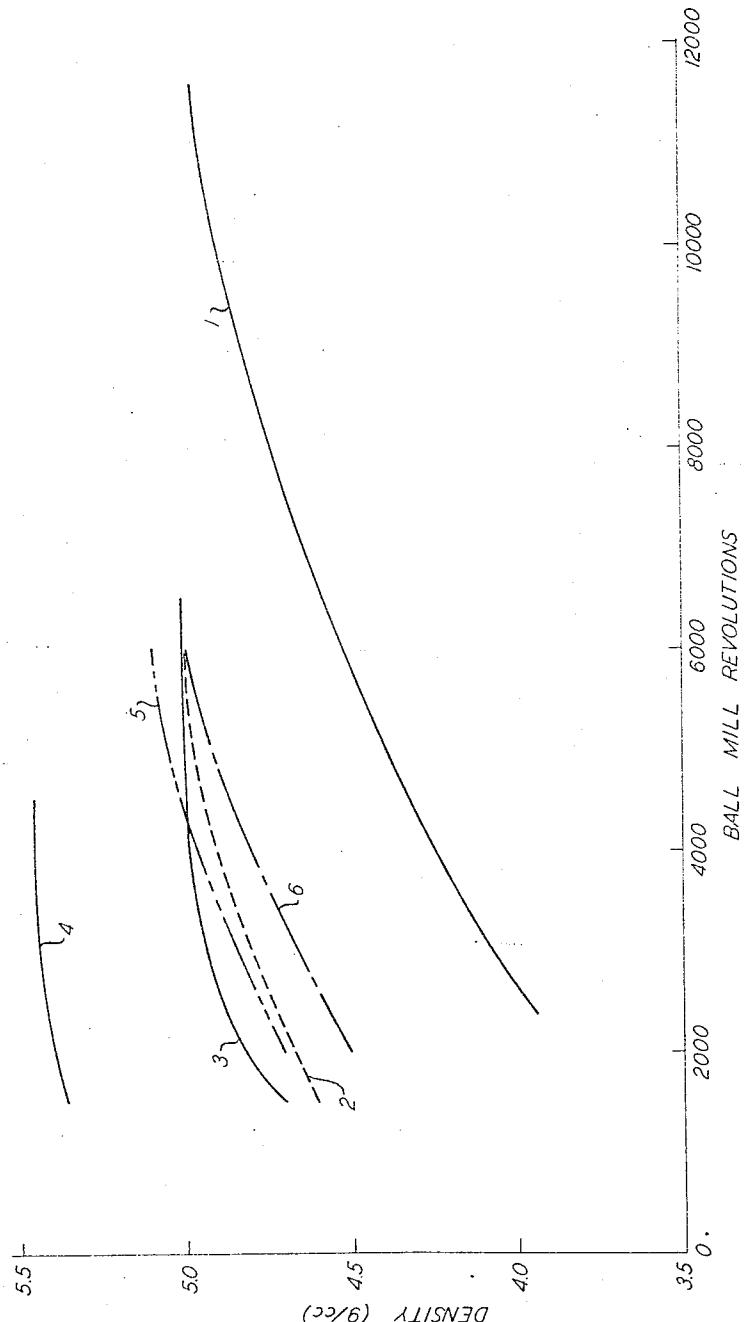
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MANUFACTURE OF GARNET CERAMIC

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MANUFACTURE OF GARNET CERAMIC

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ABSTRACT OF THE DISCLOSURE

Ceramic magnetic yttrium-iron garnet and related compositions of controlled stoichiometry have been difficult to make because of the iron contribution made by ball milling apparatus. Improved stoichiometry results from the use of iron-deficient initial ingredients coupled with removal of a sample during ball milling with the sample yielding a measured parameter, such as density, which serves as an indicator of required additional ball milling to attain stoichiometry.

This invention relates to the preparation of polycrystalline magnetic materials having the garnet structure. These materials have the nominal chemical composition $Y_3FE_5O_{12}$ and partial substitutions thereof in which elements such as aluminum partially replace iron, and type 4*f* rare earths partially replace yttrium.

The role of ferrimagnetic materials in circuitry is universally recognized. Ferrite materials are utilized in circulators, isolators, phase shifters, and inductor cores, to name a few devices. In general, these materials are possessed of useful magnetic properties, may be prepared by expedient processing techniques, have chemical and physical integrity, and are otherwise suitable. It is difficult to imagine a present-day microwave technology without ferrites.

