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# Large-scale chemical synthesis of shape and size controlled $BaFe_{12-x}Sc_xO_{19}$ platelets for in-plane oriented thick screen printed films

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Scandium (Sc) doped, single phase $BaFe_{12-x}Sc_xO_{19}$ ($x=0.3$ and 0.8) were prepared at large scale (10 g) by a modified chemical coprecipitation technique. The scanning electron micrograph analysis shows the formation of nearly uniform hexagonal platelets with an average size of $<1$ $\mu$m. The sizes of the platelets were controlled by sintering temperature. The screen printed, in-plane oriented films were annealed at different temperatures to produce a dense and thick ferrite film. The hysteresis loops for $x=0.3$ show a squareness ratio of 0.9 and the saturation magnetic moment of 3700 G and the coercivity of 250 Oe. The saturation magnetic moment was decreased with increase of Sc substitution. Ferromagnetic resonance measurements exhibited a peak-to-peak derivative linewidth ($\Delta H$) of ~800 Oe at 34 GHz for $x=0.3$ and at 37 GHz for the $x=0.8$ film. The Lande spectroscopic splitting factor ($g$) value for the screen printed films was found to be 1.92 for $x=0.3$ and 2.01 for $x=0.8$. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2839599]

## I. INTRODUCTION

The design of $X$-band circulators and phase shifters requires the low anisotropy field compared with the pure barium ferrite ($H_k \sim 17$ kOe), high Néel temperature, high remanance and saturation magnetization, and low FMR linewidth ($<300$ Oe). The Sc doping will stabilize the valence state of $Fe^{3+}$ and will avoid the high loss tangents.[1] The anisotropic field can vary over a wide range as a function of the level of substitution.[2] In addition to the composition, shape, size, and thickness, orientation of the particles has a significant effect on the microwave absorption properties. Since the single domain[3] size of the barium hexaferrite is about 1 $\mu$m, preparing the size and shape controlled particles using the bottom-up approach is more desirable than the conventional ceramic method. Here, we prepared the Sc doped hexaferrites $BaFe_{12-x}Sc_xO_{19}$ ($x=0.3$ and 0.8) by using the modified coprecipitation method. The particles were screen printed, in-plane oriented, and annealed as thick films and we studied their structural, magnetic, and microwave properties.

## II. EXPERIMENTAL

The $BaFe_{12-x}Sc_xO_{19}$ particle processing experiments were carried out using the iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.9%, Sigma Aldrich), barium chloride ($BaCl_2 \cdot 2H_2O$, 99.9%, Sigma Aldrich), and scandium(III) acetate hydrate ($(CH_3CO_2)_3Sc \cdot xH_2O$, 99.9%) as raw materials and dissolved in distilled water with the required ratio. The mixed metal precursor solution was introduced slowly into the mixture of $NaOH-Na_2CO_3$ alkaline solution. When an alkaline solution was added, an intermediate precursor containing $BaFe_{12-x}Sc_xO_{19}$ was formed. The particles were thoroughly washed several times with distilled water and then filtered. The filtered intermediate particles were dried at 100 °C for 12 h. In order to obtain single phase crystallographic characteristics and magnetic properties, a post-thermal annealing is required. Samples are heated in air at a rate of about 6 °C/min. The temperature is then maintained at 1000–1100 °C for 5 h, after which a natural cooling is carried out. The sintered samples were dispersed either using a roller mill or a planetary ball mill while maintaining the particle shape. The hexagonal platelet shaped particles were suspended within an epoxy and screen printed on a dielectric substrate ($Al_2O_3$) with a thickness of about 1–2 mm. Particles in the still green film were oriented along the in-plane direction under an external dc magnetic field of 15 kOe. The screen printed and in-plane oriented green compact were annealed at various temperatures to make highly dense thick films for the further characterization. Due to the space constraints we are herewith presenting the data for $x=0.3$ and $x=0.8$.

The crystallographic phase of the particles was analyzed using the $\theta$-$2\theta$ x-ray powder diffraction (XRD) (Rigaku-Cu $K\alpha$ radiation, $\lambda=1.545\,06$ Å) technique. The surface morphology of the particles and films was examined by scanning electron microscopy (SEM) (Hitachi S-4100). Chemical analyses have been carried out using an induction coupled plasma spectrophotometer (ICP 20P VG Elemental Plasma Quad2) as well as a SEM-EDAX (energy dispersive analysis x-ray spectra) facility. The magnetic properties were measured using a vibrating sample magnetometer (VSM) (ADE Technologies). FMR measurements were performed in both out-of-plane and in-plane FMR conditions by using a $TE_{01}$ rectangular waveguide at room temperature in $K_a$-band fre-

