Topochemical growth of textured polycrystalline barium hexaferrite from oriented antiferromagnetic $\alpha$-FeOOH nanorods

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Abstract
Nanorods of goethite, i.e. $\alpha$-FeOOH, were mixed with BaCO$_3$, dispersed in a polymer solution, and oriented under a 90 kOe magnetic field during polymerization. The orientation arose principally from the interaction of the magnetic field with the anisotropic antiferromagnetism of the goethite particles. The oriented antiferromagnetic particles act as seeds for the topochemical growth of BaFe$_{12}$O$_{19}$ ferrite grains along the [0001] direction. The degree of grain orientation was determined using magnetic measurements and orientation distribution functions and pole figures determined by electron backscatter diffraction analysis.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetic orientation of paramagnetic or diamagnetic materials has attracted a great deal of interest due to the significant enhancement realized in functional properties of highly crystallographically textured optical, electronic, thermal, mechanical and magnetic materials [1, 2]. Some non-ferromagnetic materials, such as polymers, carbon, cellulose fibers, carbon nanotubes and assorted crystallites, usually suspended in a liquid medium, have been shown to be aligned under magnetic fields. This phenomenon results from the interaction of magnetic fields with anisotropic features of these materials including uncompensated spins on surfaces, magnetic susceptibility, demagnetizing fields and other sources [3]. This magnetic orientation technique has been successfully applied to non-magnetic textured ceramic materials even under ‘dry’ ceramic processing conditions [4].

Ba M-type hexaferrite (henceforth BaM) has the magnetoplumbite structure and a stoichiometry of BaFe$_{12}$O$_{19}$. The magnetoplumbite structure has 32 atoms/f.u. and 64 atoms in a single unit cell. One property of this compound that is of particular value in microwave device design is the strong uniaxial anisotropy in which the magnetic easy direction aligns along the crystallographic $c$ axis. The high magnetic anisotropy field, $H_A \sim 17\,000$ Oe, can be adjusted by appropriate substitution for the Ba ion, allowing for tuning of the ferromagnetic resonance (FMR) frequency from $\sim 1$ to 100 GHz. This extraordinary degree of freedom makes BaM a choice material for many microwave and mm wave device applications, including monolithic microwave integrated circuit (MMIC) applications [5]. In many MMIC applications high crystallographic orientation is a requirement that necessitates the use of single crystals or highly oriented polycrystalline materials having low microwave FMR linewidths [6, 7]. Despite being considered a mature class of materials, the hexaferrites have received increased attention due to the needs of next-generation microwave devices and systems, especially in
areas of military and commercial communication and radar technologies.

In the present study, we have employed a magnetic orientation technique in which BaM crystallites nucleate and grow on antiferromagnetic $\alpha$-FeOOH seed particles having rod-like morphology. The $\alpha$-FeOOH nanorods, oriented while suspended in solution during polymerization, enable the topochemical growth of highly oriented BaM ferrite grains during a subsequent high temperature sintering. The resulting topochemical growth yields [0001]-textured ferrite grains, which were verified by both static magnetic measurements and the electron backscatter diffraction (EBSD) measurements. The EBSD technique provides advanced analysis of anisotropic crystalline materials in which high resolution chemical and structural mappings provide information on grain orientation and crystal quality. Such information is essential to not only the optimization of growth processes, but also in elucidating the microstructural dependence of magnetic properties [8].

2. Experimental details

The processes described herein begin with the ball milling for 4 h of a mixture consisting of 1 mol BaCO$_3$ (99.0% purity) and 12 mol $\alpha$-FeOOH (99.0% purity); this ratio leads to a stoichiometric M-type hexaferrite after sintering having the composition BaFe$_{12}$O$_{19}$. The $\alpha$-FeOOH nanorods have widths of 50–100 nm and lengths of 300–500 nm, corresponding to aspect ratios ranging from 3:1–10:1. The mixture was subsequently combined with a polymer solution followed by orientation of the goethite by the application of magnetic fields up to 90 kOe during chemical polymerization of the monomer matrix.

