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The Molten Salt Synthesis of Single Magnetic Domain $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ Crystals

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This report sets down a synthetic process utilizing molten NaCl–KCl as a solvent whereby $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ submicron crystals are prepared which possess near-theoretical magnetic properties. The present process, unlike previous preparations, yields a high-magnetic quality product as a direct result of the synthesis. No special treatment steps are required to enhance the product magnetic properties. Control of the Fe(II) content and the crystallite perfection resulting from the use of molten salt solvents are responsible for the high magnetic quality.

Introduction

The use of ferrites with the magnetoplumbite structure ($MFe_{12}O_{19}$, M = Pb, Ba, Sr) as permanent magnet materials began with the work of J. J. Went, et al. (*1*), in 1952. The crystal structure was initially determined by Adelsköld (*2*), and was subsequently refined by a number of workers (*3*). A discussion of the crystal structure and magnetic ordering, as well as the relation of the physiochemical properties to those of other ferrite compounds, are given by Smit and Wijn (*4*).

Solid State Synthesis

The conventional preparation of $MFe_{12}O_{19}$ is the high-temperature, solid state reaction of an iron oxide (Fe_2O_3, Fe_3O_4) and an MO (carbonate, etc.) yielding compound. Although the crystallographic stoichiometry is $MO:Fe_2O_3 = 1:6$, the practice is to prepare reactant mixtures with a ratio of 1:4.5 to 1:5.6 so as to compensate for evaporative loss of MO (particularly PbO), or iron oxide pick-up during subsequent processing operations. Chemical homogeneity can be enhanced by milling this product to a small particle size and repeating the solid state reaction schedule.

An improved variation of this process is to start with an aqueous solution of M^{2+} and Fe^{3+} and coprecipitate the cations as their hydroxides, carbonates, or salts of some organic anion. The precipitate is then heated to high temperature to form the desired compound by solid state reaction. This method is superior to the previous method in that it results in a more complete reaction. Even greater degrees of preparative sophistication have been applied in attempts to produce, on a commercial basis, magnet materials with superior physiochemical properties (*5*, *6*).

The above techniques produce a product which is predominantly $MFe_{12}O_{19}$ with varying quantities of MO, Fe_2O_3, and other impurities, either as the result of intentional additions or from incomplete solid state reaction. The important powder magnetic properties are σ_s (saturation magnetization) and H_{ci} (intrinsic coercive field). They may vary from the theoretical values obtained with careful preparation to fractions of the theoretical value obtained in commercial operations. The intrinsic values of saturation magnetization at 298° K are 74.3 $emug^{-1}$ for $SrFr_{12}O_{19}$ and 72.0 $emug^{-1}$ for $BaFe_{12}O_{19}$ (*7*). The intrinsic coercive field for coherent rotation of magnetization in single magnetic domain crystals has been investigated theoretically by Stoner and Wohlfarth (*8*). The room temperature values of H_{ci} of 0.5–1.5 μm particles of $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ were calculated to be 6700 and 6000 Oe, respectively (*7*, *9*). The single magnetic domain size of $MFe_{12}O_{19}$ apparently depends on whether the domain size is measured on distinct, small (~1.0 μm) crystallites, sintered compacts of crystallites, or large single crystals. Crystals with dimensions appreciably greater than ~1.0 μm, such as those obtained in solid state reactions, exhibit lower values of H_{ci} (by as much as a factor of ten) than anticipated from the calculated values or realized in very special cases to be discussed below.

The solid state synthesized $MFe_{12}O_{19}$ crystals are reduced to single magnetic domain dimensions by milling the as-prepared material. Milling has been observed to result in physical damage to the crystallites by creating vacancies, dislocations, and irregular crystallite surfaces, all of which lead to values of H_{ci} below the theoretical value (*10* a–c). Nevertheless, there can be a net increase in the value of H_{ci} through the milling process.

Significant increases in the H_{ci} values of single magnetic domain crystallites have been achieved by several treatment schemes. One method is to heat-treat the milled crystallites at high temperature (700–1250°C) to anneal out vacancies and dislocations (*10*a, b, *11*a, b). H_{ci} values of 3000 Oe or more have been attained in this way in powders having initially lower H_{ci} values. It is assumed that the high-temperature anneals will not alter the gross crystal-surface imperfections.