Despite their excellence, however, ferrite compositions are subject to several well recognized drawbacks. Reproducibility has always been a problem. The obtaining of a uniform stoichiometric product is virtually impossible. Extreme dependence on temperature and other processing conditions give rise to these and other compositional gradients. All of these variations result in line-width broadening and concomitant losses for many circuit applications.

Several years ago a new ferrimagnetic material emerged. While not found in nature, this material is isostructural with naturally occurring garnets, and it was so named. The prototype material $Y_3Fe_5O_{12}$ was and is called yttrium-iron garnet. Compositional variations not affecting structure, generally made for the purpose of varying saturation magnetization, have been reported. These include partial substitutions of, for example, aluminum, vanadium, or gallium for iron, and partial or complete substitutions of any of the 4*f* rare earths, in accordance with the periodic table of Mendelyeev, for yttrium.

From the very start it was recognized that these ferrimagnetic garnet compositions were in certain respects superior to the ferrites. For example, it was recognized that the fact that this composition is a true chemical compound would afford far closer compositional control than that permitted in ferrite mixed crystals. Other advantages were expected to accrue from the fact that the stoichiometry permitted no divalent iron, and from the observation that other crystalline phases were unlikely to occur within expedient compositional ranges.

The above advantages were, in fact, realized and single crystal garnets have been in specialized device use for some time. Of course, crystal garnets are far more expensive than ordinary fired ferrites, for which reason use has been limited to those very demanding circumstances where the expense could be justified.

While it was expected, too, that ferrimagnetic element tolerances could be improved by the use of ceramic garnets, this expectation has not been realized. In practice, it has been found that small, generally unavoidable composition variations from the nominal formula produced significant variations in magnetic and electrical properties. Materials so produced have not generally represented the desired improvement over the ferrites.

It is known that such compositional variations are, in large part, concerned with the increasing iron content brought about by the introduction of abraded iron during ball milling. Recognized this, workers in the field have sought to overcome this problem by the use of iron deficient starting materials. While this was a proper approach, a technique for the precise control of iron had not been developed. It was possible to produce materials that do not have excess iron by this technique but preparation of uniformly stoichiometric material has not proven expedient.

In accordance with this invention, a processing technique has been discovered which may yield ferrimagetic garnet compositions which are substantially stoichiometric, and in which such characteristics as dielectric constant and dielectric loss may be maintained to very close tolerances.

A problem toward which this invention is directed is that of determining a suitable relationship between one or more processing parameters and some characteristic coinciding with stoichiometry to aid as a processing control. In accordance with the preferred embodiment herein, this relationship takes the form of a density-pulverizing dependency. In accordance with this species, use is made of the empirical relationship between density and, for example, number of ball mill revolutions. Very briefly, such a relationship, possibly in graphical form, is prepared by ball milling a critically iron deficient material, withdrawing samples at spaced intervals during milling, firing and sintering such samples in accordance with a standard procedure, and relating the two parameters. This procedure is carried to initiation of an asymptotic density or else the curve is extrapolated to such level on the basis of an empirically determined curve form. It remains only to note the interval in terms of revolutions between the measured density of a withdrawn sample and the final value to tailor the process to produce a stoichiometric product.

Variations are apparent. While the relationship must be determined anew for each new composition, once determined it may serve as a guide for successive batches of any certain composition. For extremely discriminating need, it may be desired to determine the relationship for each batch. In commercial practice this is not a burdensome procedure since a single batch may contain as much as forty pounds or more.

The described procedure has resulted in ceramic garnet material meeting the most demanding requirements. Dielectric loss, tan δ, has been kept to values as low as 0.0005 and less, stoichiometry has been maintained at near nominal with an analyzed iron plus iron substitute content of 5 ± 0.1 and better per formula unit, and the dielectric constant has been controlled within 2 percent and better. Parameters other than density have also been utilized with some success. For compositions in which iron is partially substituted, for example by aluminum, it has been found that a further element of control is afforded. Here, it is found that the saturation moment $4\pi M_S$ can be changed by heat treatment. Such a practice, which under certain circumstances results in an increase

in the saturation value, is sometimes usefully employed as a step subsequent to the final sintering. A preferred embodiment of this invention is defined accordingly.

A description of the invention is expedited by reference to the drawing in which the figure is a series of curves plotted on coordinates of density and ball milling revolutions. The coordinate units are density in grams per cubic centimeter on the ordinate and number of ball mill revolutions on the abscissa.

