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Growth of self-textured barium hexaferrite ceramics by normal sintering process and their anisotropic magnetic properties

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ABSTRACT

In this report a simple and low-cost technique for growing highly textured barium hexaferrite ceramics without the need for flux or seed crystals to achieve grain orientation is demonstrated. Plate-like shaped barium hexaferrite particles were synthesized using a solid-state reaction process and then aligned under a weak magnetic field, followed by uniaxial compaction. The aligned hexaferrite particles appear to serve as seeds, forming textured grains during sintering. The development of texture was verified by X-ray diffraction (XRD), electron backscatter diffraction (EBSD), and vibration sample magnetometer (VSM) measurements. The prepared high-quality hexaferrite ceramics exhibited good anisotropic magnetic properties, comparable to those of single crystal counterparts. A mechanism for the formation of the self-textured grain growth of the barium hexaferrite ceramics, which involves grain boundary and lattice diffusion and interface reaction processes, is proposed.

1. Introduction

Barium containing M-type hexaferrites with the stoichiometry of $BaFe_{12}O_{19}$ (BaM) have been widely investigated because of their unique anisotropic magnetic properties, which are suitable for a variety of micro-wave and millimeter-wave applications [1–5]. In the past decade, there has been widespread interest in the fabrication of barium hexaferrite single crystals, because they exhibit high saturation magnetization and large magneto-crystalline anisotropy along the crystallographic *c*-axis [6,7]. Such high performance single crystals can enhance device functionality, while meeting the demands of device miniaturization for better systems integration. However, synthesizing these single crystals is a very expensive and complicated undertaking, due to their high temperature melting point, and the high reactivities of the constituents. For these reasons, high-performance textured hexaferrites are considered to be a promising alternative, because they exhibit properties comparable to those of the single crystal hexaferrites [5,8,9].

Several processing techniques, including tape casting [10], screen-printing of multilayers [11], hot forging [12], and template grain growth [13,14], have been employed to produce textured ceramics. However, as yet, these processes have been sparingly utilized in the synthesis of some perovskite and bismuth layer-structured ferroelectrics and tungsten bronze-type structures. In previous studies where they were employed, quite a wide range of variation in the degree of texturing of the ceramics has been reported, depending on the processing conditions. Further, the synthesis of textured hexaferrites is a time-consuming process, and also requires special processing conditions, such as a strong external magnetic field during the sintering process [5,7,9,15].

In the present study, we modified the template grain growth approach to prepare highly-textured hexaferrite ceramics, using simple normal sintering with optimized process parameters. Plate-like shaped BaM particles, prepared using a solid-state reaction process, were aligned under a weak magnetic field, and then uniaxially compacted, to orient them along their c-axis. These aligned particles serve as seeds to form the textured grain growth during sintering. EBSD, XRD and VSM measurements were employed to verify the grain orientation. The texturing of the hexaferrite ceramics leads to enhanced anisotropic magnetic properties.

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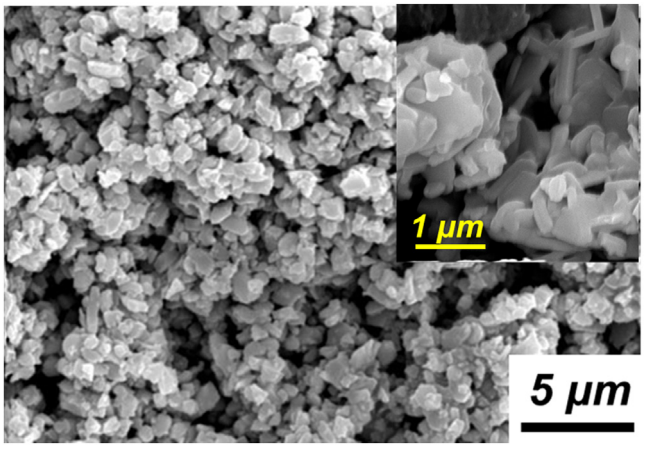

Fig. 1. SEM micrograph of barium hexaferrite powder prepared by the solid-state-reaction method. Inset: plate-like structures were observed in the powder particles.

2. Experimental

Barium hexaferrite powder with the composition $BaFe_{12}O_{19}$ was made using a conventional solid-state-reaction (SSR) method, as follows. High-purity (>99.9%) $BaCO_3$, and Fe_2O_3 (both from Sigma Aldrich Co., USA) fine powders were mixed in the desired stoichiometric ratios and ball-milled at room temperature for 15 h using yttrium stabilized zirconia balls in isopropanol solution. The slurry was dried using a rotary evaporator at 80 °C and then calcined at 1200 °C for 2 h for phase formation.

Fig. 1 shows a scanning electron microscope (SEM) micrograph of the as-prepared powder particles. The shapes of the majority of the powder particles were observed to be plate-like in structure with an average size of 1 μm. These particles were transferred into a glass jar and oriented using a magnetic field that was swept across the jar for 1 h. The field used was measured to be ~3–4 kOe, which is slightly higher than the coercive magnetic field strength of BaM. This allowed the particles within the applied magnetic field to align with each other. After removing the magnetic field, the powder was uniaxially pressed at load of 0.2 MPa into circular pellets of 10 mm diameter and a thickness of 2 mm. The aligned particles rearranged themselves perpendicular to the applied pressing direction by sliding [16] and served as seeds to grow textured barium hexaferrite ceramics.