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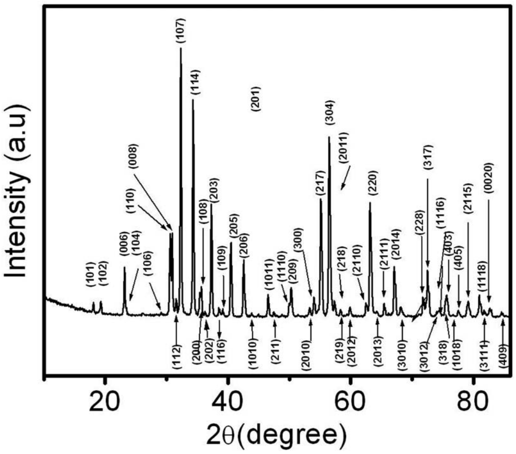

FIG. 1. X-ray diffractogram of representative $BaFe_{11.2}Sc_{0.8}O_{19}$ powder sample.

quency. The FMR data allow us to calculate the effective magnetization, anisotropy field, Lande spectroscopic splitting factor, and FMR linewidth.

## III. RESULTS AND DISCUSSION

The x-ray diffraction pattern in Fig. 1 confirmed the formation of pure single phase Sc doped Ba hexaferrite having the magnetoplumbite structure.[4] Chemical analysis and SEM-EDAX analysis showed that the samples had the required stochiometric ratios of Ba, Fe, and Sc. The sizes of the platelets were controlled by the sintering temperature as shown in Fig. 2. When the particles were sintered at 1000 °C, the average particle size is about 350 nm [Fig. 2(a)]. However, when the particles were sintered at 1150 °C for 2 h, the average particle was increase to 1 $\mu$m [Fig 2(b)]. The hexagonal platelet morphology was well maintained even after low energy ball milling and this type of hexagonal platelet shape is highly desired in achieving the *c*-axis particle orientation in the screen printed films. The screen printed films were then sintered at different temperatures to produce a dense and thick film and the magnetic properties are shown in Table I. The density of the film was 2.5 $g/cm^3$. The hysteresis loops for the as-prepared and screen printed, in-plane oriented $BaFe_{11.7}Sc_{0.3}O_{19}$ film show a squareness ratio $(S=M_r/M_s)$ of 0.88, a coercivity of 230 Oe, and the saturation magnetic moment $(4\pi M_s)$ of 3700 G. After sintering at 700 °C for 1 h the film becomes hard and dense and the in-plane orientation was stabilized without deteriorating the magnetic properties. Similar experiments were carried out for the $BaFe_{11.2}Sc_{0.8}O_{19}$ thick films. After sintering at 700 °C for 1 h, the squareness was stabilized with a small increase in coercivity [Fig. 3]. When the sintering temperature was increased the squareness starts to decrease and the coercivity increased. Here we have taken into account two important parameters: (i) The saturation magnetic moment decreases with increasing the substitution of Sc due to the occupation of nonmagnetic Sc at the octahedral sites $(4f_{VI})$ belonging to the *R* structural block of barium hexaferrite. As a part of the Sc ions $4f_{VI}-12k$ interactions, a decrease in magnetic moment has been observed because the antiferromagnetic order among up and down sublattices are cancelled, so that $12k$ ions with different numbers of magnetic $4f_{VI}$ neighbors have different magnetizations.[5] (ii) Optimal

