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(54) **PROCESS FOR THE PREPARATION OF SEMICONDUCTING CERAMICS COMPOSED OF METAL OXIDES, IN PARTICULAR OF TIN OXIDE, ESPECIALLY FOR VARISTORS**

(75) Inventors: **Mehrdad Hassanzadeh**, Clapiers (FR); **Celine Machado-Bailly**, Blois (FR); **Renaud Metz**, Villeurbanne (FR); **Ramon Puyane**, Montpellier (FR)

Correspondence Address:
MCKENNA LONG & ALDRIDGE LLP
1900 K STREET, NW
WASHINGTON, DC 20006 (US)

(73) Assignee: **AREVA T&D SA**, Paris (FR)

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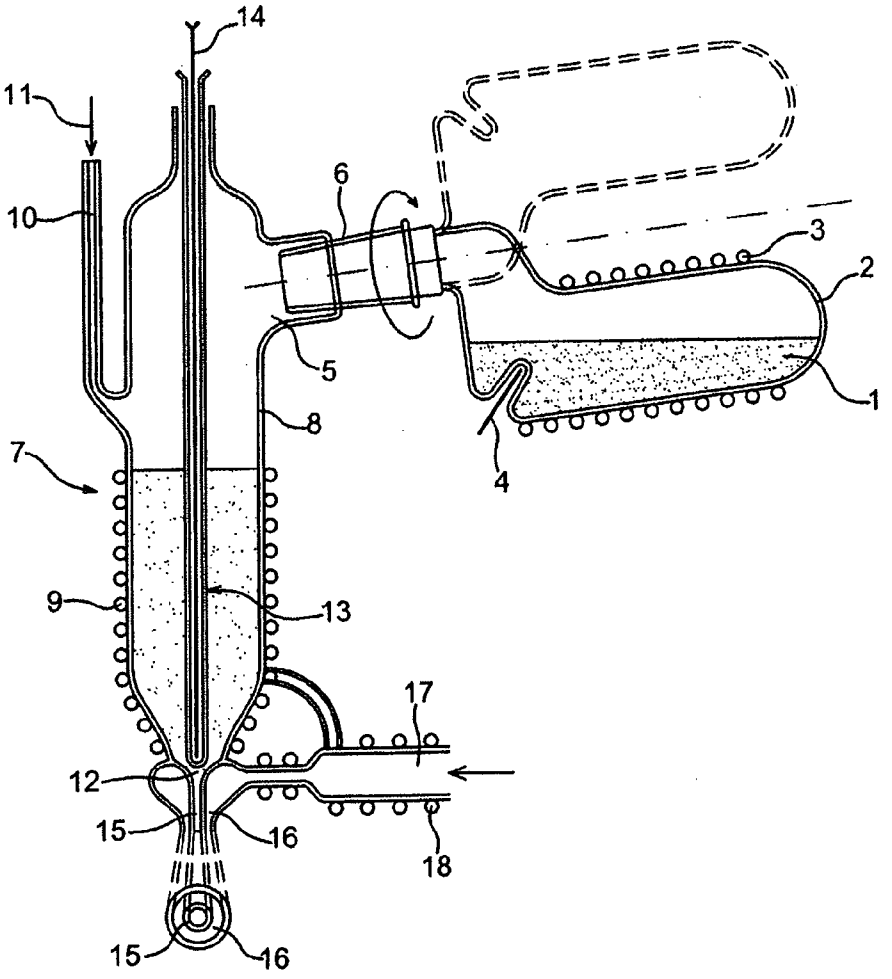
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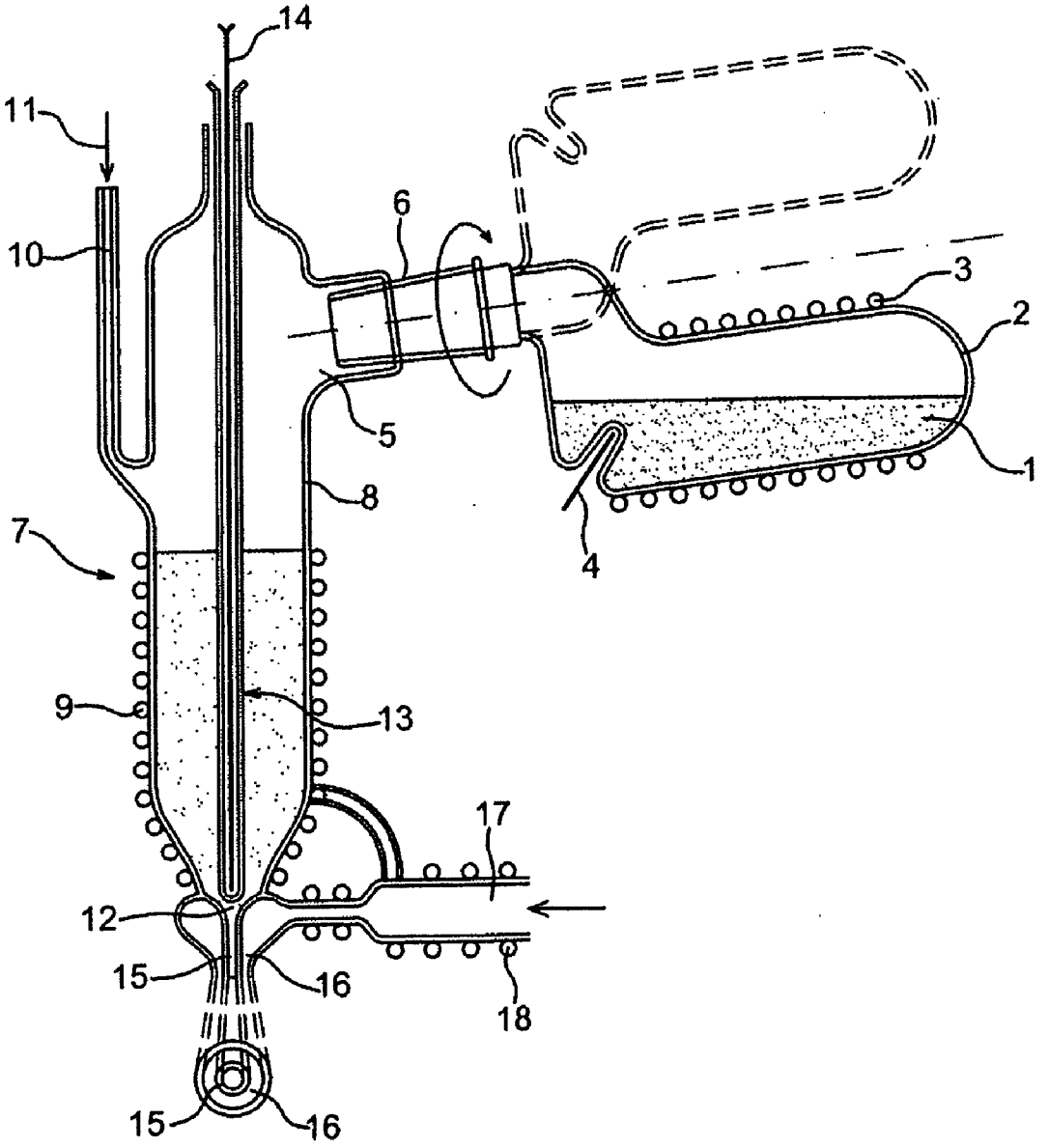
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(57) **ABSTRACT**

Process for the preparation of a semiconducting ceramic based on doped tin oxide SnO_2 by a process of "PADO" (Precursor Alloy Direct Oxidation) type applied to an alloy of tin and of doping metals or by a process of "PADO" type applied to tin, the doping metals being added in the form of oxides to the powder subjected to sintering.




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PROCESS FOR THE PREPARATION OF SEMICONDUCTING CERAMICS COMPOSED OF METAL OXIDES, IN PARTICULAR OF TIN OXIDE, ESPECIALLY FOR VARISTORS

TECHNICAL FIELD

[0001] The invention relates to a process for the preparation of semiconducting ceramics composed of metal oxides, more specifically of semiconducting ceramics, composed of one or more base metal oxides, such as tin oxide SnO_2 and of one or more doping metal oxides.

[0002] Such semiconducting ceramics, whether bulk or else in the form of thin layers, are used in particular to manufacture resistors which are nonlinear as a function of the voltage and in particular varistors, which are used, for example, in low-, medium- and high-voltage lightning arresters or voltage-limiting components associated, for example, with an item of electrical or electronic equipment.

[0003] The technical field of the invention can thus be defined very generally as that of ceramics based on metal oxides and of their preparation and more particularly as that of ceramics exhibiting a resistance which is nonlinear as a function of the voltage, such as varistors.

[0004] Resistors which are nonlinear as a function of the voltage, such as varistors, based on silicon carbide, selenium rectifiers and p-n junction diodes made of silicon or germanium, have been widely used for the voltage stabilization of electrical circuits or the suppression of normally high overvoltages induced in electrical circuits.

