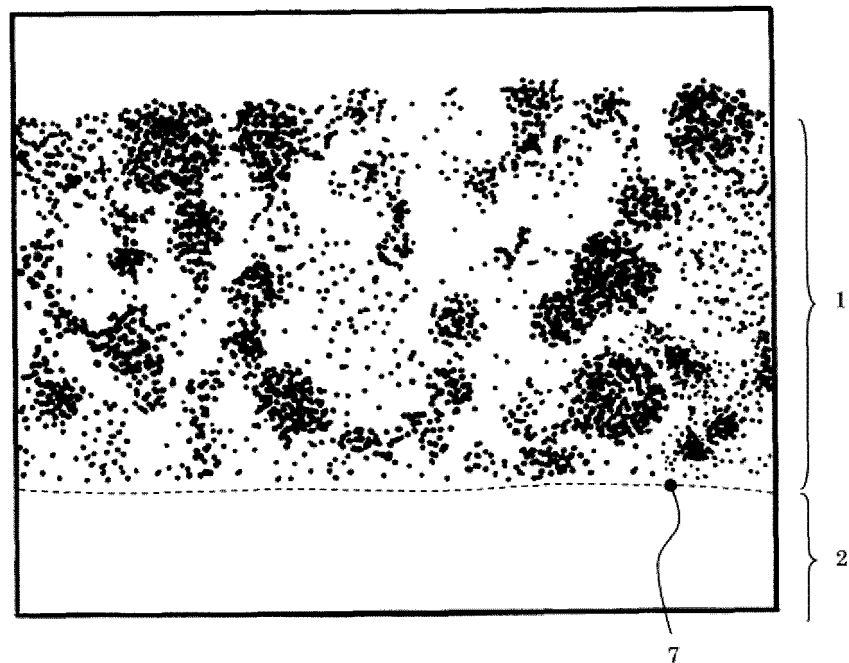


FIG. 5

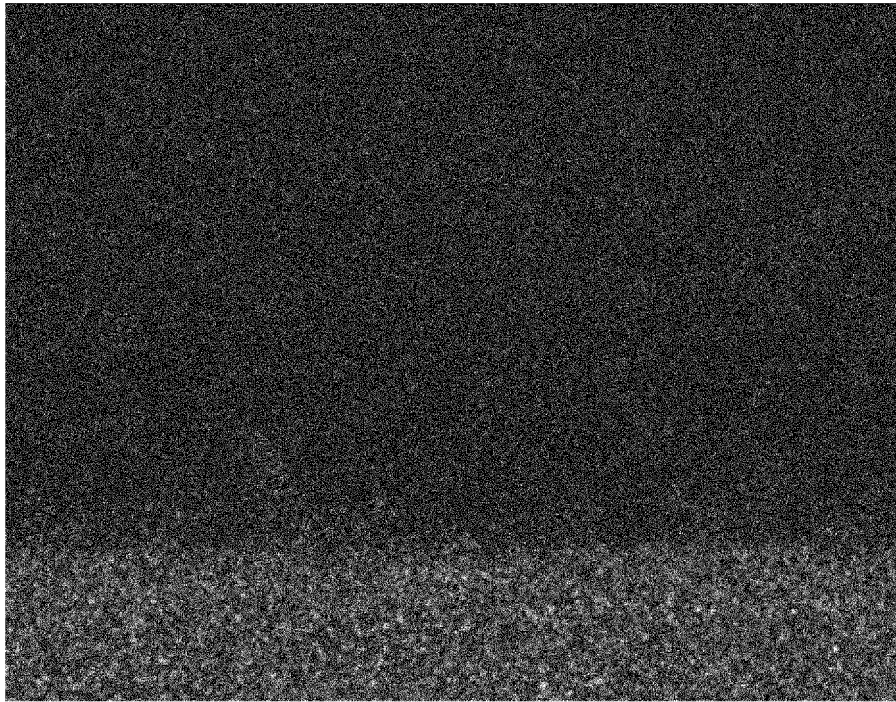


FIG. 6

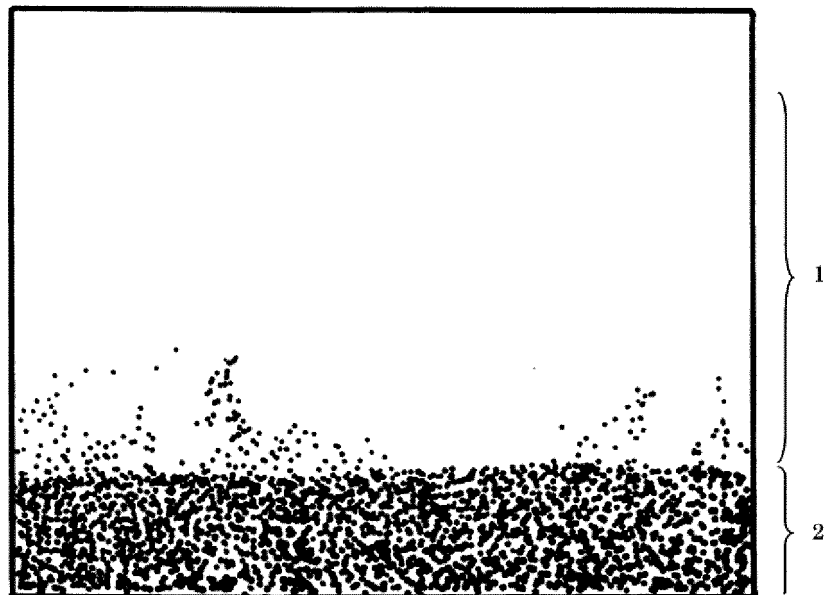


FIG. 7

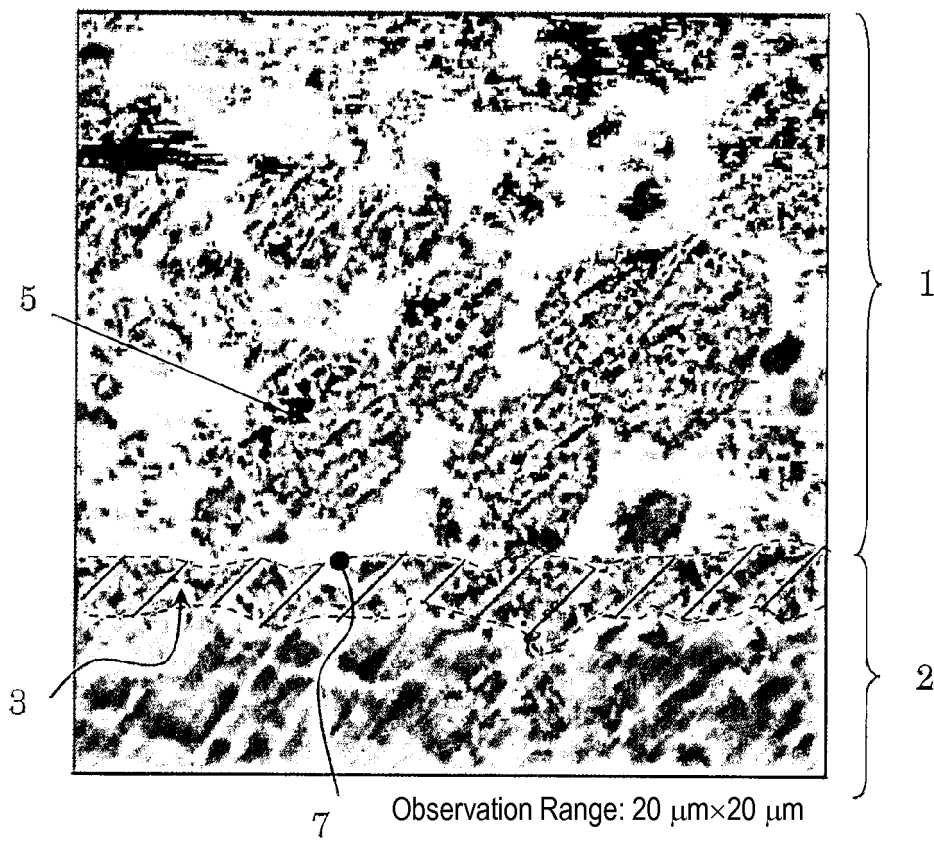


FIG. 8

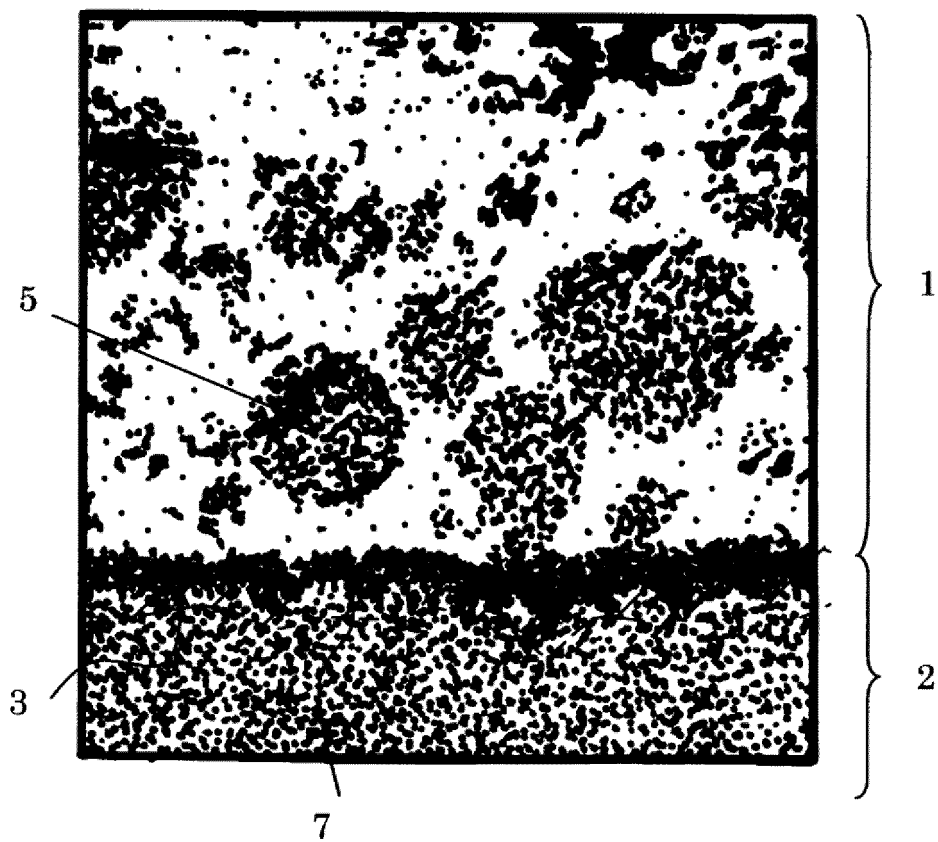


FIG. 9

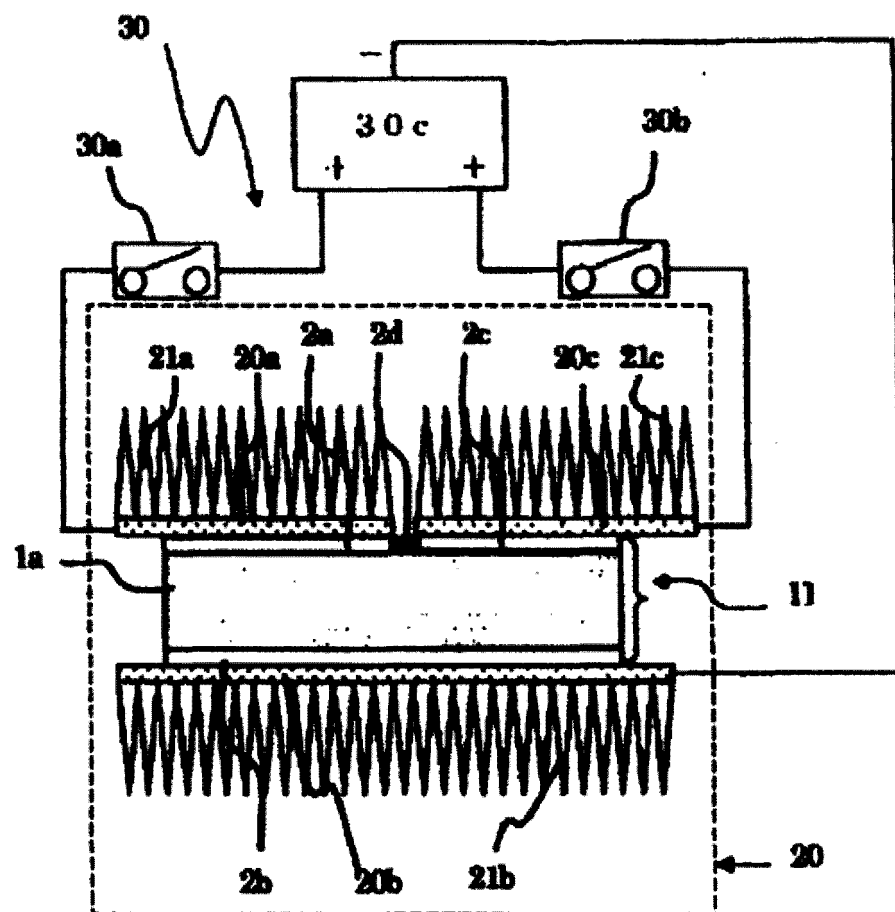
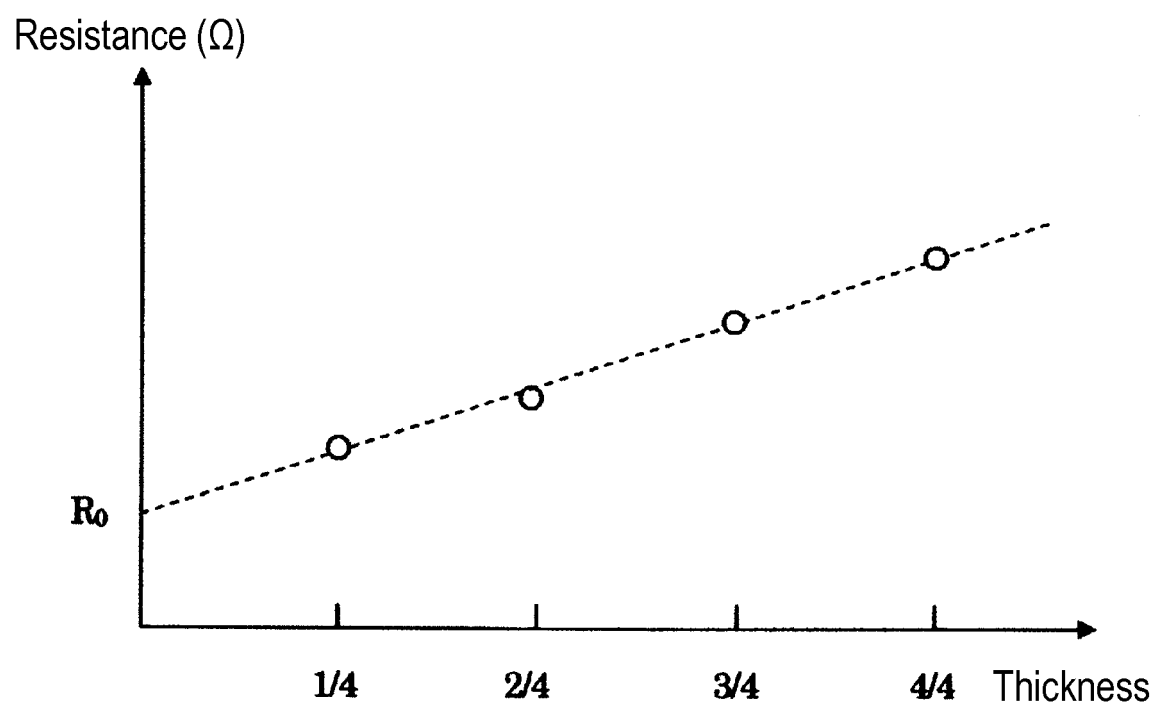


FIG. 10



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/067548

A. CLASSIFICATION OF SUBJECT MATTER

