

[54] **METHOD OF MAKING
MAGNETICALLY-ANISOTROPIC
PERMANENT MAGNETS**

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1970, abandoned.

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[58] Field of Search **252/62.58, 62.63; 264/61,**
264/DIG. 58, 24, 86, 56

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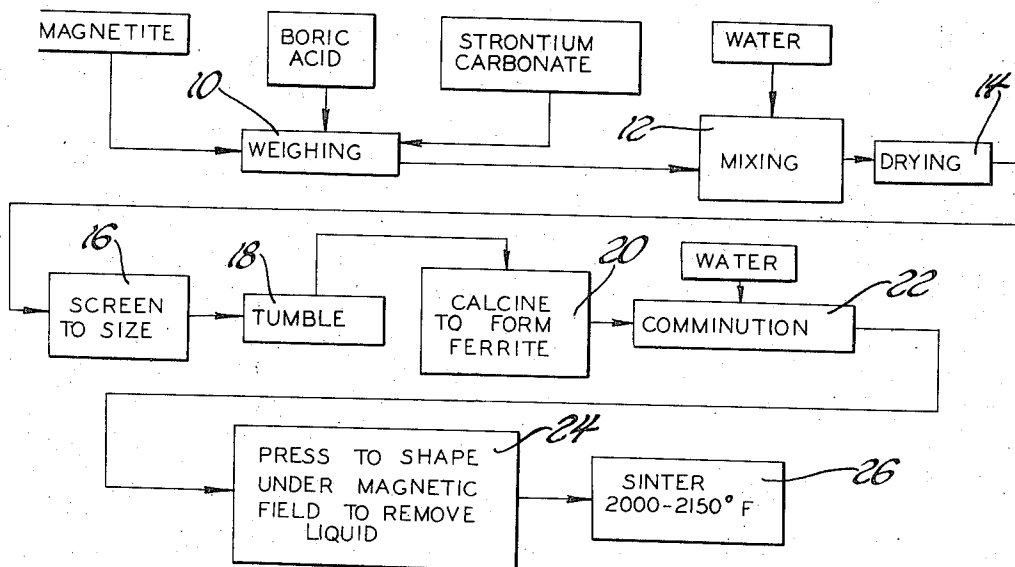
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[57]

ABSTRACT

A method of making a permanent magnet of the hard ferrite type having a formula $[SrO.6 Fe_2O_3] SrO.6-Fe_2O_3$ is disclosed. The process comprises the critical step of adding a compound selected from the group consisting of boric acid and boric oxide to magnetite and a source of SrO during the mixing [a] and milling step prior to calcining of the mixture. Superior magnets are produced over those achieved by the process where the boric acid or boric oxide is introduced after calcining of magnetite and a source of SrO.