[0005] The electrical characteristics of such a nonlinear resistor are in particular:

[0006] the nonlinearity coefficient α; the higher a is, the better the performance of the material,

[0007] the maximum acceptable electric field before breakdown E_s (in V/mm); the higher it is, the better the performance of the material. This field E_s corresponds to a voltage before breakdown V_s.

[0008] Currently, resistors are essentially composed of sintered bodies of zinc oxide ZnO optionally comprising one or more additives or doping agents chosen, for example, from metal oxides.

[0009] Thus, the documents FR-A-2 174 174, FR-A-2 174 175, FR-A-2 174 176 and FR-A-2 194 026 disclose varistors formed of a sintered body essentially composed of ZnO with, as additives, Bi_2O_3, Sb_2O_3 and Co_3O_4.

[0010] However, it was suggested, in 1973 and then in 1974, to employ tin oxide SnO_2 in the manufacture of varistors, first of all as doping agent and then as main oxide constituting the ceramic.

[0011] The document JP-A-49 105196 (1974) discloses an improvement in the electrical properties of varistors made of ZnO by doping a mixture of ZnO, NiO_2, BaO and TiO_2 with 1 mol % of SnO_2; this mixture is subsequently compacted and sintered at 1350° C. in air.

[0012] The documents JP-A-48 099695 (1973) and JP-A-49 041897 (1974) provide formulations which can be expressed, for example, by: Bi_2O_3 7 parts; $(ZnO)_{0.87}(SnO_2)_{0.12}(YF_3)_{0.01}$ 100 parts, and which make it possible to achieve electrical characteristics of varistors which are highly varied, simply by modifying the Bi_2O_3 content.

[0013] Thus, values of the nonlinearity coefficient α of 10 to 51.3 and voltages V_s of 235 to 889 V are obtained.

[0014] The documents JP-A-49 108590 (1974) and JP-A-49 047898 (1974) provide, for the first time, compositions for varistors predominantly based on SnO_2 instead of ZnO, although the latter oxide is, however, still present in minor amounts. These compositions comprise SnO_2 (up to 70 mol %), ZnO and Sb_2O_3 doped with Bi_2O_3, V_2O_5, Nb_2O_5, Cr_2O_3 or Mn_2O_3.

[0015] These compositions make it possible to obtain high nonlinearity coefficients, the maximum value indicated for the latter being 30.

[0016] Later, compositions for varistors based on SnO_2, this time completely devoid of ZnO, are disclosed in the documents JP-A-49 129192 (1974) and JP-A-49 129193 (1974). These compositions are defined generally by the following compositions as mol %: 40 to 99.85 of SnO_2, 0.05 to 30 of Sb_2O_3 and 0.1 to 50 mol % of CoO.

[0017] The ceramics prepared from a mixture composed of 99.9 mol % of SnO_2, 0.05 mol % of Sb_2O_3 and 0.05 mol % of Bi_2O_3 or from a mixture composed of 99.85 mol % of SnO_2, 0.05 mol % of Sb_2O_3 and 0.1 mol % of CoO, compacted and sintered, have electrical properties of varistors which are relatively mediocre, with α and V_s values respectively of less than 10 and 25 V.

[0018] However, it may be considered that varistors based on SnO_2 have only really taken off since 1995, with the studies mentioned in the paper by S. A. Pianaro, P. R. Bueno, E. Longo and J. A. Varela, "A new SnO_2-based varistor system", which describes in particular a varistor composition comprising, as mol %: 98.9% of SnO_2, 1% of CoO, 0.05% of Nb_2O_5 and 0.05% of Cr_2O_3.

[0019] This composition exhibits advantageous electrical properties, in particular a nonlinearity coefficient α of 41 and a maximum electrical field before breakdown E_s of 400 V/mm, which are associated with monophase structures, the grain boundaries of which are apparently devoid of precipitated phases.

[0020] The document BR-A-96 00174-7 discloses metal oxide compositions for varistors composed essentially of tin oxide (SnO_2) doped with various metal oxides, such as cobalt oxide and niobium oxide.

[0021] A typical composition comprises from 97.5 to 99.45% of tin dioxide (SnO_2), from 0.5 to 2.0% of cobalt oxide (CoO) and from 0.05 to 0.3% of niobium oxide (Nb_2O_5). These compositions are subsequently subjected to sintering at a temperature of 1300 to 1350° C. to give a ceramic.

[0022] As regards their process of preparation, the semiconducting ceramic materials for semiconducting ceramic pellets or varistors used for protecting from overvoltages are generally prepared from their constituent oxides in the pulverulent form.

[0023] Thus, the semiconducting ceramic materials most widely used at the moment, which are based on ZnO, are prepared from pulverulent oxides composed of the predomi-

nant oxide, which is ZnO, and doping oxides, such as nickel, chromium, manganese, magnesium, bismuth, antimony, silicon or cobalt oxides, and the like.

[0024] Generally, the conventional chemical processes for the preparation of ceramic materials thus consists in weighing the constituent oxides, in mixing them and in milling them, and in then forming a mixture in an aqueous medium in order to obtain a slip.

[0025] This slip is atomized and dried (spray drying) to form agglomerates of a few hundred microns, which are subsequently shaped by pressing and then sintered at high temperature.

[0026] Finally, metal electrodes are deposited and the component is coated, on its other surfaces, with a material which provides electrical insulation and physicochemical and mechanical protection.

[0027] However, this type of process is complex to carry out and requires large milling and heating devices. Furthermore, it is difficult to obtain good chemical homogeneity as the intimate mixing of the milled components, at best micrometric in size, can never be perfect.

[0028] It is in order to overcome the disadvantages of the conventional processes for the preparation of ceramics, in particular of semiconducting ceramics for varistors, described above and in particular in order to obtain a powder which is homogeneous at the molecular level formed of alloyed metal oxides that the process referred to as the "PADO" or Precursor Alloy Direct Oxidation process has been provided.

[0029] The PADO process is disclosed in the document FR-A-2 674 157 and, with some variations in comparison with the document FR-A-2 674 157, in the document EP-A1-0 580 912 and in the document U.S. Pat. No. 5,322,642.

[0030] In the PADO process, the base components or starting materials for producing the powder intended to give the semiconducting ceramic are no longer metal oxides but alloys or mixtures of metals which are only subsequently oxidized, either in the solid phase or in the liquid phase or in the vapour phase.

[0031] The PADO process, disclosed, for example, in the document FR-A-2 674 157, comprises the following successive steps:

[0032] placing the various chosen metals in a crucible;

[0033] melting the said metals under a reducing atmosphere while mixing the liquid for the purpose of homogenizing it;

[0034] casting the liquid alloy in an ingot mould in the said reducing atmosphere;

[0035] allowing the ingot obtained to cool;

[0036] reducing the ingot to a powder with a predetermined particle size, each of the particles of which is homogeneous;

[0037] oxidizing the said particles.

[0038] The ingot obtained can be reduced to a powder by milling or to chips by machining, so that the ingot, the powder or the chips can be left under an appropriate atmosphere for the purpose of their oxidation.

[0039] It is also possible to melt the ingot to give a liquid alloy which is sprayed for the purpose of obtaining solid fine components or grains of homogeneous composition which are subsequently oxidized.

[0040] Once the powder has been obtained, it is compacted in the form of pellets by cold pressing, followed by sintering at high temperature.

[0041] According to claim **10** of this document, the product obtained by the process is composed of an alloy of zinc oxide and of doping products composed of oxides of at least some of the following metals: Ni, Cr, Mg, Mn, Bi, Sb, Si and Co (on page 5, line 32, it is copper which is mentioned); tin is not mentioned.

[0042] The document EP-A1-0 580 912 discloses more fully a process of "PADO" type for the manufacture of a homogeneous powder formed of metal oxides from alloys of metals in which the following successive steps are carried out:

[0043] placing, in a crucible, the various metals provided for in order to form the alloy;

[0044] melting the said metals under a neutral or reducing atmosphere while mixing the liquid for the purpose of homogenizing it;

[0045] recovering the liquid alloy;

[0046] obtaining, from the alloy, a powder with a predetermined particle size, each of the particles of which is homogeneous;

[0047] oxidizing the said particles.

[0048] In order to prepare a ceramic, for example a semiconducting ceramic, based on metal oxides, the powder formed of oxides which is obtained is compacted, for example in the form of a pellet, and the compacted product is sintered at a temperature of greater than or equal to 800° C.

[0049] This process applies in particular to the manufacture of semiconductors based on zinc oxide which are doped with oxides of Ni, Cr, Mg, Mn, Bi, Sb, Co (or Cu); again, tin is not mentioned.

[0050] The powder with a predetermined particle size can be obtained by direct spraying of the liquid alloy recovered or else by casting the liquid alloy in an ingot mould in a neutral or reducing atmosphere, followed by melting the ingot to give a liquid alloy which is sprayed for the purpose of obtaining solid fine components or grains of homogeneous composition.

