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MANGANITE COMPOSITION

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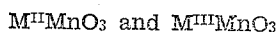
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This invention relates to magnet cores and particularly to cores constituted by manganites.

A manganite is an oxygen compound of manganese and a second bivalent or trivalent metal. More particularly, manganites as referred to hereinafter in the specification and in the claims are compositions which have the general formulae



According to the invention, the magnet cores are constituted by essentially homogeneous mixed crystals of two or more of the foregoing manganites. The term "mixed crystal" refers to the crystalline combination or two or more such manganites which are solid solutions of the manganites having a common chemical characteristic. More specifically, the mixed crystal is a new chemical compound of the individual manganite having a substantially homogeneous crystalline structure.

The mixed crystals are preferably composed in a stoichiometric ratio of two or more manganites but it is not essential that they be in exact stoichiometric ratio, and the mixed crystals may contain a slight excess or deficiency of oxygen and a slight excess or deficiency of manganese, and still be satisfactory for the purposes of the invention.

The mixed crystals of the manganites may also contain additional compounds such as ferrites, chromites, titanates and aluminates, without departing from the inventive concept.

The mixed crystals of the manganites do not all have a purely cubic crystalline structure since the ratios of the axes and the axial angles of the crystal system may slightly depart from those of the cubic crystal system.

In describing the invention, particular reference will be made to lanthanum manganite. However, the invention is not restricted solely to the case where lanthanum manganite is one of the constituents of the mixed crystal. The purpose of describing the invention in connection with lanthanum manganite is that the perovskite structure of the mixed crystal requires a large ion at the position of the M^{III} in the crystal lattice which is furnished most conveniently by the lanthanum ion.

In this connection it is to be noted that there are other manganites which may have no perovskite structure individually but which, when combined in the form of mixed crystals, exhibit a perovskite structure. For example, yttrium and strontium manganite, each taken individually, have no perovskite structure, but when combined in the form of a mixed crystal, exhibit a perovskite structure.

Instead of lanthanum manganite, it is also possible to use other manganites of trivalent metals having a perovskite structure, such as

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praseodymium manganite and neodymium manganite.

Other manganites which are suitable for the purpose of the invention and which will be described more completely in the examples to be given later, are manganites of strontium, barium and lead, and in connection with desired magnetic properties to a lesser degree, those of calcium and cadmium, even though not all of these materials, taken individually, exhibit a perovskite structure.

However, in determining the formation of mixed crystals having a perovskite structure, there is a definite limit for the replacement of the lanthanum in lanthanum manganite. For example, the lanthanum in lanthanum manganite may be replaced by strontium to the extent of approximately 70% at most, and at most by 50% by barium or lead. Exceeding the limit set for the substitution by other constituents results in a crystal phase different than the perovskite phase.

Partially substituting another manganite for lanthanum manganite has the effect of varying the curie point of the mixed crystal manganite, the curie point being that temperature at which, for all practical purposes, the material exhibits no ferromagnetic properties, i. e., it is paramagnetic. By replacing some of the lanthanum manganite in the mixed crystal with strontium, barium and/or lead manganite, a curie point exceeding room temperature can be readily obtained. Mixed crystals including 25 to 50 mol. per cent of strontium, barium, or lead manganite, respectively, and containing 75 to 40 mol. per cent of lanthanum manganite, has a curie point between 60 and 90° C., which is above normal ambient temperatures, in which event these materials are suitable for magnet cores.

In this connection it is to be noted that various mixed crystals of manganites exhibit a curie point which is below 0° C. and consequently such materials have no ferromagnetic properties at normal ambient temperatures. A comparatively pure lanthanum manganite containing 4% of manganese which is tetravalent, has a curie point below -200° C. If the perovskite structure is retained and no second phase exists in the material, the said material may contain more than 25% manganese in tetravalent form, so that a material of the formula $LaMnO_{3.125}$ may, for example, be obtained having a curie point in the neighbourhood of -20° C. By partly replacing the lanthanum in the lanthanum manganite by one of the bivalent metals, the curie point can be raised to a temperature above 0° C. If the lanthanum is replaced by strontium, barium and/or lead, it is possible to obtain material at ambient temperatures having an initial permeability of 100 to 200 which was measured at

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4 kc./sec. and a magnetic saturation of approximately 60 gauss cm.³/g.