A second method to increase the value of H_{ci} is to etch away surface flaws and irregularities of the 1.0 μm crystallites with dilute mineral acid solutions (*12*a–c). Becker (*13*) has observed that the material remaining after dissolving as much as 60% of a $BaFe_{12}O_{19}$ powder sample possessed an $H_{ci} \simeq 5400$ Oe. This value represents 90% of the theoretical H_{ci} value and, coupled with $\sigma_s \simeq 72.0$ emug^{-1}, represented the closest approach to theoretical magnetic properties for solid state prepared $MFe_{12}O_{19}$.

Molten Salt Syntheses

Molten salt fluxes have been utilized to prepare $MFe_{12}O_{19}$ where the preparation of large single multidomain crystals was required. A number of workers (*14–17*) used molten $Na_2Fe_2O_4$ to prepare crystals of $BeFe_{12}O_{19}$ by slow-cooling techniques. Relatively large crystals with a thin hexagonal platelet morphology were obtained in each case. There is no mention of the preparation of 1.0 μm crystals using this solvent. Similar results were obtained using molten $BaFe_2O_4$ as the solvent (*18–20*). Other molten salt systems that have been used to prepare multidomain single crystals of $MFe_{12}O_{19}$ are PbO (*21*a, b), PbO–PbF_2 (*22*a, b), and Bi_2O_3 (*23*). Several workers have successfully used molten solvents in the system BaO–B_2O_3, the composition being BaO-rich with a BaO:B_2O_3 ratio of 3.10–4.60:1 (*24*). A rather unique technique which uses a molten salt both as a solvent and as a reactant is that of Brixner (*25*). In this preparation, either molten $SrCl_2$ or $BaCl_2$ is used as a solvent for Fe_2O_3. Air oxidation, or more likely atmospheric H_2O hydrolysis, of MCl_2 at 1350°C results in the formation of MO, which in turn reacts to form $MFe_{12}O_{19}$, followed by formation of large single crystals as the solution supersaturates with $MFe_{12}O_{19}$.

None of the above molten salt syntheses produced single magnetic domain crystals of high-crystalline perfection and near-theoretical magnetic properties. Other work has been reported where synthesis was achieved using molten salts as the reaction medium. Wickham (*26*) has reported the preparation of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ using Na_2SO_4–K_2SO_4 as the solvent, and MCO_3 and Fe_2O_3 as the reactants. The reactants and products were only partially soluble in the molten salt at 845°C. The product of the reaction sequence was composed of extremely fine crystallites of $MFe_{12}O_{19}$ embedded in the solidified salt matrix. The $MFe_{12}O_{19}$ was retrieved by dissolving the Na_2SO_4–K_2SO_4 matrix with H_2O. There was no information given as to the crystallite size or magnetic properties of the product.

Shirk and Buessen (*27*) have reported the synthesis, based on the observations of Tanigawa and Tanaka (*28*), of a homogeneous glass in the system BaO–B_2O_3–Fe_2O_3, with the specific molar ratios 0.265 B_2O_3–0.405 BaO_2–$_3$0.33 Fe_2O_3. This material was observed to be paramagnetic, indicating that no $BaFe_{12}O_{19}$ had been formed in this step. The glass was then given a specific heat treatment which precipitated a second phase which was freed from the surrounding glass matrix using acetic acid. X-ray diffraction showed this phase to be $BaFe_{12}O_{19}$. Although the saturation magnetization was not measured, it may be assumed to be near the theoretical value, since the material was ≥95% pure. The H_{ci} was as high as 5350 Oe, which equaled that of etched, solid state-reacted $BaFe_{12}O_{19}$. This work represents the first example of the direct preparation of a $MFe_{12}O_{19}$ compound possessing near-theoretical magnetic properties.

The present work was to develop a molten salt synthesis for $MFe_{12}O_{19}$ which would yield a high-magnetic quality product directly; i.e., a monodispersed powder composed of crystallographically and chemically perfect hexagonal crystallites with a maximum basal plane dimension of 1.0 μm.

A 50 mole% KCl–50 mole% NaCl eutectic at 800°C is reported to dissolve ~20–25 mole% of Fe_2O_3 and certain other transition metal oxides (*29*). SrO and BaO have at least a small solubility in alkali halides melts. An unanswered question is the solubility of the product in the solvent, which if too great, would require special quenching techniques to yield the small crystallite size desired.

A "basic" and a "modified" synthetic process were investigated.