[0051] The "PADO" process, for example disclosed in the document FR-A-2 674 157 and in the document EP-A1-0 580 912, makes it possible, without having recourse to one or more milling and mixing stages, which are often sources of pollution, to obtain a mixture formed of a perfectly homogeneous powder formed of oxides which can never be obtained by conventional processes employing large milling and heating devices. The perfectly homogeneous powder obtained exhibits a homogeneity at a molecular level which had never been achieved until then.

[0052] However, the "PADO" process introduces an answer to the problem of homogeneity of the powders only in the context of the preparation of powders formed of oxides and then of semiconducting ceramics specifically based on zinc oxide (ZnO) and not in the case of ceramics based on other oxides, in particular of ceramics based on tin oxide (SnO_2).

[0053] This clearly emerges from the two documents mentioned above, where the only ceramic mentioned is specifically a ceramic based on zinc oxide doped with oxides, among which tin oxide is not mentioned.

[0054] There thus exist, from the viewpoint of the above, a need for a process, derived from the "PADO" process, which makes it possible to obtain powders formed of oxides and then ceramics, these being perfectly homogeneous at the submicroscopic level, indeed even at the molecular level, that is to say with segregations which are as limited as possible, which is not limited to powders and ceramics based on zinc oxide and which applies in particular to powders and ceramics based on tin oxide (SnO_2).

[0055] There additionally exists a need for a process derived from the "PADO" process which makes it possible to obtain semiconducting ceramics based on oxides exhibiting better electrical parameters, in particular α and E_s parameters, than those obtained with ZnO.

[0056] Finally, there additionally exists a need for ceramics based on oxides exhibiting an increased density and consequently improved mechanical and thermal properties, in particular as regards their mechanical strength and their ability to dissipate heat.

[0057] The aim of the present invention is to provide a process for the preparation of ceramics based on oxides of metals which meets, inter alia, the needs listed above.

[0058] The aim of the present invention is, in addition, to provide a process for the preparation of ceramics based on oxides of metals which does not exhibit the disadvantages, limitations, failings and drawbacks of the processes of the prior art, in particular of the "PADO" process, and which solves the problems of the processes of the prior art.

[0059] These aims, and others also, are achieved, in accordance with a first embodiment of the invention, by a process for the preparation of a ceramic comprising, preferably composed of, a base metal oxide and at least one doping metal oxide, in which the following successive steps are carried out:

[0060] tin metal (Sn), and one or more (other) doping metals and/or one or more salts of these (other) doping metals are placed in a crucible;

[0061] the tin and the said doping metals and/or salts of doping metals placed in the crucible are melted under a neutral or reducing atmosphere while mixing the molten tin and doping metals and/or salts of doping metals, in order to obtain a homogeneous liquid mixture or alloy of metals;

[0062] starting from the said homogeneous liquid mixture or alloy of metals, a powder formed of alloy of metals with a predetermined particle size is prepared, directly or after an optional operation of particle size classification, for example a sieving operation, each of the particles of which is homogeneous;

[0063] all the said particles of the powder formed of alloy of metals with a predetermined particle size or a predetermined particle size fraction of the powder are completely or partially oxidized, in order to obtain a homogeneous powder formed of oxides of the metals which is completely or partially oxidized, coalescence of the particles being avoided;

[0064] the homogeneous powder formed of oxides which is completely or partially oxidized is shaped;

[0065] the shaped powder is sintered.

[0066] In this first embodiment, the process according to the invention can be defined as a process of "PADO" type applied to tin and more specifically to an alloy of tin and of doping metals and which is employed in order to prepare ceramics formed of doped tin oxide.

[0067] The process according to the invention thus exhibits all the advantages of the PADO process already mentioned above.

[0068] It was indicated above that it proved to be the case that the "PADO" process makes it possible to prepare oxide-based powders and ceramics, the grains of which are chemically homogeneous at the submicroscopic scale, indeed even molecular scale, only in the specific case of powders and ceramics based on zinc oxide (ZnO).

[0069] The process according to the invention, in this first embodiment, is not described in the documents of the prior art, where the preparation of ceramics based on SnO_2 by the PADO process is not mentioned. A fortiori, the preparation of ceramics based on SnO_2 comprising doping oxides, preferably specific doping oxides in specific proportions, is not described either.

[0070] Nothing could allow it to be anticipated in the prior art that this PADO process could also be successfully employed to prepare powders and then ceramics based on tin oxide (SnO_2).

[0071] This is because the teachings which can be deduced from the successful use of the PADO process with zinc oxide (ZnO) cannot under any circumstances be applied to tin dioxide (SnO_2) as very significant differences in behaviour exist between these oxides which in fact renders completely unpredictable and random the change from one oxide to the other; zinc oxide exhibits, for example, a metal/oxygen ratio of 1, whereas, for tin, this ratio is equal to 2.

[0072] The success of the "PADO" process, proven only with zinc oxide, did not mean in any way that this process might be applied to tin oxide.

[0073] In addition, by virtue of the use of tin oxide SnO_2, the varistors obtained exhibit better electrical characteristics than the varistors of the prior art, in particular obtained by the "PADO" process, for example better α and E_s properties than those obtained with varistors based on zinc oxide.

[0074] The electrical characteristics of the varistors prepared by the process according to the invention according to this first embodiment are also better than those of the varistors based on tin dioxide of the documents JP-A-49 108590, JP-A-49 047898, JP-A-49 129192, JP-A-49

129193, JP-A-05 129106 and JP-A-05 129167, the α values of which are low and always less than 30.

[0075] To sum up, it may be indicated that the present invention relates neither to the process for the preparation of an alloy nor to the atomization of the latter. The invention may be defined generally as being the application of the "PADO" process to SnO_2. The physicochemical history of a powder is determining in the chemistry of the solid. Consequently, the results obtained with the process of the invention were unpredictable and absolutely uncertain as a person skilled in the art knows that the chemistry of tin is very different from that of zinc.

[0076] In the case where the oxidation of the particles of the powder formed of alloy of metals is only a partial oxidation, this characteristic of partial oxidation of the metals or of the Sn metal (see below as regards the 2nd embodiment) also fundamentally distinguishes the process according to the invention from the processes for the preparation of semiconducting ceramics of the prior art and in particular from the processes of "PADO" type, such as those disclosed, for example, in the documents FR-A-2 674 157 and EP-A-0 580 912, in which a complete oxidation is carried out.

[0077] In other words, in the process according to the invention, the powder to be compacted is, when a partial oxidation has been carried out, a composite composed of metal (metals) and of metal oxide(s).

[0078] Basically, in the process according to the invention and when a partial oxidation is carried out, the compacted powders are mixtures of metal (metals) and of metal oxides obtained by partial oxidation of the metal powders.

[0079] For this reason, the raw ceramic (before sintering and after shaping) comprises tin metal and other metals, which is never the case in the prior art and which is not under any circumstances suggested by the prior art.

[0080] It may be said that, in this case, a metal-ceramic composite is subjected to sintering.

[0081] This partial and incomplete oxidation is a preferred characteristic of this first embodiment of the process according to the invention but also of the second embodiment (see below). It is admittedly mentioned in passing in the document EP-A1-0 580 912 that the alloy powder may be partially oxidized but, before compacting and sintering, this powder is completely oxidized, so that the ceramic before sintering does not under any circumstances comprise metal.

[0082] Surprisingly, it turns out that, by carrying out only partial oxidation of the alloy (or metal) powder, the presence of metal, for example of tin metal, in the raw ceramic makes it possible to increase the densification of the ceramic after sintering. This is well observed experimentally starting from metal particles with an initial size of the order of 20 to 40 microns in diameter as the densifications are relatively low. There is thus a change from approximately 75% to approximately 85%.

[0083] The electrical characteristics of the varistors obtained (E_s and α) when recourse has been had to a partial oxidation are also excellent, for example better than those of the Japanese documents cited above.

[0084] When the partial oxidation gives a powder with 50% to 99.9% of oxide, the above effects are particularly marked.

[0085] A percentage of 64% of oxide in particular for tin gives the best results for the densification and the electrical properties.

[0086] The oxide or oxides of doping metals can be chosen from oxides of cobalt, chromium, manganese, niobium, tantalum, transition metals, such as Zn, and lanthanide metals.

[0087] Consequently, the other doping metal or metals placed in the crucible can likewise be chosen from the abovementioned doping metals and the salts of metals placed in the crucible can likewise be chosen from the salts of the abovementioned metals.

[0088] Preferably, the oxide or oxides of doping metals are chosen from cobalt, manganese, niobium and tantalum oxides.

[0089] More preferably, the ceramic comprises, as doping metal oxides, simultaneously, at the same time, cobalt oxide, manganese oxide, niobium oxide and tantalum oxide.

[0090] The proportion by weight of the tin and of the other doping metal or metals and/or salt or salts of doping metals placed in the crucible is preferably such that it makes it possible to obtain a ceramic comprising a proportion of tin oxide of greater than or equal to 90% by weight, preferably of greater than or equal to 95% by weight, more preferably of greater than or equal to 99% by weight, better still of greater than or equal to 99.995% by weight.