Our previous work indicates that the polymer network-assisted-alignment process (PNAAP) [9] was effective in the magnetic field orientation of ferrite materials as highly oriented compacts. In this paper, this technique is utilized to align the antiferromagnetic particles prior to sintering, which results in preferred crystal growth of Ba hexaferrite grains. Firstly, we synthesize the polymer solution consisting of the following: (i) acrylamide (AM) monomers as the primary monomers from which the gel network is built; (ii) methylenebisacrylamide (MBAM) monomers which serve as cross-linking agents in the gel and (iii) ammonium persulfate (APS) which catalyzes the polymerization process by activating trimethylolxylenediamine (TEMED) that partakes in the polymerization by combining with and activating the AM or MBAM monomers. The monomers were dissolved in deionized water, producing a pre-mix solution having approximately 14.85 wt% AM, 1.85 wt% MBAM and 70 wt% deionized water. Ammonium citrate tribasic (1.0–3.0 ml/100 g of mixed raw powders) was used as a dispersant and Dow Corning Y-30 antifoam emulsion (0.05–0.10 ml/100 g of the powders) aiding in the degassing of the suspension. Secondly, the mixed powders were added to form a suspension with 30–40 vol% solid content. The suspension was then cooled to 2–3 °C to extend the idle time between the addition of the catalysts and the onset of polymerization. After 10–30 min, APS and TEMED solutions were mixed into the suspension, yielding the final mixture. Note, the optimized composition sensitively depended upon the size distribution of the raw particles. The suspension was then cast into a mold and placed into the bore of a magnet (10–90 kOe), where it remained for 1–10 h. The amounts of catalysts were chosen to provide a reasonably long idle time, allowing the particles to align within the applied magnetic field. After removing the mold, the samples were dried for 24 h in air. The dry ‘green’ bodies were then placed in a vented furnace for burnout of the gel polymer. The burnout procedure began with a 1.5 °C min$^{-1}$ heating ramp rate to 650 °C, followed by a 10 h soak time, with a 20 °C min$^{-1}$ cooling rate to room temperature. The resulting loose green bodies were uniaxially pressed using 10–20 MPa to increase the density without losing preferred particle orientation. As a last step, the green body was sintered at 1350 °C in air for a period of 10 h.

3. Results and discussion

Figures 1(a) and (b) present magnetic hysteresis loops and scanning electron microscopy (SEM) images of the samples’ morphology in cross section prior to sintering. Figure 1(a) illustrates magnetic hysteresis loops for a randomly oriented sample. As shown, in the presence of a magnetic field aligned either in-plane or perpendicular to the plane of the compact, there are no signs of anisotropy in the magnetic hysteresis loops. However, the green compact (i.e. the compressed mixture of BaCO$_3$ and $\alpha$-FeOOH) exhibits a minor ferromagnetic hysteresis loop nucleated at a field of ~2 kOe. It is subsequently dominated by antiferromagnetic behavior that presumably arises from the $\alpha$-FeOOH grains. The iron (III) hydroxide goethite ($\alpha$-FeOOH) is a common authigenic mineral in sediments. It is antiferromagnetic, but may possess weak parasitic ferromagnetism that originates from defects such as impurities, dislocations, vacancies, etc, which in turn result in spin-canting or local exchange fields [10, 11]. The $\alpha$-FeOOH has a high coercivity and low Curie temperature, typically less than 100 °C. Our measurements indicate a saturation magnetization as $4\pi M_s$ of 0.46 G and a coercivity of ~110 Oe.

In contrast to the randomly oriented sample, the field-oriented sample exhibits a clear magnetic anisotropy, as presented in figure 1(b). The magnetic orientation yields an increase in both saturation magnetization and coercivity, i.e. $4\pi M_s = 0.95$ G and $H_c = 550$ Oe, for the measurement performed with the magnetic field aligned perpendicular to the sample plane. The magnetic anisotropy is further substantiated by the corresponding measurement in which the applied field is aligned parallel to the sample plane, i.e. presumably along the magnetic hard plane. We measured the degree of magnetic anisotropy, as $\eta = M_\parallel / M_\perp$, to be 0.38.

We postulate that the measured magnetic properties are dominated by microstructural properties; the insets to figures 1(a) and (b) represent random and oriented samples, respectively. By inspection, the oriented sample reveals $\alpha$-FeOOH particles having the majority rod axes perpendicular to the external field, whereas the sample not experiencing large applied
fields during processing appears to have more random distribution of particle axes. The magnetic orientation presented in figure 1(b) is assumed to originate from the presence of anisotropic antiferromagnetic susceptibility. However, it is noteworthy that a magnetic field strength of 90 kOe may likely change either local spin configurations, especially near defects, or the original canted-spin configuration, while orienting α-FeOOH particles. The high magnetic field obviously leads to an enhancement in both magnetization and coercivity, although the role of the aforementioned weak parasitic ferromagnetism upon the measured magnetic anisotropy remains unclear.