Experimental

"*Basic*" *Molten Salt Synthesis*

Synthesis. The "basic" process consisted of dry blending the solvent, 50 mole% NaCl, 50 mole% KCl, and the reactants to prevent the formation of subsequently unreacted pockets of material that result from gross segregation of components, The reactants, α-Fe_2O_3 and the divalent metal carbonate, oxide, hydroxide, or nitrate, constituted from 10 to 80 wt% of the 50–450.0 g reaction mixture.

The blended reaction mixture was placed in a platinum, 99+% dense α-Al_2O_3 or 99+% dense ZrO_2 crucible, and introduced into an electrically heated air atmosphere furnace at 800–1100°C for 30 to 180 minutes. The optimum product magnetic properties were attained by carrying out the reaction at 1000–1050°C for 30 min or longer. These parameters were used for the majority of samples prepared. It was observed that there was incomplete solution of perhaps the reactants, but most likely, the product during this phase of the synthesis. The reacting mixture is therefore a slurry of reactants/product in the molten solvent. At the end of the period, the crucible and its contents were removed from the furnace and allowed to air-cool (~50–100 deg. min^{-1}) to room temperature. No special quench operations were found which would enhance the product magnetic quality above that attained by this simple cooling process. The product $MFe_{12}O_{19}$, usually $BaFe_{12}O_{19}$, was freed from the solidified cake by dissolving the NaCl–KCl solvent with H_2O. The product powder was collected by filtration, or sedimentation in a magnetic field, washed, and dried. Chemical analysis showed 0.00–0.10 wt% of Na^+ and 0.00–0.07 wt% K^+ in the resulting $MFe_{12}O_{19}$. The Na and K is most likely residue from the NaCl–KCl leach, rather than occluded or dissolved salt in the $MFe_{12}O_{19}$.

Results

1. $MFe_{12}O_{19}$ physiochemical properties. The quality of the product was determined in terms of the following parameters.

(i) *Chemical purity.* Phase purity was determined by Debye–Scherrer X-ray diffraction analysis, the experimentally determined minimum level of detection being ~3 wt% for α-Fe_2O_3, the major contaminant. Wet chemical analysis for M^{2+} and Fe^{3+} was frequently used to verify and refine the X-ray data.

(ii) *Magnetic properties.* σ_s was measured at room temperature using a commerical vibrating sample magnetometer. Values of H_{ci} were measured by orienting the crystallites magnetically in a molten wax matrix and measuring the hysteresis loop of the cooled compact.

(iii) *The crystallite size amd morphology.* A correlation was made between crystallite size and morphological features and measured H_{ci} and chemical purity.

The quality of the product varied from pure $MFe_{12}O_{19}$ ($BaFe_{12}O_{19}$) with essentially no impurity phase, $H_{ci} = 4300$ Oe and theoretical saturation magnetization, to essentially no reaction or reaction to a poor magnetic quality product, $H_{ci} \sim 20$–200 Oe, containing unreated material as the impurity phases. The bulk of the investigation was applied to elucidating the factors which led to such radically different results in what appeared to be a relatively straightforward process.

2. Solvent purity and composition. Variations in the chemical purity of the molten salt solvent materials from especially prepared, chemically pure material to commercial, tonnage-quantity grades revealed that the impurities usually found in these chemicals had no effect on the magnetic quality of the product $MFe_{12}O_{19}$, except for fluoride ion, which will be discussed in more detail below.

Experiments with salts other than NaCl–KCl were less successful than those employing the NaCl–KCl mixtures. Solvents incorporating lithium salts invariably formed $LiFe_5O_8$. Solvents utilizing a mixture of alkali-halide and an alkaline earth halide ($SrCl_2$, $BaCl_2$) did yield the corresponding ferrite, but with H_{ci} values $\leqslant 900$ Oe. Solvents composed of mixed alkali halide-alkali sulfate, applying Wickham's observations (*26*), produced $MFe_{12}O_{19}$ with lower values of H_{ci} than did the NaCl–KCl systems. Solvents such as $NaPO_3$, $Na_2B_4O_7$, and Na_3AlF_6 were totally unsatisfactory in that the products were apparently not $MFe_{12}O_{19}$, and the solvents were difficult to separate from the product material.