[0091] In other words, the proportion by weight of the other doping metal or metals and/or salt or salts of doping metals placed in the crucible is such that it makes it possible to obtain a ceramic comprising, as complement to 100% by weight of tin oxide, less than 10% by weight, preferably less than 5% by weight, more preferably less than 1% by weight and better still less than 0.005% by weight of oxides of doping metals.

[0092] This percentage of SnO_2 in the final ceramic being observed, the proportion of the other doping metal or metals and/or salt or salts of doping metals in the crucible is such that it makes it possible preferably to obtain a ceramic comprising, as complement to 100% by weight of tin oxide, one or more among the following oxides in the following proportions by weight:

[0093] 0.1 to 3% of cobalt oxide,

[0094] 0.01 to 3% of chromium oxide,

[0095] 0.01 to 3% of manganese oxide,

[0096] 0.01 to 0.5% of niobium oxide,

[0097] 0.01% to 0.5% of tantalum oxide,

[0098] 0.01 to 0.5% of one or more transition metal oxides,

[0099] 0.01 to 0.5% of one or more lanthanide metal oxides, such as lanthanum oxide.

[0100] This is because the inventors have demonstrated that the PADO process was employed with even better results in preparing ceramics based on tin oxide if the latter preferably received the addition of oxides of specific doping agents, these oxides being more preferably in the specific proportions cited above.

[0101] In other words, the unexpected adapting of the "PADO" process to ceramics based on SnO_2 is carried out optimally if specific doping agents are preferably added to the ceramics.

[0102] This optimization is even better if these specific doping agents are added in specific proportions, which thus constitutes a twofold selection.

[0103] The fact that the "PADO" process can be applied to SnO_2 with results which are further improved provided that, preferably, such doping agents are selected and the fact that this improvement is even more obvious in such specific ranges of contents are in no way mentioned in the prior art.

[0104] The addition of these specific doping agents, preferably in these specific proportions, further improves the electrical properties, which are already intrinsically improved by the use of SnO_2 instead of ZnO, and the other properties, such as the density.

[0105] Oxides of doping agents which are particularly preferred are chosen from cobalt, manganese, niobium and tantalum oxides, such as Co_3O_4, MnO_2, Nb_2O_5 and Ta_2O_5, preferably in the proportions mentioned above.

[0106] A preferred ceramic will comprise the addition of all four of these doping oxides, preferably in the proportions mentioned above.

[0107] For example, this ceramic will have the following composition by weight (as % by weight):

[0108] SnO_2: 98.24%;

[0109] Co_3O_4: 0.05%;

[0110] MnO_2: 1.69%;

[0111] Nb_2O_5: 0.01%;

[0112] Ta_2O_5: 0.01%.

[0113] Generally, the SnO_2 makes it possible to use a smaller number of doping agents, these doping agents being used in amounts which are lower overall and these doping agents in addition being chosen from doping agents which are less polluting, less toxic and cleaner.

[0114] In comparison with the ceramics based on ZnO, the relative content of doping agents with respect to the base metal oxide or reference oxide is generally 10 times less (10 times less doping agents) in ceramics based on SnO_2.

[0115] Thus, the % of doping agents is of the order of 2%, in particular 1.76%, in the above example, whereas it is generally of the order of 10% in the case of ZnO formulations. Furthermore, toxic doping agents, such as antimony oxide, are preferably not employed.

[0116] The alloy powder with a predetermined particle size can be prepared by cooling, preferably rapidly or suddenly (quenching), the homogeneous liquid mixture or alloy of metals, so as to solidify it, while retaining the chemical homogeneity of the mixture or alloy of liquid metals (high temperature), and by then dividing the solidified homogeneous alloy of metals to give a powder formed of alloy of metals with a predetermined particle size.

[0117] The cooling of the homogeneous liquid mixture or alloy of metals so as to solidify or set it can be carried out by casting the liquid mixture or alloy of metals in an ingot mould under a neutral or reducing atmosphere and by then cooling the ingot obtained.

[0118] The dividing of the solidified homogeneous alloy can be carried out in the liquid phase by melting it again to give a homogeneous liquid alloy of metals which is sprayed or atomized by a stream of gas or of liquid and rapidly cooled (quenched).

[0119] The powder formed of alloy of metals with a predetermined particle size can also be prepared directly from the homogeneous liquid alloy of metals resulting from the second stage of the process by spraying or atomization with a stream of gas or of liquid and rapid cooling ("quenching").

[0120] It is found that the homogeneity of the powder is improved by quenching the stream of metal in a liquid coolant.

[0121] The stream of gas can be a stream of neutral or reducing gas, such as hydrogen, nitrogen, argon or their mixtures.

[0122] The stream of gas can be a stream of oxidizing gas, such as air, air enriched in oxygen, or oxygen optionally enriched in water vapour.

[0123] The dividing of the solidified homogeneous alloy of metals can also be carried out in the solid phase by abrasion or milling.

[0124] The powder formed of alloy of metals can optionally be separated into several particle size fractions.

[0125] The powder formed of alloy of metals may be completely oxidized, that is to say that the oxidized powder comprises 100% by weight of oxide.

[0126] Alternatively, the oxide powder may be only partially oxidized.

[0127] In this case, the powder formed of alloy of metals may be partially oxidized to a percentage of 50 to 99.90% by weight, preferably of 55 to 80 or 85% by weight, more preferably of 60 to 70% by weight, that is to say that the oxidized powder comprises from 50 to 99.90% by weight of oxide, preferably from 55 to 80 or 85% by weight of oxide and more preferably from 60 to 70% by weight of oxide.

[0128] Preferably, the powder formed of alloy of metals is partially oxidized to a percentage of 64% by weight.

[0129] The complete or partial oxidation of the particles of the powder formed of alloy of metals with a predetermined particle size can be carried out by bringing the said particles into contact with an oxidizing gas from a temperature and/or for a period of time which is (are) sufficient to produce a desired percentage of oxides of metals in the powder, for example for the oxidation to be complete.

[0130] For example, in the case of tin, a residence of one minute at 900° C. is sufficient to oxidize a monolayer of metal particles with a mean diameter of 20 to 40 microns.

[0131] These experimental conditions for the oxidation are to be specified by a thermogravimetric analysis. For example, in the case of pure tin, a temperature of 900° C. for 15 minutes makes it possible to completely oxidize the tin to give tin oxide.

[0132] In other words, a stationary temperature phase is observed, the particles being maintained at this temperature for a period of time sufficient for the oxidation to be complete.

[0133] The degree of oxidation of the particles is, in the case of tin, controlled or conditioned essentially by the temperature of the stationary oxidation phase and not by its duration, as in the case of zinc.

[0134] It was completely unexpected that, in the case of a mixture or alloy based on tin, mastery of the complete oxidation is obtained by essentially controlling the temperature of the stationary oxidation phase and not its duration, as is the case for zinc and its alloys.

[0135] This means that it is thus possible to obtain, for example, complete oxidation, whatever the duration of the stationary phase, on condition of being positioned at the appropriate temperature.

[0136] The oxidizing gas can be chosen from gases comprising oxygen optionally enriched in water vapour and/or in carbon dioxide, such as air, air enriched in oxygen, oxygen, or air enriched in carbon dioxide and/or in water vapour; or mixtures of CO and of CO_2.

[0137] The operation of bringing the particles into contact with the oxidizing gas can be carried out at a temperature of greater than or equal to 400° C., for example from 400 to 950° C.

[0138] The duration of this contacting operation is generally from 6 hours to 1 second, preferably from 4 hours to 2 seconds.

[0139] The contacting operation can thus be carried out, for example, for 4 hours at 400° C. or 2 seconds at 900° C.

[0140] In the process according to the invention, in this first embodiment, the aim is to prepare a powder comprising oxides (case of partial oxidation) or composed of oxides (case of complete oxidation) which is finely divided, which is homogeneous, which has segregations which are as limited as possible, which is isotropic and which has a surface condition which has to facilitate the subsequent densification.

[0141] The powder has a particle size which is generally submicronic in mean size (for example, mean diameter) of the particles.

[0142] The completely or partially oxidized homogeneous powder can be shaped by compacting it in the form of pellets, for example by cold pressing.

[0143] The sintering can be carried out at a temperature of 1100 to 1350° C. for a period of time generally of greater than or equal to 30 minutes, preferably from 30 minutes to 2 hours.

[0144] The above aims and yet other aims are achieved, in accordance with a second embodiment of the process of the invention, by a process for the preparation of a semiconducting ceramic comprising, preferably composed of, a base metal oxide and at least one doping metal oxide, in which the following successive steps are carried out:

[0145] tin is placed in a crucible;

[0146] the tin is melted, so as to obtain liquid tin;

[0147] a tin powder with a predetermined particle size is prepared from the liquid tin, directly or after an optional operation of particle size classification (sieving);

[0148] all the tin powder with a predetermined particle size or a predetermined particle size fraction of the powder is completely or partially oxidized;

[0149] one or more doping metal oxide(s) is (are) added to the partially or completely oxidized tin powder;

[0150] the partially or completely oxidized tin powder and the doping metal oxide(s) are mixed;

[0151] the mixture of partially or completely oxidized tin powder with the doping metal oxide(s) is shaped;

[0152] the shaped powder is sintered.