5 Claims, 3 Drawing Figures



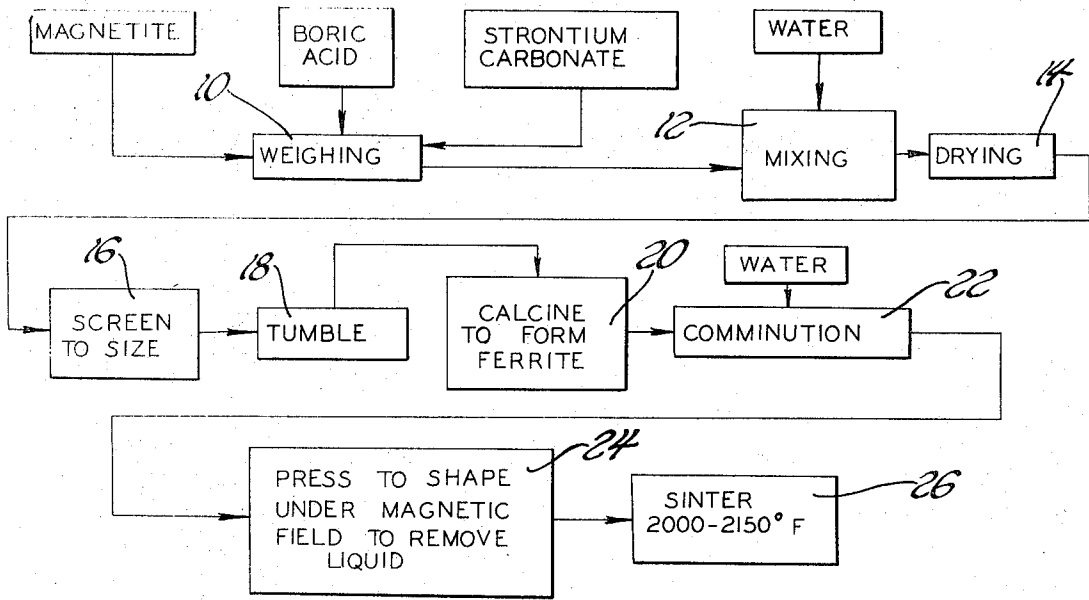


Fig. 1

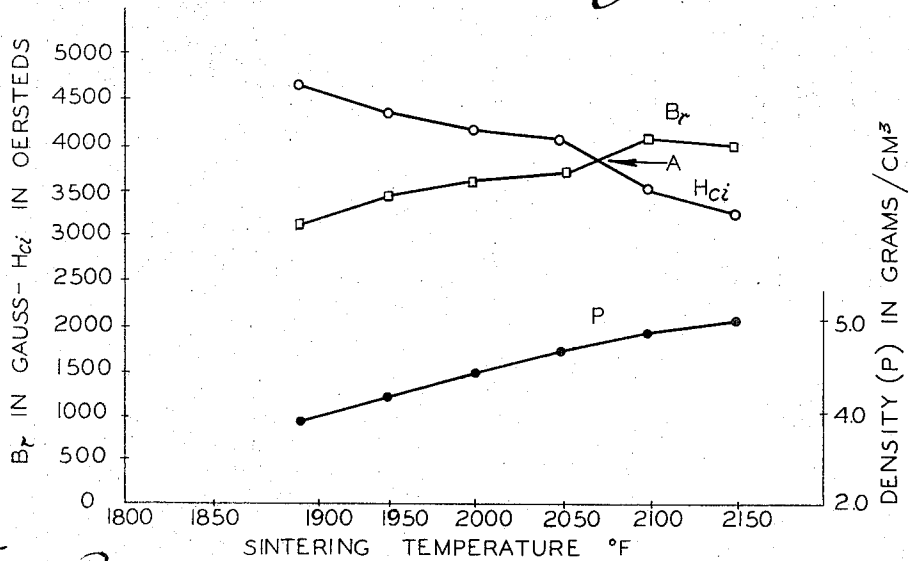


Fig. 2

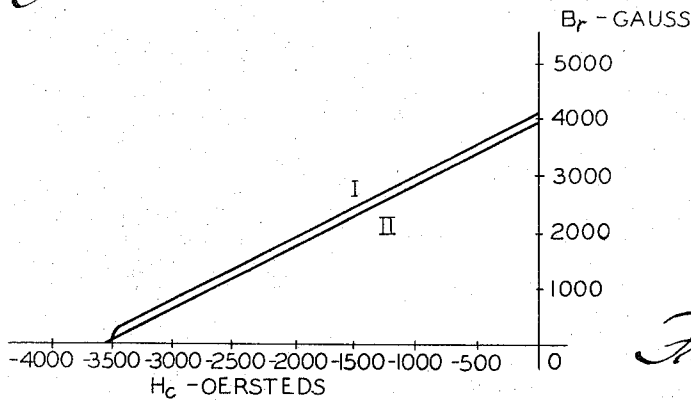


Fig. 3

METHOD OF MAKING MAGNETICALLY-ANISOTROPIC PERMANENT MAGNETS

This application is a Continuation-In-Part of Ser. No. 51,751, filed July 2, 1970, now abandoned.

This invention relates to hard ferrite magnets and, more particularly, to a method of making magnetically-anisotropic permanent magnets of the hard ferrite type having improved magnetic properties.

The term "hard" ferrites, as used herein, refers generally to ferrite having a hexagonal crystalline lattice of the structure of the mineral magnetoplumbite and a formula $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$. The term "permanent" magnets, as used herein, refers to those magnets formed of hard magnetic materials in which, once magnetized, the magnetization is retained in the absence of a magnetizing field and they themselves serve to supply an external field.