3. Reactant stoichiometry and purity. Variations in the ratio of MO: Fe_2O_3 in the reaction mixture were investigated, MO concentrations less than stoichiometric resulted in the presence of unreacted α-Fe_2O_3 in the product $MFe_{12}O_{19}$. Similarly, excess of MO over the stoichiometric amount required yielded MO as a distinct, nonmagnetic impurity phase. In neither case was H_{ci} of the product affected by the presence of one reactant in excess to the 20% studied. A chemical analysis of material with $H_{ci} = 3500$ Oe and theoretical saturation magnetization revealed that this material did indeed possess the stoichiometry MO:Fe_2O_3::1.0:6.0. As a precaution, a 10 mole % excess of MO was used to ensure complete reaction of the Fe_2O_3. The excess MO could be removed by rendering the leach solution acidic (pH = 5) with nitric acid. The contact of the mildly acidic leach medium with the ferrite resulted in no changes in the $MFe_{12}O_{19}$ properties due to acid etch.

Variations in the component chemical purity to within the limits normally observed in commercial materials and the identity of the MO precursor failed to yield any information as to the source of the observed variation in $MFe_{12}O_{19}$ magnetic quality.

The final variable explored was the iron oxide reactant. Initial and highly successful experiments were conducted using A.C.S. analytic reagent α-Fe_2O_3. The product in these syntheses was $MFe_{12}O_{19}$ with $H_{ci} = 2900$–3700 Oe and theoretical saturation magnetization. In an attempt to further improve product magnetic quality, a 99.999 wt% pure α-Fe_2O_3 was used. The resultant product possessed the theoretical saturation magnetization, but H_{ci} was now 1000–1800 Oe. Examination of the crystallites of both products under the scanning electron microscopy revealed them to be virtually identical. Both products consisted of hexagonal platelets with maximum basal plane dimensions of 1.5 μm or less and thicknesses of 0.5 μm or less.

A third iron oxide was prepared by precipitat-

TABLE I

SPECTROCHEMICAL ANALYSIS OF REACTANT IRON OXIDES AND PRODUCT $BaFe_{12}O_{19}$

Impurity (w/o)	99.999 w/o α-Fe_2O_3	Analytic reagent α-Fe_2O_3	In-house prepared α-Fe_2O_3	$BaFe_{12}O_{19}$[a] I	$BaFe_{12}O_{19}$[b] II
Cr	0.001	0.001	0.001	0.001	0.001
V	N.D.[c]	0.001	0.001	N.D.	N.D.
Ti	0.1	<0.01	<0.01	0.01	<0.01
Cu	<0.01	0.001	0.001	0.001	0.001
Zn	<0.1	<0.01	<0.01	<0.01	<0.01
Pb	N.D.	N.D.	N.D.	N.D.	0.01
Mo	0.05	0.05	0.05	0.001	0.001
Mg	0.001	N.D.	N.D.	0.001	N.D.
Ag	0.01	0.001	0.001	0.001	0.001
C	≤0.001	N.D.	≤0.001	N.D.	≤0.001
Ni	0.001	0.001	<0.001	0.001	<0.001
Mn	N.D.	0.001	0.1	N.D.	0.001
Ca	<0.01	<0.01	<0.01	<0.01	<0.01
Si	0.001	0.001	0.001	0.001	0.001

[a] $BaFe_{12}O_{19}$ prepared with 99.999 w/o α-Fe_2O_3.

[b] $BaFe_{12}O_{19}$ prepared with analytical reagent α-Fe_2O_3.

[c] N.D. = None Detected.

ing $Fe(OH)_3$ from an aqueous solution of technical grade ferric chloride hexahydrate. The $Fe(OH)_3$ was filtered, washed, dried, and ground to −325 mesh. The $MFe_{12}O_{19}$ resulting from this reactant had an $H_{ci} = 3400\text{–}4300$ Oe, but it was similar in all other respects to that obtained using the commercial analytic reagent α-Fe_2O_3.

An emission spectrochemical analysis was performed on the three reactant iron oxides, as well as on their product $BaFe_{12}O_{19}$, the results of which appear in Table I. As may be seen from the data, there are no major compositional differences between the reactants and their products, or between the reactants themselves. To verify that the small impurity concentrations were not significant, $BaFe_{12}O_{19}$ samples were prepared from each of the reactants with one to two w/o of one or more of the impurities present as the oxide or chloride. With the exception of Cr(III), which substituted in the ferrite lattice, there was no observed detriment or benefit to the product from these impurities. It was concluded that impurities were not, to within the scatter of the magnetic measurements, responsible for the wide product magnetic quality variation observed.