[0153] The doping metal oxide(s) added to the completely or partially oxidized tin powder are chosen from cobalt, chromium, manganese, niobium and tantalum oxides, transition metal oxides, such as zinc oxide, and oxides of lanthanide metals, such as lanthanum oxide.

[0154] Preferably, the oxide(s) of doping metals are chosen from cobalt, manganese, niobium and tantalum oxides.

[0155] More preferably, the ceramic comprises, as doping metal oxides of, simultaneously, at the same time, cobalt oxide, manganese oxide, niobium oxide and tantalum oxide.

[0156] The doping metal oxide(s) are added to the partially or completely oxidized tin powder in a percentage by weight such that it makes it possible to obtain a ceramic comprising a proportion of tin oxide of greater than or equal to 90% by weight, preferably of greater than or equal to 95% by weight, more preferably of greater than or equal to 99% by weight and better still of greater than or equal to 99.995% by weight.

[0157] In other words, the doping metal oxide or oxides can thus be added to the partially or completely oxidized tin powder in a percentage by weight such that it makes it possible to obtain a ceramic comprising, as complement to 100% by weight of tin oxide, less than 10% by weight, preferably less than 5% by weight, more preferably less than 1% by weight and better still less than 0.005% by weight of oxides of doping metals.

[0158] This percentage of SnO_2 in the final ceramic being observed, the doping metal oxide(s) are added to the partially or completely oxidized tin powder in a percentage by weight such that it makes it possible to obtain a ceramic comprising, as complement to 100% by weight of tin oxide, one or more among the following oxides in the following proportions by weight:

[0159] 0.1 to 3% of cobalt oxide,

[0160] 0.01 to 3% of chromium oxide,

[0161] 0.01 to 3% of manganese oxide,

[0162] 0.01 to 0.5% of niobium oxide,

[0163] 0.01% to 0.5% of tantalum oxide,

[0164] 0.01 to 0.5% of one or more transition metal oxides,

[0165] 0.01 to 0.5% of one or more lanthanide metal oxides, such as lanthanum oxide.

[0166] Oxides of doping agents which are particularly preferred are chosen from cobalt, manganese, niobium and tantalum oxides, such as Co_3O_4, MnO_2, Nb_2O_5 and Ta_2O_5, preferably in the proportions mentioned above.

[0167] A preferred ceramic will comprise the addition of all four of these doping oxides, preferably in the proportions mentioned above.

[0168] For example, this ceramic will have the following composition by weight (as % by weight):

[0169] SnO_2: 98.24%;

[0170] Co_3O_4: 0.05%;

[0171] MnO_2: 1.69%;

[0172] Nb_2O_5: 0.01%;

[0173] Ta_2O_5: 0.01%.

[0174] All the advantages and effects related to the use of specific doping agents preferably in specific proportions mentioned in the context of the first embodiment can be repeated in full for the second embodiment of the invention and in particular as regards the advantages and effects provided by the use of cobalt, manganese, niobium and tantalum oxides, preferably in specific proportions.

[0175] The metal powder, for example tin powder, with a predetermined particle size can be prepared in the liquid phase by melting the bulk tin to give a liquid metal which is sprayed or atomized by a stream of gas or of liquid and cooled, quenched.

[0176] The liquid tin can be sprayed or atomized by a stream of neutral or reducing gas, such as nitrogen.

[0177] The tin powder with a predetermined particle size can be prepared in the solid phase by abrasion or milling.

[0178] The tin powder can be separated into several particle size fractions.

[0179] The tin powder may be completely oxidized to a percentage of 100%.

[0180] Alternatively, the tin powder may be only partially oxidized.

[0181] In this case, the tin powder may be oxidized to a percentage of 50 to 99.90% by weight, preferably of 55 to 80 or 85% by weight, more preferably of 60 to 70% by weight, that is to say that the oxidized powder comprises from 50 to 99.90% by weight of oxide, preferably from 55 to 80 or 85% by weight of oxide, more preferably from 60 to 70% by weight of oxide; better still, the powder is oxidized to a percentage of 64% by weight.

[0182] For example, in the case of tin, a residence of one minute is sufficient to oxidize a monolayer of metal particles with a mean diameter of 20 to 40 microns at 900° C.

[0183] The tin powder can be partially or completely oxidized by bringing the said powder into contact with an oxidizing gas from a temperature and/or for a period of time which is (are) sufficient to produce a desired percentage of tin oxide in the powder.

[0184] As has already been mentioned above for the first embodiment of the process of the invention, the control of the degree of oxidation is, in the case of tin, essentially controlled by the temperature of the stationary phase and not by its duration, as in the case of zinc.

[0185] The operation in which the particles are brought into contact with the oxidizing gas can be carried out at a temperature of greater than or equal to 400° C., for example from 400 to 950° C., for a period of time of 1 second to 6 hours, preferably of 2 seconds to 4 hours.

[0186] The oxidizing gas can be chosen from gases comprising oxygen optionally enriched in water vapour and/or in carbon dioxide, such as air, air enriched in oxygen, oxygen, or air enriched in carbon dioxide and/or in water vapour; or mixtures of CO and of CO_2.

[0187] Analogously to the first embodiment, the process according to the invention in the second embodiment can be defined as a process of "PADO" type applied to tin which is employed in order to prepare ceramics based on doped tin oxide, the doping metals being added in the form of oxides to the powder subjected to the sintering and not in the form of metals or of salts to the crucible at the beginning of the process.

[0188] All the arguments mentioned in the context of the first embodiment in connection with the unexpected application of the "PADO" process to tin can be applied in full to the second embodiment of the process of the invention.

[0189] The two embodiments of the process according to the invention are related by the same inventive concept, which is the surprising application of the PADO process to tin in order to prepare ceramics for varistors.

[0190] In addition, this second embodiment of the process of the invention comprises a specific sequence of steps, themselves specific, which is neither described nor suggested in the prior art.

[0191] First, in the process according to this second embodiment, use is made specifically of pure bulk tin and not of a tin alloy, as in the prior art.

[0192] A partial or complete oxidation of the tin powder is then carried out.

[0193] The following step of the process, which consists in adding one or more doping oxides to the partially or completely oxidized tin powder, is also specific to the process according to the invention in this embodiment.

[0194] It should be noted that the comments expressed above for the first embodiment which relate to the use of an only partial oxidation of the alloy powder apply in full to the second embodiment in the case where a partial oxidation of the tin powder is carried out (and not of alloy as in the first embodiment). In particular, the powder subjected to sintering then comprises tin metal, tin oxide and the oxides of doping metals added.

[0195] In particular, similar improvements in the densification and in the electrical properties are obtained.

[0196] The invention will be better understood on reading the detailed description which will follow given by way of illustration and without implied limitation and made with reference to the appended drawing, in which:

[0197] FIG. 1 is a diagrammatic view in vertical section of an atomization device for preparing a powder formed of alloy of metals with a predetermined particle size, each of the particles of which is homogeneous.

[0198] The first embodiment of the process according to the invention will now be described in detail.

[0199] This process can be defined as being a "PADO" process adapted to a specific alloy based on Sn.

[0200] In the first step of the process according to the invention, in its first embodiment, tin, as base metal, that is to say as metal, the oxide of which is the base oxide of the ceramic to be prepared, and one or more other doping metals mentioned above and/or more salts of these doping metals, preferably in the proportions defined above, are placed in a crucible or any other receptacle suitable for the melting of metals.

[0201] The term "base metal oxide" (this base metal oxide being, in the present case, tin oxide SnO_2) as used in the present description is used generally to indicate that this oxide is predominant by weight in the final sintered ceramic, that is to say that this oxide generally represents 50% by weight or more, preferably more than 50% by weight, of the final ceramic; the more preferred proportions of the base metal oxide (greater than or equal to 90, 95, 99 or 99.995% by weight) have been given above.

[0202] The term "doping agent" is a term commonly used by a person skilled in the art in this field of the art.

[0203] The term "salt" is such as commonly used in inorganic chemistry and includes chlorides, nitrates, and the like, but also in particular oxides.

[0204] The final ceramic can optionally comprise, in addition to the base metal oxide and the doping metal oxide, in particular, impurities and/or other additives. The term "impurities" is understood to mean substances which occur by chance, without being desired, in the ceramic and the term "additives" is understood to mean substances deliberately added to the ceramic in order to obtain one or more specific properties. Preferably, the semiconducting ceramic is composed of a base metal oxide and at least one doping metal oxide.

[0205] Subsequently, in a second step, the tin and the said doping metals and/or salts of doping metals are melted under a neutral or reducing atmosphere, for example hydrogen, while mixing the molten metals in order to obtain a homogeneous liquid mixture or alloy of metals (tin and doping metals).