Substitution of Al, Cr, Ti, Fe, Co or Ni, for example, for part of the Mn, generally involves a lower curie temperature. For this reason only a limited substitution of these metals is desirable.

The mixed crystals of the manganites may be prepared by reaction of a mixture of the constituent metal oxides or compounds which decompose into these oxides upon heating, or compounds which in addition to one or more of the desired metal oxides contain only volatile components. The constitution of this mixture, the reaction temperature, the partial oxygen pressure of the ambient atmosphere at the reaction temperature, and the partial oxygen pressure of the cooling atmosphere all determine the oxygen content of the mixed crystal thus formed.

The magnet cores according to the invention are produced by conventional techniques employed in the ceramic industry, the material being used in the form of powder during the sintering and cooling operations and the conditions being such as to prevent conversions adversely affecting the magnetic properties, such as the formation of undesirable second phases in the material. After shaping the initial mixture, the preparation of the desired mixed crystals and the sintering operation required for the manufacture of the magnet cores may alternatively be effected in one operation. Finally, the mixed crystals in question may be fabricated into magnet cores with the use of a binder.

The invention will be described in connection with the following examples which indicate several preferred embodiments of the invention.

EXAMPLE I

A mixture of 130 gms. of lanthanum carbonate, 29.5 gms. of strontium carbonate and 115 gms. of manganese carbonate is sintered in air at 900 to 1000° C. for several hours. After cooling, the mixture is ground and molded into the desired shape, followed by sintering in air at a temperature between 1370 and 1450° C. for three hours. The magnet core obtained consists of essentially homogeneous mixed crystals of 80 mol. percent lanthanum manganite and 20 mol. percent strontium manganite. In a similar manner, mixed crystals of 70 mol. percent lanthanum manganite and 30 mol. percent strontium manganite, of 60 mol. percent lanthanum manganite and 40 mol. percent strontium manganite and of 50 mol. percent lanthanum manganite and 50 mol. percent strontium manganite are produced. If the composition contains more than 40 mol. percent of MnMnO₃, it is desirable to use an atmosphere having a higher partial pressure of the oxygen or even pure oxygen. Several magnetic properties are stated in the following table.

Table I

Composition lanthanum manganite (mol. percent)	Strontium manganite (mol. percent)	Curie temperature, °C.	Magnetic saturation at 20° C. (gauss. cm. ³ /g.)	Initial permeability, 4 kc./sec. and 20° C.
80.....	20	45	20	100 95
70.....	30	95	65	
60.....	40	95	61	
50.....	50	80	47	

EXAMPLE II

A mixture of 130 gms. lanthanum oxide, 39.5 barium carbonate and 115 gms. manganese car-

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bonate is sintered in air at 900 to 1000° C. for several hours. After cooling, the mixture is ground and moulded into the desired shape, followed by sintering in air at a temperature between 1370 and 1450° C. for three hours, thus obtaining a magnet core consisting of essentially homogeneous mixed crystals of 80 mol. percent lanthanum manganite and 20 mol. percent barium manganite. In a similar manner, mixed crystals of 75 mol. percent lanthanum manganite and 25 mol. percent barium manganite, of 70 mol. percent lanthanum manganite and 30 mol. percent barium manganite and of 65 mol. percent lanthanum manganite and 35 mol. percent barium manganite are formed. Several properties are stated in the following table.

Table II

Composition lanthanum manganite (mol. percent)	Barium manganite (mol. percent)	Curie temperature, °C.	Magnetic saturation (gauss. cm. ³ /g.) at 20° C.
80.....	20	25	5
75.....	25	43	34
70.....	30	65	55
65.....	35	80	55

EXAMPLE III

A mixture of 160 gms. lanthanum carbonate, 44.3 gms. strontium carbonate, 103.5 gms. manganese carbonate and 5.1 gms. aluminium oxide is sintered in air at 900 to 1000° C. for several hours. After cooling, the mixture is ground and moulded into the desired shape, followed by sintering in air at a temperature between 1370 and 1450° C. for three hours. The magnet core obtained may be conceived to consist of essentially homogeneous mixed crystals of 60 mol. percent lanthanum manganite, 10 mol. percent lanthanum aluminate (LaAlO₃) and 30 mol. percent strontium manganite. The curie-temperature is 43° C. and the magnetic saturation 17 gauss. cm.³/g. at 20° C.