The current widespread use of the permanent magnets is due, in general, to their desirable magnetic properties and their relatively low cost. Of the magnetic properties desired in permanent magnets one of the most important is a high coercive force. A high coercive force is needed to assure the magnetic stability in the presence of relatively high demagnetizing fields. This is an important consideration for dc motor applications, an important use of permanent magnets today, where demagnetizing fields can be high. Two other magnetic properties of importance in permanent magnet applications are residual flux density or remanence which remains when the "saturating" magnetizing force is reduced to zero and maximum magnetic energy product which is a measure of the maximum magnetic energy the given magnet can develop in its magnetic gap. Materials having the highest possible energy product, remanence and coercive force are used as permanent magnets.

Since the introduction of hard ferrite type permanent magnets, the ferrite technology has been directed to increasing the maximum energy, remanence and coercive force. The first major advance in this field came with the discovery that the maximum energy could be increased about threefold by orienting the ferrite particles along a preferred magnetic axis using a magnetic field. The orientation is accomplished by dispersing the hard ferrite particles in a slurry or other mobile state and then pressing the material into a body while under the influence of a directional magnetic field to align the ferrite particles whereby their easy direction of magnetization is more or less parallel to the applied field. Following orientation, the pressed body is sintered to produce the finished magnet which is then magnetized in the direction of orientation.

Since this discovery, efforts to increase the magnetic properties of oriented ferrite magnets have proceeded in two directions. The first is to increase magnetic properties by increasing the purity of the ferric oxide (Fe_2O_3) used in producing the ferrite. Since ferric oxide is the principal ingredient of the starting composition, it was thought that by increasing the purity of Fe_2O_3 improved properties would result. This technique has resulted in an improvement of the properties, but has also resulted in increasing the cost of fabricating ferrite magnets. The second approach is to increase maximum energy product and remanence by raising the sintering temperature of the oriented magnet to the range 2,250° to 2,400° F. However, past experience has

shown that the increase in the remanence on raising of the sintering temperature is accompanied by a decrease in coercive force. The first effect is apparently due to an increase in apparent density of the body while the second effect appears to be a result of grain growth.

Various additives such as silica, alumina, titania, or boric acid have been added to the ferrite prior to sintering to inhibit grain growth accompanying sintering with some beneficial effects. For example, commercial permanent magnets made with such an additive and sintered in the range of 2250° to 2400° F have a remanence, B_r , generally in excess of 3500 gauss and a maximum energy product, $(BH)_{max}$, approaching 3.5×10^6 gauss-oersteds. However, the coercive force H_c is found to decrease usually falling below 2000 oersteds which is undesirable in certain commercial applications where strong demagnetizing fields are present. For many such applications, it is desirable to have not only the remanence greater than 3500 gauss and the maximum energy product greater than 3.0×10^6 gauss-oersteds, but also the coercive force in excess of 3000 oersteds. In addition, the magnets should be relatively inexpensive to produce.

Accordingly, it is among the principal objects of our invention to provide an inexpensive magnetically-anisotropic permanent magnet having improved magnetic properties and a method of making the same using magnetite ore instead of ferric oxide.

It is another object of our invention to provide a method of making improved hard ferrite compositions for use in making permanent magnets wherein relatively high magnetic properties are obtainable at relatively low sintering temperatures.

It is a further object of our invention to provide a method of making magnetically-anisotropic permanent magnets of the hard ferrite type using relatively inexpensive, raw grade magnetite ore, having a maximum energy product in excess of 3.0×10^6 gauss-oersteds, a remanence in excess of 3500 gauss and a coercive force in excess of 3000 oersteds.

These and other objects are accomplished, in the preferred embodiment of our invention, by an improved ferrite manufacturing process including the steps of mixing magnetite (Fe_3O_4) and strontium carbonate with a minor addition of boric acid in water, milling the compounds to form a homogeneous mixture thereof, drying the homogeneous oxide mixture, screening the resulting cake, tumbling the mixture to form a free-flowing powder, and then calcining the mixture at about 2100° F to form a ferrite. The calcined ferrite is then comminuted in water to a particle size which is ceramically workable and pressed into a body of desired shape while under the influence of a directional magnetic field to remove the water and orient the ferrite particles in the magnetic field. The pressed body is then sintered at a temperature in the range of 2000° to 2150° F to form a permanent magnet having the aforementioned unusually high magnetic properties.