[0206] During this melting step, the salt or salts optionally present may decompose, for example if they are nitrates. The possible contamination caused by this decomposition is very slight, as the actual result of the very low content of doping agents.

[0207] This first step and this second step are conventional steps which can easily be carried out by the man skilled in the art, for example using the device (oven) described in the document FR-A-2 674 157 (FIG. 1) and in the document EP-A1-0 580 912, to the description of which reference may be made.

[0208] In the third step of the process in its first embodiment, a powder formed of alloy of metals with a predetermined particle size, each of the particles of which is homogeneous, is prepared from the said homogeneous liquid mixture or alloy of metals.

[0209] The said predetermined particle size can be obtained directly or else on conclusion of an optional sieving operation.

[0210] This powder formed of alloy of metals can be prepared directly by spraying or atomizing, without preliminary cooling, the liquid alloy prepared in the second step by a stream of gas or of liquid.

[0211] Use may be made, in carrying out the direct atomization of the liquid alloy, of the device described in FIG. 3 of the document EP-A1-0 580 912.

[0212] Alternatively, it is possible, first of all, to cool the homogeneous liquid mixture or alloy of metals, so as to solidify it, and then to divide this solidified homogeneous alloy of metals to give a powder formed of alloy of metals with a predetermined particle size.

[0213] The cooling operation can be carried out by casting the liquid alloy of metals in an ingot mould under a neutral or reducing atmosphere and by then cooling the ingot obtained, likewise under a neutral or reducing atmosphere.

[0214] Alternatively, the alloy, if it has been produced in a silica container sealed under vacuum comprising the various metals, this container having been subsequently heated in an oven and regularly agitated in order to obtain a homogeneous liquid mixture, can finally be cooled by a quenching intended to solidify the alloy obtained.

[0215] The solidified homogeneous alloy of metals, such as an ingot, can be divided by again melting this solid alloy (which is, for example, in the form of an ingot) in order to give a homogeneous liquid alloy of metals which is sprayed by a stream of gas or of liquid.

[0216] The liquid used for the atomization can be water.

[0217] The gas used for the atomization or spraying can be a reducing or neutral gas chosen, for example, from hydrogen, nitrogen, argon and their mixtures.

[0218] The gas used for the atomization or spraying can be an oxidizing gas, such as air, optionally enriched in oxygen and/or in water vapour, or oxygen, so that the fine particles of molten alloy are sprayed to give fine particles which are at the same time partially oxidized and cooled.

[0219] Preferably, in this embodiment of the invention, use is made of a reducing or neutral gas; for this reason, fine particles or droplets of alloys are then cooled and stored in a nonoxidized or very superficially oxidized metal state. In all cases and whatever the gas used for the spraying, in this embodiment of the process of the invention, the alloy particles are necessarily subsequently subjected to complete or partial oxidation prior to shaping and sintering.

[0220] In the case where the gas used is an oxidizing gas, the spraying is generally carried out at a temperature of 400 to 1000° C., whereas, in the case where the gas used is a neutral or reducing gas, the spraying is generally carried out at a temperature of 230 to 1000° C.

[0221] The dividing, atomizing or spraying of the alloy can be carried out with a device such as that described in the

documents FR-A-2 674 157 (FIG. 2) and EP-A-0 580 912 (FIG. 2), to the description of which reference may be made.

[0222] The dividing, atomizing or spraying in the liquid phase can also be carried out by atomizing the mixture, alloy or liquid with a stream of gas, for example with nitrogen gas, using the device described in FIG. **1**.

[0223] This device comprises three parts: a part intended for the melting of the alloy (or of the metal, in the case of the second embodiment of the invention: see below); a chamber which is the atomizer proper, which is provided at its base with a spray nozzle; and a tube or rod for blocking the spray nozzle and for measuring the temperature at this nozzle.

[0224] The entire device is heated via electrical resistors and flushed with neutral gas, such as argon (other than the atomizing gas), in order to protect the liquid from any premature oxidation which might promote segregation of the oxides.

[0225] More specifically, the alloy or the metal (**1**) is melted in a receptacle (**2**) heated via a heating resistor (**3**) and equipped with a thermocouple (**4**). This receptacle is fitted into a branch connection (**5**) equipped with a ground adapter (**6**) situated in the side wall (**8**) of the atomizer (**7**); the latter has the form of a substantially elongated vertical cylindrical chamber.

[0226] The adapter (**6**) makes it possible to rotate the receptacle (**2**) containing the alloy (or the metal) between two positions: a first "bottom" position (in solid lines), in which the alloy (or the metal) is heated and melted, and a second "top" position (in dotted lines), in which the molten liquid alloy (or metal) can be transferred into the chamber of the atomizer. The molten alloy is kept molten in the lower part of the chamber of the atomizer (**7**) by heating electrical resistors (**9**). A pipe (**10**) which emerges in the side wall of the chamber of the atomizer conveys a stream of inert gas (**11**), such as argon, into the chamber and prevents any oxidation of the molten alloy or metal.

[0227] A flow orifice (**12**) for the liquid alloy (or metal) occurs at the base of the chamber of the atomizer, which orifice is blocked by a rod or tube (**13**) equipped at its centre with a thermocouple (**14**). When it is desired to atomize or spray the molten alloy, the tube or rod (**13**) is raised and a thin stream of liquid alloy (or metal) flows via the orifice into a nozzle (**15**). The latter is surrounded by an annular cavity (**16**) which receives a side feed of stream of atomizing gas, such as nitrogen, via a pipe (**17**) also equipped with heating electrical resistors (**18**).

[0228] For this reason, the thin stream or flow of liquid alloy (or metal) which issues under the effect of gravity from the end of the nozzle is sprayed or atomized by virtue of the partial vacuum produced by the gas, such as nitrogen, stream ring which surrounds the molten alloy flowing through the nozzle (**15**).

[0229] The droplets of liquid alloy or metal are subsequently cooled, preferably rapidly cooled, that is to say quenched, in order to recover an alloy (or metal) powder. The solidified homogeneous alloy of metals (or metal), such as an ingot, can also be divided in the solid phase, for example by abrasion, milling or machining. This spraying or atomizing in the solid phase is generally carried out at the boiling point of nitrogen at 1 bar, namely −196° C.

[0230] On conclusion of the atomizing or spraying, the powder may already exhibit the desired particle size; if not, it is subjected, for example, to a sieving operation.

[0231] In addition, the alloy powder (or metal powder, in the second embodiment) can subsequently be separated into several particle size fractions by sieving or any other separation process.

[0232] All the powder or only a predetermined particle size fraction, for example the particle size fraction comprising the particles with a diameter of less than 40 μm, is subjected to the following stage of the process, which consists of a complete or partial oxidation of the alloy powder obtained above.

[0233] The term "complete oxidation" is understood to mean that the final powder obtained comprises 100% by weight of oxides.

[0234] The term "partial oxidation" is understood to mean that the final powder comprises a proportion of oxide(s) of less than 100% by weight; preferably, the proportion of oxide(s) is 50 to 99.9% by weight; preferably it is from 55 to 80% or 85% by weight; more preferably it is from 60 to 70% by weight.

[0235] This complete or partial oxidation is generally carried out while avoiding coalescence of the particles: this can be obtained by varying the physical parameters related to the technique used, such as the temperature, the pressure, the rate, and the like, or by virtue of the technology employed: for example, use may be made of a fluidized, pulverulent bed.

[0236] This complete or partial oxidation is generally carried out by bringing the alloy powder (or metal powder) into contact with an oxidizing gas from a temperature and/or for a period of time which is (are) sufficient for the oxidation to be complete or for the desired percentage of oxide(s) in the powder to be obtained.

[0237] For example, in the case of tin, a residence of one minute is sufficient to oxidize a monolayer of metal particles with a mean diameter of 20 to 40 microns at 900° C.

[0238] The oxidizing gas can be any oxidizing gas suitable for this purpose but it is generally chosen from gases comprising oxygen optionally enriched in water vapour and/or in carbon dioxide, such as air, air enriched in oxygen, oxygen, or air enriched in carbon dioxide and/or in water vapour; or mixtures of CO and of CO_2.

[0239] The operation in which the alloy (or metal) particles are brought into contact with the oxidizing gas can be carried out at a temperature ranging from 60 to 1000° C. but is generally carried out at a high temperature, namely a temperature of greater than or equal to 400° C., for example from 400 to 950° C.

[0240] This contacting operation is carried out for a period of time sufficient for the oxidation to be complete or for the desired percentage of oxide(s) in the powder to be obtained. This period of time can be easily determined by a person skilled in the art, for using oxidation curves found during

preliminary experiments, which give the exact amount of alloy oxidized as a function of the temperature and of the period of time.

[0241] The powder formed of oxide(s) which is obtained has a particle size which is generally submicronic in mean size (for example, mean diameter) of the particles.

[0242] The powder formed of oxide(s) which is obtained is subsequently shaped in a known way, for example compacted in the form of pellets of ceramics, by cold pressing, for example by uniaxial cold pressing, using an organic or inorganic binder, such as water.