As was observed previously, lattice defects can greatly affect the value of H_{ci}. Fe(II) present in the lattice is such a defect. Several samples of in-house prepared Fe_2O_3 were subjected to various heat treatments and then used to prepare $BaFe_{12}O_{19}$. The treatments and results are shown in Table II. The highest temperature most certainly generated a small equlibrium concentration of Fe(II), the upper limit of which is 1000 ppm, since wet chemical analysis, which is generally sensitive to the 0.1 wt% level, was unable to conclusively establish the presence of Fe(II). Qualitatively, the Fe_2O_3 darkened from orange-brown to a very dark brown to black.

TABLE II

THE EFFECTS OF Fe_2O_3 HEAT TREATMENT $BaFe_{12}O_{19}$ H_{ci}

Treatment of in-house prepared Fe_2O_3	$BaFe_{12}O_{19}$ H_{ci} (Oe)
300°C, 5 hr, Air atmosphere	3000
500°C, 5 hr, Air atmosphere	3450
700°C, 5 hr, Air atmosphere	3040
1000°C, 5 hr, Air atmosphere	970

It had previously been incorrectly assumed that air oxidation during the synthetic process would eliminate any Fe(II) present by oxygen diffusion into the reacting melt.

Samples of the three reactant iron oxides were subjected to Thermal Gravimetric Analysis (T.G.A.) up to 1200°C. The 99.999 w/o α-Fe_2O_3 lost less than 0.1 wt% over the entire temperature range, whereas the analytical reagent material lost 1.0–1.5 wt%. The in-house prepared α-Fe_2O_3 lost as much as 2.0 wt%, dependent on the previous heat treatment. These data, coupled with the spectrochemical analysis, led to the conclusion that weight loss is due either to physically absorbed or chemically bound H_2O. Since the bulk of the weight loss was observed above 700°C, it is concluded that the water is chemically bound, possibly as $Fe(OH)_3$ or FeOOH.

A series of samples were prepared where the depth of reaction mixture was varied from the ~1.0 cm used in all samples to this point to 10.0 cm. The object was to determine whether oxygen diffusion into the reacting system or the H_2O content of the Fe_2O_3 reactant determined the content of Fe(II) and thereby the $MFe_{12}O_{19}$ magnetic quality. It was observed that the 99.999 wt% Fe_2O_3 consistently yielded a product ($BaFe_{12}O_{19}$) with $H_{ci} = 1000\text{–}1800$ Oe, irrespective of mixture depth. The analytic reagent Fe_2O_3 gave $H_{ci} = 3600$ Oe for a mixture depth of 1.0 cm down to $H_{ci} = 1900$ Oe for an 8.0 cm deep mixture. The in-house prepared Fe_2O_3 gave $H_{ci} = 4300$ Oe for a 1.0 cm deep mixture and $H_{ci} = 3550$ Oe. for a 6.0-cm deep mixture.

The 99.999 wt% Fe_2O_3 apparently contains a detrimental amount of Fe(II), but no chemically bound H_2O. The small amount of air trapped in the reaction mixture voids is not enough to completely oxidize the Fe(II) to Fe(III). Diffusion of additional oxygen from the atmosphere into the molten reaction mass cannot compensate for the concentration of Fe(II) since O_2 has a diffusion coefficient of about 1×10^{-5} cm^2 sec^{-1}, which corresponds to a mean diffusion depth of ~0.4 cm in 60 min. Hence, the $BaFe_{12}O_{19}$ H_{ci} is uniformly low due to Fe(II) defects. The analytical reagent Fe_2O_3 apparently contains Fe(II). However, there is now some chemically bound H_2O (T.G.A. results), in addition to trapped atmospheric oxygen which, coupled with O_2 diffusion, lowers the Fe(II) content to a greater extent than in the case of the 99.999 wt% Fe_2O_3. Hence, there were fewer Fe(II) defects present and a more nearly theoretical value of H_{ci} results. The decrease of H_{ci} with sample depth indicates the importance of atmospheric oxygen diffusion into the reaction mixture to reduce the Fe(II) concentration. The in-house prepared Fe_2O_3 contains even more chemically bound H_2O than the analytic reagent Fe_2O_3, which gives a further decrease in the number density of Fe(II) defects in $MFe_{12}O_{19}$ and the highest value of H_{ci} obtained. This higher bound H_2O concentration tends to overshadow the effects of atmospheric oxygen diffusion into the reaction mixture; hence, there is a reduced dependence of H_{ci} on the reaction mixture depth. Using the value of H_{ci} as a gauge, it is possible to grade the reactant iron oxides' performance in the molten salt synthesis in terms of their Fe(II) contents and/or their bound H_2O contents which result in lower Fe(II) contents in the $MFe_{12}O_{19}$.