Prior to our invention it was believed that in order to make commercially usable hard ferrites, it was necessary to start with Fe_2O_3 which was substantially pure and which has as fine a grain size as was commercially available. However, we have found that superior magnets can be produced by a process wherein relatively low cost, natural magnetite having a relatively large grain size is mixed with a minor amount of boric acid or boric oxide and with a source of SrO and reacted to

form the hard ferrite composition which is then formed into a magnetically-anisotropic magnet.

Other objects and advantages of our invention will become apparent from the following detailed description of the invention, reference being had to the accompanying drawings of which:

FIG. 1 is a flow diagram of our improved process for making permanent magnets;

FIG. 2 is a graph showing the variation in remanence, coercive force and density with sintering temperatures of ferrite magnets made in accordance with our improved process; and

FIG. 3 is a graph showing the demagnetization portion of the hysteresis loop for two samples made by our improved process and subjected to different soak times at a sintering temperature of 2100° F.

In our improved method for fabricating hard, magnetically-anisotropic permanent magnets of the hard ferrite type, the proportions of raw materials are first weighed out as shown in FIG. 1, block 10. In accordance with the principal feature of our invention, the raw materials include predominately magnetite (Fe_3O_4) with a source of the bivalent metal oxide, SrO , such as the oxides or carbonates of strontium, and a minor addition of a source of boron such as boric acid or boric oxide. In our preferred process, strontium carbonate and boric acid are used. The addition of boric acid is in the range of about 0.3 to 1.5 percent, by weight. The addition of a boron source at the start of the process has been found critical to achieving the magnetic properties hereinafter more fully described.

One of the principal advantages of our method is that it is not necessary that the raw iron oxide, specifically magnetite, be of high purity and small grain size as is required when using Fe_2O_3 , but rather relatively low purity and large grained material is used. A suitable iron oxide for use in our process is "Meramac" iron oxide, a product of the Meramac Mining Company. "Meramac" is a technical grade iron oxide which analyzes at 93.02% Fe_3O_4 , 6.15% Fe_2O_3 , 0.1 percent silicon and 0.06 percent vanadium and less than 0.002 percent titanium, and which has a grain size on the order of 50 microns. "Meramac" currently is commercially available at a cost of 60-80 percent less than that of Fe_2O_3 currently used in ferrite fabricating processes and, therefore, the use of "Meramac" significantly reduces the cost of fabricating hard ferrite magnets.

After weighing, the raw materials are then mixed with a sufficient amount of water and milled as a slurry in a stainless steel ball mill, block 12, for an extended period of time to achieve a thorough mixture of the raw materials. As a result of milling, the grain size of the magnetite is broken down from 50 microns to about 5 microns. The resulting mixture is then dried in an oven as shown by block 14. After drying, the material is screened into granules of a desired size, block 16, which are tumbled for a short time, block 18, to make the granules free-flowing. As a next step in the process, the material is fired or calcined at an elevated temperature wherein a reaction takes place to form the hexagonal ferrite, block 20. The ferrite material is mixed with water and comminuted, block 22, in a ball mill until ceramically workable particles of an average size of 1 to 2 microns are obtained. The ground ferrite, as a slurry, is then pressed in a non-magnetic die into a predetermined shape under a strong directional magnetic field, block 24, to remove the water and simultaneously

to orient the ferrite particles in the magnetic field. If desired, other methods of orienting and forming the ferrite crystals into a body may be used, such as dispersing the particles in a flexible, organic binder and mechanically orienting the particles therein to form a flexible sheet from which the magnetic bodies are cut. Such a method is described in U.S. Pat. No. 3,110,675 to Brailowsky owned by the assignee of this invention. The pressed body is then sintered in the temperature range of about 2,000° to 2,150° F, block 26, to form the finished magnet. The fired ferrite magnet may then be magnetized or, if desired, magnetization may be performed later.

The following specific examples will make the nature of our process and the resulting improved magnetic properties more clear.