H01C7/02(2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01C7/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2014

Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 4-211101 A (TDK Corp.), 03 August 1992 (03.08.1992), paragraphs [0002], [0009] to [0019] (Family: none)	1-7, 9-14 8
Y	JP 63-60501 A (Murata Mfg. Co., Ltd.), 16 March 1988 (16.03.1988), page 2; fig. 1 (Family: none)	1-7, 9-14
Y	JP 5-109504 A (Murata Mfg. Co., Ltd.), 30 April 1993 (30.04.1993), paragraphs [0006], [0010] (Family: none)	1-7, 9-14

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

24 July, 2014 (24.07.14)

Date of mailing of the international search report

05 August, 2014 (05.08.14)

Name and mailing address of the ISA/
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Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/067548

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2005-167113 A (Murata Mfg. Co., Ltd.), 23 June 2005 (23.06.2005), paragraph [0009] (Family: none)	11-14
Y	WO 2013/051486 A1 (Hitachi Metals, Ltd.), 11 April 2013 (11.04.2013), paragraphs [0023], [0024] (Family: none)	12-14
A	JP 3-233805 A (Nichicon Corp.), 17 October 1991 (17.10.1991), entire text; all drawings (Family: none)	1-14

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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- WO 2010067866 A **[0012]**
- JP 2012169515 A **[0012]**
- JP 3233805 A **[0012]**
- JP 2013139001 A **[0170]**