The addition of as much as 2 wt% of KF to the molten salt solvent in syntheses utilizing the analytic reagent Fe_2O_3 increased the value of H_{ci} by 200–400 Oe above that for identical syntheses from which the KF was omitted. This product had, however, a value of H_{ci} below that attained with the in-house prepared Fe_2O_3. Concentrations of KF greater than 2 wt% resulted in a drastic reduction of H_{ci}. Addition of KF to syntheses using Fe_2O_3 other than the analytic reagent did not show any improvement in H_{ci}. The response of the analytic reagent Fe_2O_3 seems to correlate with the observations of Banks, et al. (*30*), that F^- will substitute for O^{2-} in the lattice and thereby stabilize the presence of divalent cation in a trivalent cation site; i.e., F^- stabilizes the presence of Fe(II) in an Fe(III) site. However, it would seem that the compensation is less than perfect, as well as there being an upper limit to the extent of the phenomenon.

4. Crystal morphology versus properties. The $MFe_{12}O_{19}$ crystallite morphology was examined using a scanning electron microscope; and it was found to be independent of the reactants, used in the synthesis. Figure 1 shows the typical morphology of crystallites synthesized from any one of the three iron oxide reactants. In all cases, the crystallites are hexagonal platelets with maximum basal plane dimensions ≤ 1.5 μm and thicknesses a small fraction of this value. There is no evidence of gross morphological differences that would account for the large differences in the measured values of H_{ci}.

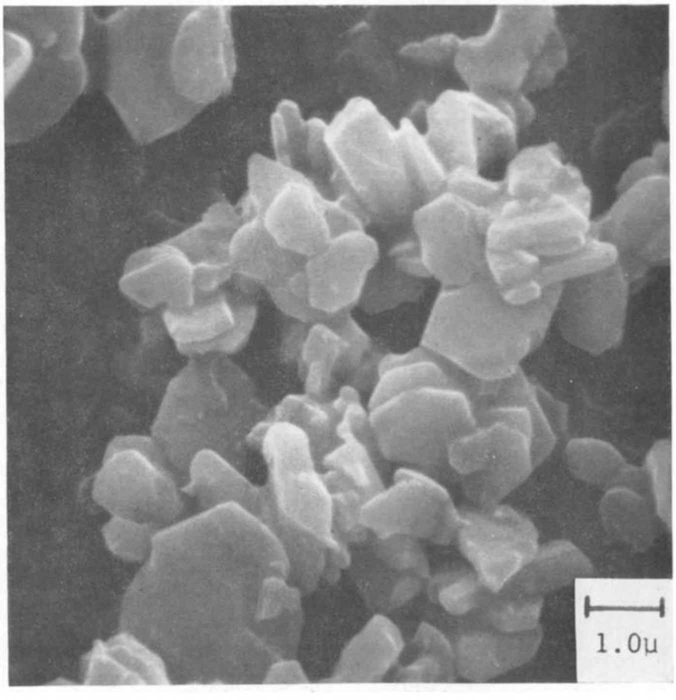

FIG. 1. $BaFe_{12}O_{19}$ prepared from analytic reagent Fe_2O_3. 10,000×.

Conclusions on the "Basic" Molten Salt Synthesis

The following conclusions may be drawn on the molten salt synthesis of $MFe_{12}O_{19}$ and its effect on the magnetic quality of the product:

Solvent. 50 mole% NaCl–50 mole% KCl is by far the best solvent. Small additions of F^-, as NaF or KF, can in certain cases, yield an improvement in product quality. Major quantities of KF or NaF may be detrimental, however.

Reactants. Any salt which decomposes to yield the required MO reactant is satisfactory. Since Fe(II) in $BaFe_{12}O_{19}$ greatly reduces H_{ci}, the Fe_2O_3 reactant must contain a negligibly small quantity of Fe(II) and/or 1.5–2.0 wt% of chemically bound H_2O.