EXAMPLE I

328.380 grams of "Meramac" iron oxide was mixed with 68.653 grams of strontium carbonate and 2.876 grams of boric acid to form a starting mixture having a composition of, by weight, 82.11 percent "Meramac", 17.17% SrCO_3 and 0.72% H_3BO_3 . The mixture was mixed and milled with water in a one-half gallon stainless steel ball mill for 14 hours, dried and screened through a 20 mesh screen. The granules were then tumbled for 15 minutes. Following tumbling, the mixture was calcined at 2150° F for 2 hours in a flowing air atmosphere. The calcined ferrite was then comminuted in water for 30 hours in a one-half gallon stainless steel ball mill having an equal number of $\frac{3}{8}$ inch and $\frac{1}{4}$ inch stainless steel balls. The comminuted particles as a slurry of about 45 to 48 percent, by weight, water were pressed in a directional magnetic field of 6,000 oersteds into cylindrical test samples one inch in diameter and one-half inch high. The density of the pressed samples was 2.75 g/cm³. The samples were then sintered in the range from 1900° to 2150° F for 30 minutes.

To demonstrate the effect of the boron addition, corresponding samples were prepared identically with the process described above, but without the boron addition. The intrinsic coercive force, H_{ci} , and remanence, B_r , of both sets of ferrite samples were then measured using a standard hysteresisgraph. Density measurements, D , were also made.

The tables below show the results of the hysteresisgraph measurements. The data shown below in Table I was obtained from the ferrite samples prepared in accordance with this invention, and the data shown in Table II was obtained from the identical samples, but prepared without the boron addition. The tabular data shown below in Table I is shown in graphical form in FIG. 2.

TABLE I

Sintering Temperature °F	H_{ci} OE	B_r G	D gr/cm ³
1900	4,615	3,080	3.84
1950	4,385	3,435	4.22
2000	4,140	3,660	4.48
2050	4,105	3,740	4.65
2100	3,575	4,100	4.86
2150	3,280	4,040	4.98

TABLE II

Sintering Temperature °F	H _c OE	B _r G	D gm/cm ³
1900	4,425	2,485	3.16
1950	4,220	2,565	3.28
2000	3,765	2,845	3.60
2050	3,905	2,895	3.64
2100	2,275	3,725	4.49
2150	1,770	3,825	4.80

Comparing the data in Table I with that in Table II it may be seen that in all respects the properties obtained in the ferrite samples prepared in accordance with this invention are superior to those prepared with magnetite and strontium carbonate, but without the boron addition. Further, from the data presented in Table I and from FIG. 2, it may be seen that the samples prepared in accordance with our improved process exhibited superior magnetic properties with a coincident numerical value of B_r and H_c_i at about 3,900 gauss and 3,900 oersteds, respectively, at a sintering temperature of about 2075° F (point A of FIG. 2). Although the samples prepared without the boron addition exhibited a relatively high intrinsic coercive force at the lower sintering temperatures and a relatively high remanence at the higher sintering temperature, the coincident numerical values of properties was only 3200 gauss and 3200 oersteds at a sintering temperature of about 2075° F.

Permanent magnets made in accordance with our process exhibit superior magnetic properties which are obtained at relatively low sintering temperatures. We have found that permanent magnets made in accordance with our process and sintered at about 2100° F are ideal for such applications as field magnets in dc motors since these magnets have a remanence of about 4100 gauss with a coercive force above 3500 oersteds.

Thus, a first feature of the invention is the use of coarse powder of natural magnetite together with boric acid as the additive.

A second feature of the invention is the timing of the boric acid introduction into the manufacturing process. We have found that it is very important to add the boric acid to the batch formula before the start of the first mixing, i.e., before the calcining operation. The introduction of the boric acid at this point results in a substantial improvement of the magnetic stability of the permanent magnets, i.e., in the improvement of the very "permanence" of the magnets which is measured by the value of the intrinsic coercive force. Such a feature of the invention can be of a decisive importance in fabrication of the ferrite magnets for applications such as the field magnets for dc motors. The following Example II demonstrates the effect of the timing on the magnetic stability as it is reflected by the intrinsic coercive force.

EXAMPLE II

Two mixtures hereinafter referred to as Mixtures A and B were prepared using the same starting material and formula composition and the same manufacturing technique as in the Example I. The Mixtures A and B differ only in the timing of the boric acid introduction into the process. The boric acid was added to Mixture A before the first mixing, thus, before the calcining.

To the Mixture B the boric acid was added after the calcining, just before the grinding operation. With the exception of the calcining temperature and the grinding time which were in this Example 2100° F and 60 hours respectively, the process was identical to that of the Example I. The measuring technique was exactly as that as in the Example I. The results obtained are set forth in Tables III and IV.