[0243] The powder shaped or compacted, for example in the form of pellets, is subsequently sintered in a known way at high temperature, generally at a temperature of 1100 to 1350° C., for a period of time of greater than or equal to 30 minutes, preferably from 30 minutes to 2 hours, for example at 1350° C. for one hour, in order to densify it.

[0244] The densified ceramics obtained on conclusion of the process according to this first embodiment can be used in varistors, they being metallized beforehand.

[0245] The second embodiment of the process according to the invention will now be described in detail.

[0246] This process may be defined in particular as being a "PADO" process applied to a pure tin and not to an alloy of tin and of doping agents.

[0247] For this reason, in a first step, pure bulk tin is provided, for example in the form of lumps or shot or ingots.

[0248] In a second step, a tin powder with a predetermined particle size is prepared from the pure bulk tin.

[0249] The tin powder with a predetermined particle size can be prepared in the liquid phase by melting the bulk tin to give a liquid metal which is sprayed or atomized with a stream of neutral or reducing gas, for example chosen from hydrogen, nitrogen, argon and their mixtures, or else with a stream of oxidizing gas.

[0250] The conditions of this atomizing or spraying in the liquid phase have been described in detail above in connection with the first embodiment; in particular, the device described in FIG. **1** can be used to carry out this step.

[0251] The tin powder with a predetermined particle size can be prepared in the solid phase by abrasion or milling under conditions already described for the first embodiment.

[0252] Likewise, it is possible, as in the first embodiment, to separate the tin powder into several particle size fractions.

[0253] All or only a predetermined particle size fraction, for example the particle size fraction comprising the particles with a diameter of less than 40 μm, is subjected to the following step of the process, which consists of a partial or complete oxidation of the metal powder obtained above.

[0254] The definitions of and the conditions for the partial and complete oxidations have already been given above in the context of the present embodiment.

[0255] The term "partial oxidation", in contrast to the prior art, where a complete oxidation is carried out, is understood to mean that only a portion of the said metal powder is oxidized and that a powder comprising, for example, both tin dioxide and tin metal is obtained.

[0256] Preferably, the tin powder is partially oxidized to a percentage of 50 to 99.9% by weight, preferably of 55 to 80% or 85% by weight, more preferably of 60 to 70% by weight, that is to say that the oxidized powder comprises 50 to 99.90% by weight, preferably from 55 to 80% or 85% by weight, more preferably from 60 to 70% by weight of oxide and the remainder of free metal, that is to say of free Sn.

[0257] More preferably, the tin powder is oxidized to a percentage of 64% by weight, that is to say that it comprises, for example, by weight, 64% of SnO_2 and 36% of tin.

[0258] The partial or complete oxidation of the metal powder, for example of the tin powder, with a predetermined particle size is carried out by bringing the said powder into contact with an oxidizing gas at a temperature and for a period of time sufficient to obtain a desired percentage (for example, within the ranges defined above) of tin oxide, which percentage can reach 100% of tin oxide in the partially or totally oxidized powder.

[0259] The gas used and the temperature conditions are analogous to those described above for the first embodiment of the process according to the invention.

[0260] The contacting operation is carried out for a period of time sufficient to produce the desired percentage of oxide in the powder; this period of time can be easily determined by a person skilled in the art, for example using oxidation curves, as has been described above.

[0261] In the following step, one or more powdered doping metal oxide(s) is (are) added to the partially or completely, totally, oxidized tin powder.

[0262] The oxide or oxides of doping metals added to the partially or totally oxidized tin powder can be chosen from all suitable oxides of doping metals.

[0263] They are generally chosen from cobalt, chromium, manganese, niobium and tantalum oxides, transition metal oxides, such as zinc oxide and lanthanide metal oxides, such as lanthanum oxide. The oxides can be commercially available oxides or oxides prepared by any known process, indeed even by the "PADO" process.

[0264] The oxide or oxides of doping metal are added to the completely or partially oxidized tin powder in a percentage by weight such that it makes it possible to obtain a ceramic comprising, as complement to 100% by weight of tin oxide, the desired percentage of the doping metal oxides.

[0265] For example, the doping oxide or oxides can be added in a percentage by weight such that they make it possible to obtain a ceramic comprising, as complement to 100% by weight of metal oxide, for example of tin oxide:

[0266] 0.1 to 3% of cobalt oxide, and/or

[0267] 0.01 to 3% of chromium oxide, and/or

[0268] 0.01 to 3% of manganese oxide, and/or

[0269] 0.01 to 0.5% of niobium oxide, and/or

[0270] 0.01% to 0.5% of tantalum oxide, and/or

[0271] 0.01 to 0.5% of one or more transition metal oxides,

[0272] 0.01 to 0.5% of one or more lanthanide metal oxides, such as lanthanum oxide.

[0273] The powders are mixed using known processes. The shaping and sintering stages are carried out under the same conditions as for the first embodiment, optionally with slight adjustments.

[0274] The invention will now be described with reference to the following examples, given by way of illustration and without implied limitation.

Example 1

[0275] This example illustrates the first embodiment of the process according to the invention, in which the "PADO" process is adapted in order to prepare tin oxide doped with oxides of certain metals in specific proportions.

[0276] In this example, a ceramic is prepared which has the following composition by weight (as % by weight):

[0277] SnO_2: 98.24%;

[0278] Co_3O_4: 0.05%;

[0279] MnO_2: 1.69%;

[0280] Nb_2O_5: 0.01%;

[0281] Ta_2O_5: 0.01%.

[0282] The "PADO" process is carried out on the five starting metals: tin and then cobalt, manganese, niobium and tantalum as doping agents.

[0283] A liquid alloy is first prepared from these five metals. It is subsequently quenched in order to set the composition of the alloy obtained.

[0284] The alloy is subsequently placed in an atomizer, where it is sprayed by a stream of nitrogen gas to give an alloy powder.

[0285] The alloy is prepared and is atomized on an experimental laboratory prototype.

[0286] Thus, the alloy is prepared in a silica container sealed under vacuum, which receives the various solid metals in the desired proportions. This container is subsequently heated in an oven at 1100° C. and regularly agitated in order to produce a homogeneous liquid mixture.

[0287] The molten alloy is then atomized, which carries out the quenching intended to solidify the alloy obtained so as to retain the homogeneity thereof acquired at high temperatures.

[0288] The alloy is atomized or divided to give a powder in an atomizer or atomizing device, such as that described in FIG. **1**.

[0289] The particle size fraction of the particles with a diameter of less than 40 μm is separated from the whole of the powder for the continuation of the process.

[0290] The powder corresponding to this fraction is subsequently completely oxidized to give an oxide powder; the complete oxidation is carried out by placing the alloy powder in an oven under an atmosphere of air and by maintaining it at a temperature of 900° C. for a period of time of 5 minutes.

[0291] Finally, this resulting powder is shaped under a pressure of 3 tonnes in a die equipped with two moving cylinders and then sintered at 1350° C. for 2 hours with a rise and a fall in temperature of 3° C./minute in order to result in a bulk ceramic.

[0292] The electrical characteristics of the ceramics obtained after metallization are as follows: the nonlinearity coefficient α is 47 (measured around 10^{-3} A/cm^2) and the threshold field E_s is 450 V/mm (measured for 10^{-3} A/cm^2).

Example 2

[0293] This example illustrates the second embodiment of the process according to the invention, in which the "PADO" process is modified by carrying out a partial (and no longer complete) oxidation of a tin powder (and no longer of an alloy powder) and in which the doping oxides are added to the oxidized powder, in this case partially oxidized powder, before the sintering.

[0294] In this example, a ceramic is prepared which has a composition by weight similar to that of Example 1:

[0295] SnO_2: 98.3%;

[0296] Co_3O_4: 0.05%;

[0297] MnO_2: 1.69%;

[0298] Nb_2O_5: 0.01%;

[0299] Ta_2O_5: 0.03%.

[0300] The "PADO" process is carried out on a starting product which is pure bulk tin. The latter is first atomized under nitrogen in order to produce a tin metal powder. The main parameters relating to the atomizing gas are a pressure of 3 bar, a flow rate of 45 l/minute and a temperature of 700° C. The atomizing device described in FIG. **1** is employed.

[0301] The powder is sieved, so as to retain only the particle size fraction of less than 40 μm. This powder is subsequently partially oxidized to 64% by weight, that is to say that it comprises, by weight, 64% of tin dioxide SnO_2 and 36% of tin.

[0302] This partial oxidation is carried out by placing the tin powder in an oven under an atmosphere of air, by raising the temperature at the rate of 3° C./minute up to 750° C. and by observing a stationary phase at this temperature for a duration limited to 5 minutes, before quenching with air.

[0303] The doping oxides (Co_3O_4, Nb_2O_5 and Ta_2O_5) in the powder form are then added in the desired amounts to the metal-ceramic powder.

[0304] This combined product is subsequently mixed and then shaped and sintered under the same conditions as Example 1 to give a ceramic.