This figure includes six curves, designated **1** through **6**, representing empirically determined data for the following compositions:

Curve 1 ---------- $Y_3Al_{1.25}Fe_{3.75}O_{12}$.
Curve 2 ---------- $Y_3Al_{0.97}Fe_{4.03}O_{12}$.
Curve 3 ---------- $Y_3Al_{0.37}Fe_{4.63}O_{12}$.
Curve 4 ---------- $Y_{2.035}Gd_{0.965}Fe_5O_{12}$.
Curve 5 ---------- $Y_3Fe_5O_{12}$.
Curve 6 ---------- $Y_{2.90}Yb_{0.10}Al_{1.00}Fe_{4.00}O_{12}$.

All of these compositions may be represented by the generalized formula $Y_{3-x}Me_xFe_{5-y}Me'_yO_{12}$ in which:

Y is yttrium,
Me is a trivalent 4*f* rare earth ion such as gadolinium or ytterbium,
Fe is iron,
Me′ is a trivalent ion such as aluminum or gallium, and
O is oxygen.

The curves reported on the figure were chosen to correspond with the examples. Such curves, or their mathematical equivalent, must be determined anew for each composition, each differing piece of apparatus, and for any significant change in processing conditions during ball milling. The procedure from which the information upon which the curves are based was derived is set forth:

The required raw materials were weighed out to within ±0.01 weight percent. The amount of iron-containing material was such as to yield an iron deficient final composition lacking about 0.01 atom iron per formula unit. To insure a homogeneous mix, the weighed oxide powders were ball milled in deionized water for a total of 2,900 revolutions (approximately an hour). The milled slurry was filtered; dried; screened; loaded into platinum lined boats; and calcined for ten hours at 1350° C. in an air atmosphere. The calcined powder was ball milled for a total of 7,500 revolutions. The mix was sampled at intervals of 2,500, 5,000 and 7,500 revolutions. The remainder of the mix was stored. The samples were pressed and sintered at 1500° C. for twenty hours in an oxygen atmosphere. The bulk density of the fired samples was measured, and a smooth curve of density versus ball mill revolutions was plotted. The curve was extrapolated to the required final density, and the additional number of ball mill revolutions needed was determined from the extrapolated curve.

The following more detailed processing description includes processing condition ranges considered suitable for the practice of this invention. It is apparent that many of the conditions so defined are merely good practice as generally followed. To the extent that such is true, the description is not to be considered limiting on the appended claim.

INITIAL INGREDIENTS

As indicated, these are conveniently in such amount as to yield an end product 1/10 atom iron deficient. In terms of common starting ingredients, Fe_2O_3, $Al(OH)_3$, Y_2O_3, Yb_2O_3, etc., this is in the range of from 1 to 3 weight percent. Since the iron deficiency equivalent to the amounts of starting ingredients eventually determines ball milling time, the limits on iron deficiency are set in terms of this processing parameter. The minimum tolerable iron deficiency is determined by the minimum number of ball mill revolutions required for homogeneity. For commercial equipment, this is about 3,000 revolutions. The equivalent iron deficiency in terms of starting ingredients is about 0.01 atom iron, resulting in a total of 4.99 in atom units per formula. The maximum desirable iron deficiency for the usual ball milling apparatus is about 0.20 atom iron, equivalent to 4.8 atoms iron in terms of formula units. Such a maximum iron deficiency is replaced by something of the order of 30,000 revolutions. Long ball milling time results in a thixotropic intermediate product, making the obtaining of a uniform end product difficult. While this phase of the process is in terms of ball milling and this is the type of procedure most commonly practiced, a fluid energy mill or other apparatus may suitably be used. It is only a requirement of the process that the milling be carried out in such apparatus as to result in the addition of iron to the mix and, in fact, use of any other apparatus, when developed, obviates the need for the inventive procedure. Although other iron apparatus is used in which it is inappropriate to specify conditions in terms of ball mill revolutions, the tolerable iron deficiency range set forth above nevertheless obtains. Such limits are still based on the need for homogeneity at one end and the avoidance of a thixotropic mix at the other.

Yttrium in the form of Y_2O_3, or other suitable material yielding this element, is incorporated in an amount such as to produce 3 atoms of yttrium per formula unit in the case of the unsubstituted yttrium-iron garnet. As with all of the other initial ingredients, incorporation is desirably within ±.01 weight percent. This is based on a stoichiometric garnet end product rather than on the iron deficient product equivalent to the starting ingredients.

Where a substitution is to be made for yttrium, its amount is to be determined by the nature of the modification which it is sought to produce. Such desiderata may include line-width, Curie temperature, etc.