Impurities: Trivalent cations (Al, Cr, Ga) which substitute for Fe(III) are the most significant in that they reduce the saturation magnetization. Divalent (Ni, Co, Mn), except Fe(II), and tetravalent (Ti, Si, . . .) impurities generally result in distinct, separable impurity phases which do not affect the magnetic properties of the principal phase. Fluoride ion may be beneficial by compensating for the presence of Fe(II) in the $MFe_{12}O_{19}$ lattice and reducing the defect effect on the value of H_{ci}.

The best product obtained from the molten salt synthesis, having theoretical saturation magnetization, phase purity, and $H_{ci} = 3400$–4300 Oe, represents a great improvement over material prepared by other workers. However, in view of the properties predicted by theory and those obtained through special treatment schemes, improvement is still possible in terms of H_{ci}. The best material cited above represents only ~65–70% of the theoretical H_{ci}, whereas special treatment schemes, such as acid etch, result in $H_{ci} = 5400$ Oe, or about 90% of theoretical. The chief problem seems to be the defects in the crystal lattice resulting from the presence of Fe(II) in the reactant Fe_2O_3, coupled with an inability to reduce this concentration during the molten salt synthesis. This problem has been surmounted by a modification to the reaction mixture preparation portion of the synthesis.

"Modified" Molten Salt Synthesis

Synthesis. A survey of commercially available iron oxides revealed none of them to possess the chemical qualities of the in-house prepared Fe_2O_3; i.e., a low concentration of Fe(II) and/or sufficient chemically bound H_2O to minimize the concentration of Fe(II) in the product. Therefore, the preparation of the desired Fe_2O_3 is required to obtain an $MFe_{12}O_{19}$ powder with a high H_{ci}.

The in-house preparation of Fe_2O_3 discussed above was suitable on a laboratory scale, but was not on a large commercial scale. The main problem was the gelatinous nature of the precipitated $Fe(OH)_3$, and the requirement that the residual NH_4^+ content be small so as to minimize the Fe(II) content generated by the reducing action of NH_4^+ during the molten salt synthesis. Initial experiments with NaOH/KOH as precipitation agents indicated that residual concentrations of base produced multi-magnetic domain crystals due to changes in the solvent (NaCl–KCl) characteristics affecting nucleation and crystal growth. The most likely explanation is the generation of a third solvent component, $Na_2Fe_2O_4/K_2Fe_2O_4$, during the molten salt synthesis.

The solution to the NaOH/KOH contamination problem, and the basis for the "modified" molten salt synthesis, lies in the addition of the base to some predetermined pH end point corresponding to the required stoichiometry for the conversion of $FeCl_3$ to $Fe(OH)_3$. A reference slurry solution was prepared containing the anticipated quantities of NaCl/KCl and Fe_2O_3, using the analytic reagent Fe_2O_3 as a reference material. This slurry-solution had a pH = 6.70, being independent of the relative ratio of NaCl to KCl or the quantity of Fe_2O_3 present.

The iron oxide was precipitated by slowly adding the NaOH/KOH solution to a vigorously stirred aqueous solution of $FeCl_3$ which had been made slightly acidic with HCl. The slurry-solution pH was constantly monitored with a glass membrane hydrogen ion-selective electrode until pH = 6.70 was reached. The slurry solution was allowed to digest for 3–18 hr at 25–100°C. The exact time and temperature could be varied without affecting the product quality. A final adjustment of pH was then made.

Previous procedures required the precipitated $Fe_2O_3 \cdot xH_2O$ be filtered and washed. However, when 50 mole% NaOH–50 mole% KOH is used as precipitation agent, the mixed chlorides generated give a 32 wt% $MFe_{12}O_{19}$ reaction mixture. This is a satisfactory composition for the molten salt synthesis in that this quantity of solvent results in a monodispersed $MFe_{12}O_{19}$ powder, where each crystallite is separated from

