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SINTERED ELECTRICAL RESISTOR

Gerard Heinrich Jonker, Gerard Willem van Oosterhout, and Jan Heinrik van Santen, Eindhoven, Netherlands, assignors, by mesne assignments, to North American Philips Company, Inc., New York, N. Y., a corporation of Delaware

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Sintered, electrical resistors on the basis of manganites with perovskite structure containing trivalent and tetravalent manganese are known. These resistors exhibit a comparatively low temperature coefficient of for example 0.6% per degree centigrade and a low specific resistance of 0.1Ω cm.

There are furthermore described the semi-conductive properties of cobaltites with perovskite structure, containing trivalent and tetravalent cobalt. Also with these materials the specific resistance and the temperature coefficient are low.

It has been found that on the basis of ferrites and chromites with perovskite structure semi-conductive resistors may be obtained, having a high temperature coefficient at a comparatively low specific resistance.

The invention relates to a sintered, electrical resistor substantially consisting of a phase of oxidic compounds with perovskite structure, containing Fe and/or Cr or else Co and Fe and/or Cr, in which at least one of the metals Fe, Cr and Co occurs in the trivalent and the tetravalent form. In the conductive phase manganese in the tetravalent form may be included. In order to obtain a high temperature coefficient, it is desirable to restrict the Co content in the conductive phase to not more than 90 atom percent, calculated on the total content of Fe, Cr, Co and Mn.

Part of the said metal ions may furthermore be replaced by other small trivalent or tetravalent metal ions, for example of Al, Ti and Ni. In order to prevent the specific resistance from becoming too high, it is desirable to restrict its content to not more than 20 atom percent.

The general formula for the chemical composition of perovskites is ABO_3, wherein A designates a large metal ion, having an ion radius according to Goldschmidt of more than 1.0 A. and B a small metal ion having an ion radius between 0.5 and 1.0 A., the sum of the valencies of A and B being 6. Both A and B may designate a mixture of metal ions which fulfil the aforesaid conditions.

It is known that the obtainment of conductivity in heteropolar crystals requires that they should contain one metal ion occurring in different valencies. This is permitted by the metal ions Fe, Cr and Co, which may occur in the perovskites in the trivalent and the tetravalent form, if a mixture of trivalent and bivalent metal ions is chosen for the large metal ions designated by A in the general formula. To this end use may be made of the trivalent metals yttrium and the so-called large lanthanides, for example La, Pr and Nd and the bivalent metals for example Ca, Sr, Ba and also Pb and Cd.

The latter two are less suitable because of the volatility of their oxides.

A mixed crystal of $LaFe^{3+}O_3$ with $SrFe^{4+}O_3$ may, for example, be formed by sintering in air La_2O_3, SrO (if desired in the form of carbonate) and Fe_2O_3 at temperatures lying between 1250° C. and 1400° C. In this case the desired concentrations of Fe^{3+} and Fe^{4+} are obtained by a choice of the ratio between La and Sr.

In general with the sintering in air the ratio between the concentrations of the trivalent and the tetravalent small metal ions, may be adjusted fairly accurately in accordance with the formula ABO_3 by means of the concentrations of the trivalent and the bivalent large metal ions, if the latter ratio exceeds about 1.5.

At a higher content of large bivalent metal ions not all oxygen positions in the perovskite lattice are occupied so that the content of tetravalent small ions is smaller. The oxygen content may be acted upon to some extent by means of the partial oxygen pressure of the gaseous atmosphere in which the sintering takes place.

If the A-position in the perovskite is completely occupied by large bivalent ions, the deviation from the formula ABO_3 may be considerable. For strontium ferrite, sintered in air at 1320° C. the composition $SrFeO_{2.63}$ has been found. Since the effect of the partial oxygen pressure is comparatively slight, stable resisters are also obtained with the perovskites having an oxygen deficiency.

It has been found that perovskite compositions containing Fe or Cr exhibit a high temperature coefficient at a comparatively low specific resistance. A greater variety in resistance properties may be obtained by combining the Fe- and Cr-containing perovskites with one another or with the other aforesaid metals.

In order to obtain a favourable temperature coefficient it is necessary that the sintered products according to the invention should be constituted mainly by the aforesaid conductive phases. Moreover, other conductive or nonconductive phases may be contained in the sintered products to a content of about 15% by volume. If desired, fluxes, for example copper oxide, zinc oxide, clay and glass may be added to a quantity of about 10% by weight.

The products according to the invention may be obtained from the composing oxides, if desired in the form of double oxides or compounds, for example carbonates, changing into oxides during sintering. The said constituents are ground, mixed, worked up to obtain a paste, for example with an organic binder, and then, subsequent to shaping, sintered in an oxygen containing atmosphere. The constituents may, as an alternative, be caused to react, subsequent to mixing, at a higher temperature: they may then be ground again and sintered subsequent to shaping.

The invention will be illustrated with reference to the examples indicated in the following table. This table indicates a few compositions of the sintered products with the corresponding specific resistances ρ in Ω cm. at room temperature, the activation energy q being indicated in e. v., which is a measure for the temperature coefficient in accordance with the formula

$$\rho=\rho_{\sim}e^{\frac{q}{kT}}$$

and the temperature coefficient itself in percent per degree centigrade at room temperature.