Figure 2, and its inset, present magnetic hysteresis loops and an SEM image of the sample surface morphology for an orientated sample after sintering at 1350°C for 10 h. The sample clearly demonstrates a strong magnetic anisotropy in magnetization along the two magnetic field orientations. Additionally, the saturation magnetization \( (4\pi M_s) \) is measured to be 4.2 kG, 6.7% lower than the expected value for single-crystal BaM, i.e. 4.5 kG [7]. A density of 4.8 g cm\(^{-3}\) was measured which is slightly lower than the single-crystal value and is likely responsible for this discrepancy. Nevertheless, a high crystalline quality is illustrated by the inset to figure 2.

The grain orientation and phase identification were obtained from x-ray diffraction (XRD) measurements using a Rigaku-U3 diffractometer with a Cu K\( \alpha \) radiation source. Figures 3(a) and (b) represent XRD patterns for pre-sintered samples processed with and without the application of the magnetic field during polymerization, respectively. Figure 3(c) is the corresponding data for the same sample in (b) after sintering at a temperature of 1350°C. Part (a) reveals the presence of randomly oriented grains, which are verified by examination of the five strongest diffraction peaks originating from the (111), (151), (002), (221) and (110) planes. In contrast to the random sample, the oriented sample of figure 3(b) demonstrates significant grain orientation resulting in enhanced amplitude of the diffraction peaks corresponding to the (110), (130) and (140) planes. Additionally, the (120) plane is also visible. For an orthorhombic structure, \((1k0)\) planes are not completely parallel and lead to a slight angle among the planes. Since the α-FeOOH particles are elongated along the [010] direction, it is predictable that the [010] direction aligns perpendicular to the applied magnetic field. As a result, XRD data are fully consistent with the SEM observations of figures 1 and 2. Figure 3(c) presents an XRD pattern for the orientated compact after sintering at 1350°C. It is unambiguous that all of the diffraction peaks can be indexed to the pure phase BaFe\(_{12}\)O\(_{19}\) structure. Moreover, it is observed that the (008), (0010), (0012), (0014), (0016), (0018) and (0020) planes are clearly detected. The presence of low amplitude diffraction peaks, e.g. (1118), (104) and (1017), is evidence for a small degree of misalignment that is discussed in greater detail in the EBSD section that follows. These data support the contention that (001) planes have aligned perpendicular to the applied magnetic field used in processing.

The nature of grain orientation and crystal quality for the topochemically grown BaM polycrystalline compact was
Figure 3. X-ray diffraction (XRD) patterns for (a) a green compact having not experienced magnetic field orientation during processing, (b) a green compact having experienced magnetic field orientation during polymerization and (c) an oriented compact sintered at 1350°C for 10 h. Here, green compact refers to the sample after polymer burnouts and before sintering. Solid and hollow circles denote BaCO₃ and α-FeOOH phases, respectively. The inset to the figures depicts a schematic of the compacted sample in which the shaded side represents the scanned surface for XRD measurements.

Further investigated using the electron backscatter diffraction technique [12]. Figure 4 shows an inverse pole figure (IPF) map orthogonal to the [0001] direction, i.e. perpendicular to the sample surface. The map provides the EBSD-determined crystallographic orientations which are depicted by the color of the stereographic triangle given below the map. The map shows predominantly shades of red, indicating the preference for [0001] texture. Several smaller ferrite grains are visible, however, acting as filler between the larger grains and these show largely random orientation.

Figure 5(a) presents the corresponding pole figure along the [0001] direction, calculated from the EBSD data of the IPF map. Figure 5(b) illustrates the orientation distribution function (ODF) for the topochemical sintered sample. The images are similar at every angular interval of 60° (ϕ1 angle: 0°–360° on presumably the c planes), which indicate a sixfold rotational symmetry to the material. These results reflect a strong [0001] texture of this hexagonal polycrystalline material.

Both the pole figure and the ODF function provide clear and unambiguous information concerning sample crystal texture. A primary [0001] orientation is clearly observed, but smaller fractions of [1010] and [2110] orientations are also present; these correspond to smaller misoriented ferrite grains. These results are superior to those earlier reported in samples processed by means of stress-induced orientation of plate-shaped α-FeOOH particles [13, 14]. Further improvements may be realized by applying either an optimal polymer solution or the use of BaCO₃ nanoparticles which we believe will enhance the degree of α-FeOOH particle orientation.