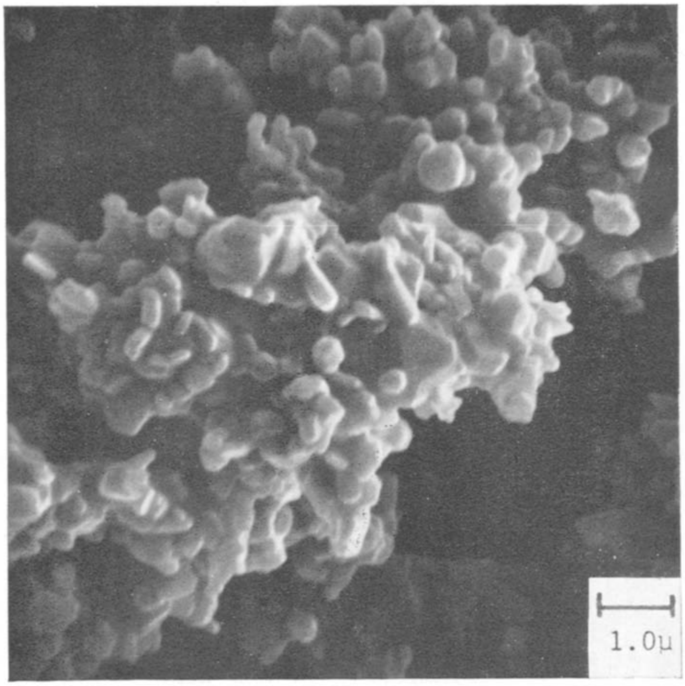

FIG. 2. $BaFe_{12}O_{19}$ prepared by the modified molten salt synthesis. 10,000×.

its neighbors by a thin layer of molten solvent. Higher concentrations (>40 wt%) of $MFe_{12}O_{19}$ result in the partial absence of this liquid layer and agglomeration of the crystallites. The required mass of MCO_3 ($BaCO_3$, $SrCO_3$) to give 110% of stoichiometry was added to the slurry solution of $Fe_2O_3 \cdot xH_2O$ in aqueous NaCl–KCl and blended. The resultant mixture was then dried in a spray-dry unit to yield an intimate mixture of the reactant and solvent components as a fine powder. This powder was then subjected to the reaction sequence determined previously; i.e., it was heated in a platinum crucible to 1025°C for 30 min in an air atmosphere.

Results. The product, freed from the solidified salt matrix, was single-phased, had theoretical saturation magnetization, and had H_{ci} values of 4900–5400 Oe for $BaFe_{12}O_{19}$ and 5970 Oe for $SrFe_{12}O_{19}$. Scanning electron microscope analysis (Fig. 2) of the crystallites revealed them to be identical to those obtained in the basic molten salt synthesis process. It was concluded that the high H_{ci} values observed result from a reduction of the defect [Fe(II)] concentration in the crystal lattice. The low Fe(II) concentration resulted from a combination of factors. There is more trapped air in the fine powder resulting from the spray-dry operation. The low temperature involved in the spray-dry operation lowers the equilibrium concentration of Fe(II) present as well as maximizing the content of chemically bound H_2O. Again, diffusion of oxygen into the reacting mixture once the solvent melts and the mixture collapses should not be significant in control of the Fe(II) content.

To determine if the intimate mixture of components and the fine particle size of the reaction mixture were of major importance, samples were prepared using commercial iron oxides slurried in the appropriate quantities of NaCl–KCl solution. With the required quantity of $BaCO_3$ added, the slurry solutions were spray dried, then reacted at elevated temperatures. In no case was the product statistically better than that obtained through the simple dry mixing of components. The intrinsic coercive field was still dependent on the depth of reaction mixture and the maximum value observed was 3700 Oe. The material was fully reacted and had the theoretical saturation magnetization. The most important factor is, therefore, that the Fe_2O_3 prepared in the present case minimizes the Fe(II) content in the product by either initially containing low Fe(II) contents and/or sufficient chemically bound H_2O to oxidize the Fe(II).

Additional experiments revealed that any ratio of NaOH–KOH, including pure NaOH, would yield equally excellent results. Further, the precipitation end-point pH could be varied from pH = 6.0 to pH = 7.10 without affecting the product magnetic quality.

Conclusions

There exists a direct synthetic process which yields $MFe_{12}O_{19}$ powders possessing near-theoretical magnetic properties. The process utilizes a molten salt solvent composed of NaCl and KCl in virtually any ratio. The main factor governing magnetic quality in this process is the presence of extremely low levels of Fe(II) in the crystal lattice. Reduction of the Fe(II) concentration is achieved through the use of a controlled Fe_2O_3 preparation starting with an aqueous $FeCl_3$ solution, using NaOH/KOH solution as precipitating agent to a fixed stoichiometric end-point as determined by pH, and limiting all pre-molten salt reaction processing to low temperature. The product characteristics of chemical purity, theoretical saturation magnetization, and H_{ci} values 90% of theoretical are equal to, or surpass, those obtained through the most elaborate preparative or treatment steps known.

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