[0305] The presence of tin metal in the raw ceramic, that is to say before sintering, made it possible to increase the densification of the ceramic after sintering from 75.2 to 85.4%.

[0306] The electrical characteristics of the ceramics obtained after metallization are as follows: the nonlinearity coefficient α is 53 (measured around 10^{-3} A/cm^2) and the threshold field E_s is 308 V/mm (measured for 10^{-3} A/cm^2).

1. A process for preparing a substantially homogenous semiconducting ceramic composition comprising base metal oxide and at least one doping metal oxide, the process comprising:

a) melting and mixing under a neutral or reducing atmosphere said base metal oxide and doping metals and/or salts of doping metals, in order to obtain a homogeneous liquid mixture;

b) preparing a powder from said homogenous liquid mixture with a predetermined particle size, directly or after an optional operation of particle size classification, each of the particles of said powder being homogeneous; and

c) completely or partially oxidizing said powder to obtain a homogeneous powder which is completely or partially oxidized, thereby preparing said substantially homogenous semiconducting ceramic composition comprising a base metal oxide and at least one doping metal oxide.

2. The process according to claim 1, wherein the oxide or oxides of doping metals are selected from the group consisting of oxides of cobalt, chromium, manganese, niobium, tantalum, and transition metals.

3. A process according to claim 1, wherein the oxide or oxides of doping metals are selected from the group consisting of cobalt, manganese, niobium and tantalum oxides.

4. A process according to claim 1, wherein the doping metal oxides are selected from the group consisting of cobalt oxide, manganese oxide, niobium oxide and tantalum oxide.

5. A process according to claim 1, wherein the proportion by weight of the doping metal or metals and/or salt or salts of doping metals in step a) is selected from the group consisting of 90% by weight, 95% by weight, 99% by weight, and 99.995% by weight.

6. A process according to claim 1, wherein the doping metal or metals and/or salt or salts of doping metals in step a) comprises one or more among the following oxides in the following proportions by weight:

0.1 to 3% of cobalt oxide,

0.01 to 3% of chromium oxide,

0.01 to 3% of manganese oxide,

0.01 to 0.5% of niobium oxide,

0.01% to 0.5% of tantalum oxide, or

0.01 to 0.5% of one or more transition metal oxides,

0.01 to 0.5% of one or more lanthanide metal oxides, such as lanthanum oxide.

7. A process according to claim 1, wherein the said doping metal or metals and/or salt or salts of doping metals in step a) comprises the following oxides in the following proportions by weight:

SnO_2: 98.24%;

Co_3O_4: 0.05%;

MnO_2: 1.69%;

Nb_2O_5: 0.01%; or

Ta_2O_5: 0.01%.

8. A process according to claim 1, wherein the powder of step b) is prepared by cooling, optionally rapidly, the liquid mixture of step a).

9. A process according to claim 8, wherein step a) further comprises casting the liquid mixture in an ingot mould under a neutral or reducing atmosphere prior to the cooling of step b).

10. A process according to claim 1, wherein step b) comprises spraying or atomizing by a stream of gas or of liquid, and quenching quenched.

11. A process according to claim 9, wherein step b) comprises spraying or atomizing with a stream of gas or of liquid, and quenching.

12. A process according to claim 10 or 11, wherein in the homogeneous liquid is sprayed or atomized with a stream of neutral or reducing gas, such as hydrogen, nitrogen, argon or their mixtures.

13. A process according to claim 10 or 11, wherein the homogeneous liquid is sprayed or atomized with a stream of oxidizing gas, such as air, air enriched in oxygen, or oxygen optionally enriched in water vapour.

14. A process according to either one of claims **8** and **9**, wherein the powder of step b) is prepared by abrasion or milling.

15. A process according to claim 1, wherein the powder of step b) is separated into several particle size fractions.

16. A process according to claim 1, wherein the powder in step c) is partially oxidized to a percentage selected from the group consisting of 50 to 99.9% by weight, 55 to 80 or 85% by weight, and 60 to 70% by weight.

17. A process according to claim 1, wherein the powder in step c) is oxidized to a percentage of 64% by weight.

18. A process according to claim 1, wherein the partial or complete oxidation of step c is carried out by bringing the said particles into contact with an oxidizing gas from a temperature and/or for a period of time which is (are) sufficient to produce a desired percentage of oxides of metals in the powder, for example for the oxidation to be complete.

19. A process according to claim 18, wherein the oxidizing gas comprising oxygen is optionally enriched in water vapour and/or in carbon dioxide.

20. A process according to claims **18** or **19**, wherein the oxidation of step c) is carried out at a temperature of greater than or equal to 400° C., for a period of time of 1 second to 6 hours.

21. A process according to claim 1 further comprising shaping the product of step c) by compacting it in the form of pellets.

22. A process according to claim 21, wherein the shaping of step d) is carried out at a temperature of 1100 to 1350° C. for a period of time of greater than or equal to 30 minutes.

23. A process for the preparation of a semiconducting ceramic comprising a base metal oxide and at least one doping metal oxide the following successive steps:

tin is placed in a crucible;

the tin is melted, so as to obtain liquid tin;

a tin powder with a predetermined particle size is prepared from the liquid tin, directly or after an optional operation of particle size classification;

all the tin powder with a predetermined particle size or a predetermined particle size fraction of the powder is completely or partially oxidized;

one or more doping metal oxide(s) is (are) added to the partially or completely oxidized tin powder;

the partially or completely oxidized tin powder is mixed with the doping metal oxide(s);

the mixture of partially or completely oxidized tin powder and of the doping metal oxide(s) is shaped;

the shaped powder is sintered.

24. A process according to claim 23, wherein the doping metal oxide or oxides added to the completely or partially oxidized tin powder are from the group consisting of cobalt, chromium, manganese, niobium and tantalum oxides and oxides of transition metals.

25. A process according to claim 23, wherein the oxide or oxides of doping metals are selected from the group consisting of cobalt, manganese, niobium and tantalum oxides.

26. A process according to claim 25, wherein the oxide or oxides of doping metals are selected from the group consisting of doping metal oxides, cobalt oxide, manganese oxide, niobium oxide and tantalum oxide.

27. A process according to claim 23, wherein the tin oxide is added in a proportion of greater than or equal to a percentage selected from the group consisting of 90% by weight, 95% by weight, 99% by weight, and 99.995% by weight.

28. A process according to claim 27, wherein the doping metal oxide(s) are added to the partially or completely oxidized tin powder in a percentage selected from the group consisting of:

0.1 to 3% of cobalt oxide,

0.01 to 3% of chromium oxide,

0.01 to 3% of manganese oxide,

0.01 to 0.5% of niobium oxide,

0.01% to 0.5% of tantalum oxide,

0.01 to 0.5% of one or more transition metal oxides, and

0.01 to 0.5% of one or more lanthanide metal oxides.

29. A process according to claim 28, wherein the doping metal oxides are added to the partially or completely oxidized tin powder in a percentage by weight such that it makes it possible to obtain a ceramic comprising, as complement to 100% by weight of tin oxide, the following oxides in the following proportions by weight:

SnO_2: 98.24%;

Co_3O_4: 0.05%;

MnO_2: 1.69%;

Nb_2O_5: 0.01%; or

Ta_2O_5: 0.01%.

30. A process according to claim 23, wherein the tin powder with a predetermined particle size is prepared in the liquid phase by melting bulk tin to give a liquid metal which is sprayed or atomized by a stream of gas or of liquid and cooled, quenched.

31. A process according to claim 23, wherein the liquid metal is sprayed or atomized by a stream of neutral or reducing gas.

32. A process according to claim 23, wherein the tin powder with a predetermined particle size is prepared in the solid phase by abrasion or milling.

33. A process according to claim 23, wherein the tin powder is partially oxidized to a percentage selected from the group consisting of 50 to 99.9% by weight, 55 to 80 or 85% by weight, and 60 to 70% by weight.

34. A process according to claim 23, wherein the tin powder is oxidized to a percentage of 64% by weight.

35. A process according to claim 23, wherein the tin powder is separated into several particle size fractions.

36. A process according to claim 23, wherein the tin powder with a predetermined particle size is partially or completely oxidized by bringing the said powder into contact with an oxidizing gas from a temperature and/or for a period of time which is (are) sufficient to produce a desired percentage of tin oxide in the powder.

37. A process according to claim 36, wherein the operation in which the particles are brought into contact with the oxidizing gas is carried out at a temperature of greater than or equal to 400° C., for a period of time of 1 second to 6 hours.

38. A process according to claim 36 or 37, wherein the oxidizing gas is chosen from gases comprising oxygen optionally enriched in water vapour and/or in carbon dioxide.

39. A process according to claim 23, wherein in which the mixture of the partially or totally oxidized tin powder and of the doping metal oxide(s) is shaped by compacting it in the form of pellets.

40. A process according to claim 23, wherein the sintering is carried out at a temperature of 1100° C. to 1350° C. for a period of time of greater than or equal to 30 minutes.

41. The composition produced according to the process of claim 1.

42. The composition produced according to the process of claim 23.

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