Aluminum, in accordance with standard practice, may be incorporated in the form of the hydroxide $Al(OH)_3$; the amount of this additive is determined in accordance with its function which is to reduce saturation magnetization. The amount is chosen so as to result in the desired deficiency of from .2 to .01 in terms of A+1FE=5 in the nominal formula unit.

Appropriate considerations apply for other starting ingredients. Gadolinium is suitably added as Gd_2O_3; ytturbium may be incorporated in the form of Yb_2O_3. The amount of any such 4*f* rare earth is such as to result in a total of 3 atoms in the yttrium site.

Other considerations are standard. Particle size of initial ingredients may be of the order of a mil or more for water soluble materials such as aluminum hydroxide, but should be below 30 microns for water insoluble starting ingredients. Particle size for some of the materials used in the examples are: Y_2O_3—1 to 13 microns; aluminum hydroxide—1/10 mil; iron oxide—1 to 2 microns.

NOMINAL COMPOSITION

In general, it is undesirable to replace in excess of about 1.6 atoms of iron (Fe=3.4 in the generalized formula above) since greater substitutions do not generally result in a good ferrimagnetic material. Tolerable impurity content is again consistent with good practice in the field and is in part determined by the end use to which the product is to be put. In general, starting ingredients having a total impurity content of 0.1 and below are readily available. Such materials resulting in a final composition having a purity level of about 99.9 are suitable. While the objectives of the invention are equally served in the preparation of materials containing greater amounts of impurity, the device demands implied by use of the invention suggest greater impurity to be undesirable.

INITIAL MIX

It has been indicated that sufficient mixing results from 2,900 revolutions of a water slurry. Dry mixing or any other appropriate technique may be substituted.

CALCINING

After the mix has been dried (if wet mixing is utilized) it is loaded into an appropriate nonreacting container which is then brought to a temperature in the range of from 1200° to 1400° C., at which it is maintained for a period of from 6 to 20 hours. Certain deviations resulting in broadening of this range may result, it having been noted, for example, that incorporation of vanadium may permit reaction at lower temperature. The minimum temperature is that required for total reaction. The maximum is determined by expediency; greater temperatures resulting in large fired agglomerates which are difficult to ball mill. The same considerations apply to the limitations set on calcining time.

BALL MILLING

The ball milling or other pulverizing procedure is designed to produce the requisite uniformity and particle size. From the standpoint of subsequent pressing, a particle size range of from one to ten microns is desired. In terms of usual industrial ball milling apparatus, this may be expressed as in the range of from 3,000 to 30,000 revolutions. Graphical data, such as that set forth in the figure, is conveniently obtained by removing samples at 2,500, 5,000, and 7,500 revolutions.

It is seen from the figure that the curve forms are regular. Data eventually obtained from these samples may be extrapolated on the curve form of any of curves 1 through 6 to an ultimate density value, this intercept being used to determine the extent of subsequent milling. For the purposes of this invention, it is preferred that the density value be set at at least 98 percent of theoretical or single crystal density.

TEST PRACTICE

Three samples at the noted intervals, each of the order of 10 grams, have been found adequate. The actual pressing and sintering procedure is not critical but is preferably such as to result in the noted 98 percent of theoretical density for a finally processed material. Lesser densities may be used but the effective discrimination is thereby reduced so that optimum tolerance materials are not obtained. In general, sludge pressing at about 1000 p.s.i. or isostatic pressing at 5000 p.s.i. have been found adequate to produce a desired minimum green density of 3.2 grams per cubic centimeter (this value being appropriate for any of the compositions described herein). Sintering of the test sample is again not critical so long as the noted density is obtained. Suitable sintering conditions are 20 hours at 1500° C. Of course, all test practices must be uniform and to close tolerance to permit comparison. In sintering, a temperature range of ±5° C. is preferred. The maximum sintering temperature, as is to be expected, is the decomposition temperature of the concerned garnet. This temperature for $Y_3Fe_5O_{12}$ is about 1510° C. The aluminum substitution composition containing about 1.25 atoms aluminum decomposes at about 1580° C.

SUBSEQUENT MILLING

The necessary amount of milling to conclusion is determined from the curve or from the mathematical data as has been indicated. In the most discriminating process, a separate curve is drawn for each batch so that the number of revolutions required is the differential between the number corresponding with the final sample (7,500 revolutions in the example above) and that corresponding with the final accepted density value. As has also been noted, some uses permit determination by use of but a single sample, the number of revolutions being read from a standard curve plotted from data obtained from a prior run.