No.	(La	Pr Nd	Ca	Sr	Ba	Pb)	(Fe	Cr	Co	Mn)	O_3	ρ in Ω cm.	q in e. v.	Temp. coeff. in percent per ° C.
1				1.00			1.00				$=SrFeO_{2.83}$	320	0.23	−3.1
2	0.80		0.20				1.00					108	0.27	−3.6
3	0.30		0.70				1.00					5.3	0.21	−2.9
4	0.20			0.80			1.00					0.265	0.04	−0.5
5	0.16				0.40		1.00					5.3	0.23	−3.1
6	0.25				0.75		1.00					27.5	0.08	−1.1
7	0.70		0.10	0.10	0.10		1.00				+2% by weight NiO	36	0.28	−3.8
8	0.80		0.20				1.00					102	0.32	−4.3
9	0.85				0.15			1.00				68	0.17	−2.3
10	0.90			0.10				1.00				135	0.21	−2.9
11	0.60			0.40			0.50	0.50				5750	0.24	−3.2
12	0.40		0.60				0.30	0.70				63	0.26	−3.6
13	0.90					0.10	0.20	0.80				290	0.19	−2.5
14	0.70				0.30		0.70		0.30			1.32	0.13	−1.8
15	0.40				0.60		0.50		0.50			2.67	0.18	−2.4
16	0.70		0.30				0.70		0.30			1.70	0.10	−1.4
17	0.40		0.60				0.50		0.50			1.15	0.14	−1.9
18	0.80					0.20	0.70		0.30			558	0.13	−1.75
19	0.70		0.30					0.70	0.30			1.95	0.30	−1.75
20	0.25				0.75		0.40			0.60		144	0.24	−3.3
21	0.60			0.40			0.70			0.30		16	0.19	−2.6
22	0.10			0.90			0.30			0.70		16	0.19	−2.6
23	0.40			0.60				0.60		0.40		0.58	0.09	−1.3
24	0.70				0.30		0.50	0.20	0.30			2.1	0.15	−2.0
25	0.60	0.10	0.10	0.10	0.10		0.50	0.30		0.20		378	0.15	−2.0
26	0.20	0.10	0.30	0.20	0.20		0.50	0.25		0.25		198	0.27	−3.6
27	0.80			0.20			0.50		0.30	0.20		502	0.29	−3.9
28	0.80			0.20			0.50		0.40	0.10	+2% by weight CuO	184	0.31	−4.2
29	0.80			0.20			0.50		0.40	0.10		230	0.31	−4.2
30	0.30				0.70		0.70		0.15	0.15		20.8	0.22	−2.9
31	0.30				0.70		0.50		0.25	0.25		55.5	0.21	−2.8
32	0.50		0.50				0.25		0.25	0.50		11.2	0.18	−2.4
33	0.50		0.50				0.25		0.25	0.50	+2% by weight ZnO	8.2	0.19	−2.6
34	0.50		0.50				0.25		0.25	0.50	+2% by weight TiO_2	6.7	0.18	−2.4
35	0.50		0.50				0.35		0.35	0.30		1.16	0.16	−2.1
36	0.50		0.50					0.25	0.25	0.50		16.3	0.21	−2.8
37	0.80			0.20			0.30	0.20	0.30	0.20		340	0.26	−3.4

What is claimed is:

1. A sintered electrical resistor having a conductive phase consisting of crystals having a perovskite structure and a composition corresponding approximately to the formula $AB_nD_{1-n}O_3$ wherein A represents a mixture of at least one trivalent metal ion selected from the group consisting of La^{+++}, Nd^{+++} and Pr^{+++} and at least one bivalent metal ion selected from the group consisting of Ca^{++}, Sr^{++}, Ba^{++} and Pb^{++}; B represents at least one trivalent metal ion selected from the group consisting of Fe^{+++}, Cr^{+++}, and Co^{+++}, D represents at least one tetravalent metal ion selected from the group consisting of Fe^{++++}, Cr^{++++}, Co^{++++} and Mn^{++++}; Mn^{++++}, Co^{+++} and Co^{++++} being present only when at least one of the other metal ions other than the metal ions represented by A in said formula is present, the elements Co, Fe and Cr being present in both the trivalent and tetravalent states, and wherein n represents a numeral having a value greater than zero but less than one.

2. The resistor of claim 1 in which the conductive phase contains Co in an amount up to 90 atom percent of the total content of Fe, Cr, Co and Mn.

3. The resistor of claim 1 wherein the conductive phase contains in addition at least one metal selected from the group consisting of Al, Ti and Ni in an amount up to 20 atom percent of the total content of Fe, Cr, Co and Mn.

4. The resistor of claim 1 wherein in addition up to 10 percent of a flux is present.

References Cited in the file of this patent

Physica, v. 16, No. 3, March 1950, pages 337–349.

Physica, v. 19, 1953, pages 120–123.