TABLE III

Sintering Temp. °F	Mixture "A"				
	B _r G	H _c OE	H _c OE	(BH) _{max} G-OE ×10 ⁻⁶	D(g/cm ³)
1950	3120	4360	2980	2.38	4.11
2000	3250	4190	3050	2.69	4.41
2050	3570	4030	3330	3.05	4.62
2100	3780	3810	3540	3.36	4.79
2150	3840	3570	3450	3.53	4.86

TABLE IV

Sintering Temp. °F	Mixture "B"				
	B _r G	H _c OE	H _c OE	(BH) _{max} G-OE ×10 ⁻⁶	D(g/cm ³)
1950	3110	3860	2930	1.97	4.28
2000	3400	3780	3110	2.80	4.53
2050	3570	3660	3280	3.00	4.77
2100	3780	3500	3320	3.30	4.86
2150	3830	3280	3110	3.52	4.95

Examination of the Tables shows clearly that as compared with the addition of the boric acid after calcining, the addition of the boric acid before calcining results in a significant improvement of the magnetic stability of the ferrite magnets. Comparing the H_c_i values of the Mixtures A and B it is apparent that the improvement takes place in the whole range of useful sintering temperatures.

Referring now to the demagnetizing curves shown in FIG. 3, it will be further seen that magnets made in accordance with our process have essentially straight line demagnetizing curves, which is ideal for dc motor applications. The two curves of FIG. 3, designated as curves I and II, are for two samples prepared according to our process and sintered at 2100° F for 30 and 15 minutes, respectively. The pertinent data for each sample is as follows:

Sample I

Sintering Temperature (°F)	2100°
Soak Time (min.)	30
B _r (gauss)	4100
H _c (oersteds)	3500
H _c _i (oersteds)	3575
(BH) _{max} (gxoe)	3.84×10 ⁶

Sample II

Sintering Temperature (°F)	2100°
Soak Time (min.)	15
B _r (Gauss)	3900
H _c (oersteds)	3600
H _c _i (oersteds)	3825
(BH) _{max} (gxoe)	3.53×10 ⁶

From the foregoing, it will be apparent that our improved process for making magnetically-anisotropic permanent magnets of the hard ferrite type yields magnets having superior properties which may be produced at a relatively low cost.

Although our invention has been described in terms of certain specific embodiments, it is to be understood that other forms may be adopted within the scope of our invention.

We claim:

1. A method of making a permanent magnet of the hard ferrite type having a hexagonal crystalline lattice with a magnetoplumbite structure and a formula $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$, comprising the steps of mixing and milling magnetite with a source of SrO and about 0.3 to 1.5 percent, by weight, of a compound selected from the group consisting of boric acid and boric oxide to form a homogeneous mixture thereof, calcining said mixture, comminuting said calcined mixture to form particles thereof having an average size of about 1 to 2 microns, orienting and forming said particles into a body and sintering said body at a temperature in the range of 2000° to 2150° F.

2. The method of claim 1 wherein said mixture is calcined at about 2100° F.

3. A method of making a permanent magnet of the hard ferrite type having a hexagonal crystalline lattice with a magnetoplumbite structure and a formula $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$, comprising the steps of mixing and milling magnetite with a source of SrO and about 0.3 to 1.5 percent, by weight, of a compound selected from the group consisting of boric acid and boric oxide to form a homogeneous mixture thereof, calcining said mixture, comminuting said calcined mixture to form particles thereof having an average size of about 1 to 2 microns, compacting said particles while under the influence of a directional magnetic field into a body anisotropic in a principal direction, and sintering said body at a temperature in the range of 2000° to 2150° F.

4. A method of making a permanent magnet of the hard ferrite type having a hexagonal crystalline lattice with a magnetoplumbite structure and a formula $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$, comprising the steps of mixing and milling magnetite having an average grain size on the order of about 50 microns with a source of SrO and about 0.7 percent, by weight, boric acid to form a homogeneous mixture thereof, calcining said mixture of about 2100° F, comminuting said calcined mixture to form particles thereof having an average size of about 1 to 2 microns, compacting said particles while under the influence of a directional magnetic field to form a body anisotropic in a principal direction, and sintering said body in the range of 2000° to 2150° F.

5. The method of claim 4 wherein said body is sintered at about 2100° F.

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