FIRING

Final firing conditions are any appropriate to the desired end product and may take the form of the conditions specified under "Test Practice."

HEAT TREATMENT

As a final optimum step, any garnet composition containing at least 0.01 atom substituted for iron may be heat treated and annealed or quenched to tailor the saturation magnetization to a desired level. This procedure has been found to have little effect on density, dielectric constant, or dielectric loss. In accordance with this practice, the magnetic moment can be changed by a short heat treatment (less than one-half hour) with magnetic moment increasing for samples treated in the temperature range of from 1000° C. to 1250° C., with no dependency on previous heat treatment history or density. Heat treatment over the range of from 1250° C. to 1500° C. does depend on density with magnetic moment increasing for density values of 95 percent or higher and with magnetic moment decreasing for density values of 95 percent or lower. Again, there is no dependency of magnetic moment on previous heat treatment history. Heat treatment over the range of 700° C. to 1000° C. produces variations in moment which do depend on previous heat treatment histories. Optimum practice depends on desired results. It is clear that where a maximum value of $4\pi M_S$ is desired, heat treatment should be carried out over the range of from 1000° C. to 1500° C.

In general, higher temperatures than those indicated should be avoided since dielectric loss, tan δ, tends to increase somewhat, probably due to the introduction of lattice defects.

The following table sets forth six examples, denoted 1 through 6, these examples corresponding with curves 1 through 6 on the figure. Values noted under appropriate headings in the table are nominal composition, weight percent of noted initial ingredients (these values in iron deficient terms with no allowance made for iron pickup) density in grams per cubic centimeter, saturation magnetization in gauss, dielectric constant ϵ', dielectric loss tan δ, and line-width ΔH in oersteds. The final parameter ΔH is in terms of the variation in applied field resulting in an absorption of 3 db, in accordance with one conventional practice.

Ex. No.	Nominal Composition	Weight percent, starting ingredients	Density (g./cc.)	Saturation moment $4\pi M_S$ (gauss)	Dielectric constant ϵ'	Dielectric loss tan δ	Line-width ΔH (oersted)
1	$Y_{3.00}Al_{1.25}Fe_{3.75}$	Y_2O_3, 46.09; $Al(OH)_3$, 13.27; Fe_2O_3, 40.64.	4.97	235	14.8	<.0005	<49
2	$Y_{3.00}Al_{0.97}Fe_{4.03}$	Y_2O_3, 46.06; $Al(OH)_3$, 10.29; Fe_2O_3, 43.65.	5.00	450	15.1	<.0005	<50
3	$Y_{3.00}Al_{0.37}Fe_{4.63}$	Y_2O_3, 45.99; $Al(OH)_3$, 3.92; Fe_2O_3, 50.09.	5.03	1150	15.8	<.0005	<50
4	$Y_{2.035}Gd_{0.965}Fe_{5.00}$	Y_2O_3, 28.61; Gd_2O_3, 21.78; Fe_2O_3, 49.61	5.50	1200	16.2	<.0005	80±10
5	$Y_{3.00}Fe_{5.00}$	Y_2O_3, 46.0; Fe_2O_3, 54.0	5.10	1780	16.3	<.0005	<60
6	$Y_{2.99}Yb_{0.10}Al_{1.00}Fe_{4.00}$	Y_2O_3, 44.1; Yb_2O_3, 2.6; $Al(OH)_3$, 10.5; Fe_2O_3, 42.8.	5.02	400	15.0	<.0005	<80

The invention has been described in terms of a limited number of illustrative embodiments. Certain variations

have been noted from time to time. Other variations are apparent. The invention is considered to derive from the monitoring of a final parameter noted as a means of determining the amount of subsequent processing required to produce a stoichiometric end product. The inventive processes are, of course, suitably applied only to a practice in accordance with which abraded iron is added to the composition. The claim is to be so construed.

What is claimed is:

1. Process for making a stoichiometric iron-containing ferrimagnetic garnet ceramic comprising mixing such starting ingredients as will yield the elements of the said composition, the amounts of the said starting ingredients being equivalent to an iron deficiency of from about 0.01 atom to about 0.20 atom per formula unit and otherwise stoichiometric mix of the said composition, calcining the resulting mix, pulverizing the calcined product in apparatus constructed of iron-containing material under

conditions such that iron is introduced into the mix from said apparatus, withdrawing a sample before completion of the pulveriing, pressing and sintering the said sample, measuring the density of said sintered sample and continuing pulverizing until the desired density or stoichiometry is obtained as indicated by previously gathered empirical data relating density to required additional pulverizing.

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