As previously conjectured, we believe that the anisotropy measured in the green compacts are due to an anisotropic susceptibility of the α-FeOOH particles. Taking the magnetic energy of a rod in an external magnetic field as

\[ E(\theta, H) = -(nH^2/2)[\chi_\perp + (\chi_\parallel - \chi_\perp) \cos^2 \theta] \]

where \( \chi_\parallel \) and \( \chi_\perp \) are the parallel and perpendicular components of the molar susceptibility relative to the rod axes, and \( \theta \) is the angle between the rod axis and the applied field \( H \). The magnetic orientation is based upon the minimization of \( E(\theta, H) \). Since the α-FeOOH nanorods possess anisotropic antiferromagnetic susceptibility (i.e. \( \chi_\perp > \chi_\parallel > 0 \) and \( \Delta \chi = \chi_\parallel - \chi_\perp = -3 \times 10^{-4} \)) [15], the long axis of the rods should align perpendicular to the applied magnetic field. This conjecture is indeed consistent with our experimental observations, as depicted in the inset to figure 1(b). The orientation of α-FeOOH nanorods enables a topochemical oriented growth during a one-step sintering process. The
following chemical processes occur concomitantly:

\[ 2 \alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2O_3 + H_2O \]
\[ 2\text{BaCO}_3 + 12 \alpha\text{-Fe}_2O_3 + (0.5 - x)O_2 \]
\[ \rightarrow 2\text{BaFeO}_3-x + 11 \alpha\text{-Fe}_2O_3 + 2\text{CO}_2 \]
\[ 2\text{BaFeO}_3-x + 11 \alpha\text{-Fe}_2O_3 \rightarrow 2\text{BaFe}_{12}O_{19} + (0.5 - x)O_2. \]

Because \( \alpha\text{-FeOOH} \) has an orthorhombic unit cell and the particles are elongated along the [010] direction [16], topochemical crystalline growth of BaM evolves along the following steps:

[001]\( \alpha\text{-FeOOH} \parallel [0001] \alpha\text{-Fe}_2O_3 \parallel [0001] \text{BaFe}_{12}O_{19}. \)

Therefore, a structural evolution occurs concomitantly with \( \alpha\text{-FeOOH} \) converting to \( \alpha\text{-Fe}_2O_3 \). \( \alpha\text{-FeOOH} \) is of orthorhombic structure: space group, \( Pbnm \) (62); \( a = 4.608 \text{ Å}, b = 9.956 \text{ Å} \) and \( c = 3.0215 \text{ Å} \), whereas \( \alpha\text{-Fe}_2O_3 \) belongs to a rhombohedral crystal system: space group, \( R3c \) (167); \( a = 5.02 \text{ Å}, b = 5.02 \text{ Å} \) and \( c = 13.73 \text{ Å} \). Specifically, the elongated axes of \( \alpha\text{-FeOOH} \) rods become the (0001) axes of the corresponding \( \alpha\text{-Fe}_2O_3 \) particles, which subsequently transforms to oriented [0001] \( \text{BaFe}_{12}O_{19} \) grains. The demonstrated topochemical orientation process results in polycrystalline specimens having strong preferred crystal texture by means of a final one-step sintering step. However, note that the grain orientation not only relies on magnetic field orientation, but also is very sensitive to the subsequent processes, such as polymer burnout, compaction and sintering conditions. Among those processes, it is noticed that a compaction process is critical to retain a high degree of the grain orientation. Nevertheless, this technique provides an advantage to present technologies that require two or more sintering steps to obtain a product of similar quality.

4. Conclusions

In summary, we report results of a new technique for the processing of highly textured polycrystalline ferrite materials. Antiferromagnetic rod-shaped goethite (\( \alpha\text{-FeOOH} \)) particles were employed to create a template for the nucleation and growth of textured BaM hexaferrite by an alignment of \( \alpha\text{-FeOOH} \) particles under the application of magnetic fields. The oriented \( \alpha\text{-FeOOH} \) particles were combined with \( \text{BaCO}_3 \) powders and consolidated in a polymer matrix. After a final one-step sintering, the BaM hexaferrite exhibits a high degree of grain orientation, which was evident in x-ray diffraction and
electron backscatter diffraction measurements. In particular, this topochemical growth has potential to be a valuable fabrication technique for a wide range of textured ceramics.

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References