EXAMPLE IV

A mixture of 114 gms. lanthanum oxide, 44.3 gms. strontium carbonate, 82.6 gms. manganese peroxide and 4 gms. of ferrioxide is sintered in air at 900 to 1000° C. for several hours. After cooling, the mixture is ground and moulded into the desired shape, followed by sintering in air at a temperature between 1370 and 1450° C. for three hours. The magnet core obtained may be conceived to consist of essentially homogeneous mixed crystals of 65 mol. percent lanthanum manganite, 5 mol. percent lanthanum ferrite and 30 mol. percent strontium manganite. The curie-temperature is 70° C. and the magnetic saturation 39 gauss. cm.³/g. at 20° C.

EXAMPLE V

A mixture of 114 gms. lanthanum oxide, 22.1 gms. of strontium carbonate, 29.6 gms. of barium carbonate and 115 gms. manganese carbonate is sintered in air at 900 to 1000° C. for several hours. After cooling, the mixture is ground and moulded into the desired shape, followed by sintering in air for three hours at a temperature between 1370 and 1450° C. The magnetic core obtained consists of essentially homogeneous mixed crystals of 70 mol. percent lanthanum manganite, 15 mol. percent strontium manganite and 15 mol. percent barium manganite, the curie temperature being 70° C., and the magnetic saturation in gauss. cm.³/g. at 20° C. being 57. The initial

permeability with 4 kc./sec. and at 20° C. was found to be 180.

EXAMPLE VI

A mixture of 114 gms. of lanthanum oxide, 80 gms. of lead carbonate and 115 gms. of manganese carbonate is sintered in air for several hours at 900 to 1000° C. After cooling, the mixture is ground and moulded into the desired shape, followed by sintering in air at a temperature gradually increasing from 1100 to 1300° C. for three hours. The magnet core obtained consists of essentially homogeneous mixed crystals of 70 mol. percent lanthanum manganite and 30 mol. percent of lead manganite, the curie-temperature being 90° C. and the magnetic saturation in gauss. cm.³/g. at 20° C. being 36.

While we have thus far described our invention with specific examples and methods of preparation, other modifications thereof will be obvious to those skilled in the art without departing from the spirit and scope of the invention.

What we claim is.

1. A new composition of matter consisting essentially of homogeneous mixed crystals of a manganite having the formula $M^{++}MnO_3$, M^{++} being a metal selected from the group consisting of strontium, barium, and lead, and a manganite having the formula $M^{+++}MnO_3$, M^{+++} being a metal selected from the group consisting of lanthanum, praseodymium and neodymium, said mixed crystals having a perovskite crystal structure.

2. A new composition of matter as claimed in claim 1 in which the mixed crystals include a material selected from the group consisting of a ferrite and an aluminate.

3. A new composition of matter as claimed in claim 1, in which the mixed crystals contain approximately between 25 to 50 mol. percent of a manganite selected from the group consisting of strontium manganite, barium manganite and lead manganite, and approximately 75 to 50 mol. percent of lanthanum manganite.

4. A new composition of matter as claimed in

claim 1, in which the mixed crystals include a ferrite.

5. A new composition of matter as claimed in claim 1, in which the mixed crystals include an aluminate.

6. A new composition of matter consisting of essentially homogeneous mixed crystals constituted by approximately between 60 to 80 mol. percent of lanthanum manganite and approximately 20 to 40 mol. per cent of strontium manganite.

7. A new composition of matter consisting of essentially homogeneous mixed crystals of approximately between 65 and 80 mol. per cent of lanthanum manganite and approximately between 20 and 35 mol. per cent of barium manganite.

8. A new composition of matter consisting of essentially homogeneous mixed crystals of 60 mol. per cent of lanthanum manganite, approximately 10 mol. per cent of lanthanum aluminate and approximately 30 mol. per cent of strontium manganite.

9. A new composition of matter consisting of essentially homogeneous mixed crystals of approximately 65 mol. per cent of lanthanum manganite, approximately 5 mol. per cent of lanthanum ferrite and approximately 30 mol. per cent of strontium manganite.

10. A new composition of matter consisting of essentially homogeneous mixed crystals of approximately 70 mol. per cent of lanthanum manganite, approximately 15 mol. per cent of strontium manganite and approximately 15 mol. per cent of barium manganite.

11. A new composition of matter consisting of essentially homogeneous mixed crystals of approximately 70 mol. per cent of lanthanum manganite and approximately 30 mol. per cent of lead manganite.

References Cited in the file of this patent

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