Next, the density of the green body was increased by cold isostatic pressing (CIP) at 200 MPa. As a last step, the specimens were sintered at an optimized temperature for 4 h soak time. The sintered disc specimens were machined to dimensions of 1 mm (thickness) × 5 mm (length) × 5 mm (width), and used for characterization. The densities were measured by Archimedes' principle, using *o*-Xylene (density = 0.879 g/cm^3 at 20 °C) as the liquid media.

The specimens were polished and etched with hydrofluoric acid 48 wt.% in water and then washed with flowing water. The etched specimens were then dried, Au-sputter-coated and examined under a scanning electron microscope (SEM; JEOL, JSM-5800, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS) to analyze their microstructure and elemental distribution.

The phase and grain orientation analyses were carried out using an XRD (Rigaku D/MAX-2500, Japan) system operated at 40 kV and 100 mA with CuK_α (1.5406 Å) source, and an EBSD (Oxford Instruments, NordlysNano, UK) attached to a field emission scanning electron microscope (FESEM; JEOL, JSM-7001F, Japan). The sample was hot-mounted by conductive resin and the mechanical automatic-polishing was performed using 9, 3, 1 μm diamond and 0.04 μm colloidal silica suspensions. EBSD mapping was performed at an acceleration voltage of 10 kV to avoid image drift by electron charging. The hit rate for identifying the Kikuchi patterns during orientation mapping was over 90%, irrespective of the measuring conditions, such as magnification and working distance. The EBSD results were post-processed using Aztec 3.2 (Oxford Instruments, UK) and OIM 7.3 (EDAX, USA) software. The room temperature magnetic properties were recorded on a LakeShore VSM with a 736 VSM controller. The field increment per data point was fixed at 20 Oe, while sweeping the field from −15 kOe to 15 kOe.

3. Results

The grain size and shape of the sintered samples were characterized by SEM analysis, as shown in Fig. 2. Top view SEM micrographs of the polished and etched surfaces, i.e., the compacted surfaces of the samples, are shown in Fig. 2(a) and (b), respectively, for the specimens sintered at 1200 °C and 1300 °C for 4 h; these are designated ST1200 and ST1300. For the ST1200 samples the measured density values were 4.95 (±0.16) g/cm^3, and the density values were 5.17 (±0.02) g/cm^3 for ST1300. The grain size was calculated from the average length of the grains using the image analyzer software, ImageJ [17]. Variation in the average grain size (d) with sintering temperature (T_s) is shown in Fig. 2(c). In the ST1200 sample, the grains were small and elongated, and grain size varied from 2 to 5 μm. This is about 2–5 times larger than the size of the as-prepared powder particles. However, after sintering at higher temperatures (1300 °C), near the eutectic temperature of the BaM [1], the microstructure consisted of abnormally grown grains (AGG), as shown in Fig. 2(b).

In the case of the AGG samples, only an average size of abnormal grains was considered for calculation of the d value. The error bar represents the mean deviation in grain size. Duplex microstructures (see the magnified microstructures in Fig. 2(b)-ii and iii, comprised of a mixture of small hexagonal grains of about 2–6 μm) and large abnormal grains with sizes of about a few hundreds of micrometers, were observed in the high temperature (1300 °C) sintered samples. It should be noted that while the formation of duplex (or bimodal) microstructure is a characteristic feature of the AGG process, and has been encountered in many ceramic systems [8,18,19], self-texturing during the AGG process is a unique behavior of the barium hexaferrite ceramic samples prepared in the present work. After sintering the hexaferrite ceramics, grain boundaries with different shapes were identified, as indicated by the white and red arrows in Fig. 2(b).

To identify the chemical composition of the samples, EDS analysis was conducted. The ratios of Fe/Ba were measured for the entire scanned area of the sample, as well as at the interface regions (solid pink arrow) between the large grain and small-grain regions of the duplex microstructure. The results are presented in Fig. 1(d). Within the detection error range of the EDS the measured Fe/Ba ratio is about 12, which is a good match to the stoichiometric composition of the barium hexaferrite system.

Fig. 3(a) represents the XRD patterns of specimens ST1200 and ST1300. The patterns were taken from a radial surface (the surface normal to the compaction direction) of the specimens. Based on the standard diffraction data [JCPDS data card no.: 84-0757], all of the diffraction peaks can be indexed on the basis of the hexagonal unit cell of space group $P6_3/mmc$ symmetry, which suggests that the specimens possess pure $BaFe_{12}O_{19}$ phases without any detectable impurities [20], as had already been verified by chemical EDS analysis.

The lattice parameters determined by the *CrytalSleuth* software [21] were found to be: a = b = 5.91 Å, c = 23.28 Å and V = 704.0 Å^3. These sample values are relatively close to those reported for the bulk polycrystalline ceramics: a = b = 5.89 Å, c = 23.19 Å and V = 696.2 Å^3 [22]. The XRD pattern of sample ST1200 revealed

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