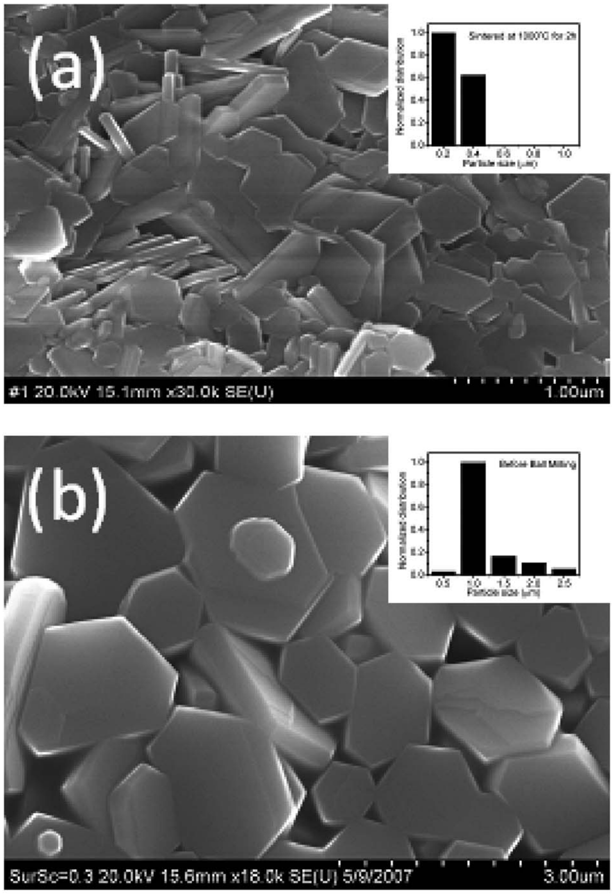

FIG. 2. Scanning electron micrographs of $BaFe_{11.7}Sc_{0.3}O_{19}$ sintered at (a) 1000 °C for 2 h, (b) 1150 °C for 2 h, (b) the insets of the figures show the particle size distribution.

TABLE I. Magnetic properties of in-plane oriented $BaFe_{12-x}Sc_xO_{19}$ ($x=0.3$ and 0.8) thick films annealed at various temperatures.

| $x=0.3$ | Squareness (in plane) | Squareness (out of plane) | Coercivity (in plane) (Oe) | Coercivity (out of plane) (Oe) |
|---|---|---|---|---|
| Before sintering | 0.88 | 0.07 | 242 | 348.44 |
| 700°C for 1 h | 0.88 | 0.06 | 258 | 388 |
| 900°C for 1 h | 0.86 | 0.09 | 255 | 363 |
| 1000°C for 1 h | 0.85 | 0.1 | 254 | 322 |
| 1050 °C for 1 h | 0.84 | 0.14 | 260 | 358 |
| 1100 °C for 1 h | 0.81 | 0.19 | 179 | 388 |

| $x=0.8$ | Squareness (in plane) | Squareness (out of plane) | Coercivity (in plane) (Oe) | Coercivity (out of plane) (Oe) |
|---|---|---|---|---|
| Before sintering | 0.79 | 0.22 | 929 | 970.01 |
| 700 °C for 1 h | 0.8 | 0.22 | 992 | 923 |
| 900 °C for 1 h | 0.78 | 0.28 | 1870 | 1593 |
| 1000 °C for 1 h | 0.64 | 0.42 | 2157 | 2064 |
| 1050 °C for 1 h | 0.65 | 0.41 | 2545 | 2010 |
| 1100 °C for 1 h | 0.61 | 0.42 | 232 | 2194 |

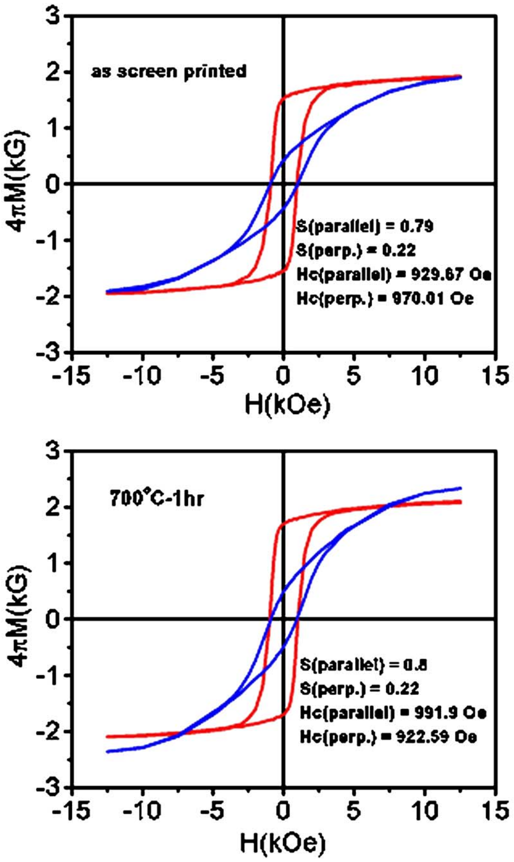

FIG. 3. (Color online) The hysteresis loops of the $BaFe_{11.2}Sc_{0.8}O_{19}$ after annealing at 700 °C for 1 h. The inequivalency in the in-plane measurement near the maximum field is related to the pole gap.

sintering temperature varies for the different amount of Sc substitution as shown in Table I. Even though the reason is unclear at present, we speculate that the number of Sc ions occupying the *R* structural block may influence the sintering temperature to keep better in-plane orientation.

FMR measurements were performed by applying a swept dc magnetic field parallel to the film plane (along the *c*-axis), i.e., parallel FMR configuration. The frequency was fixed during each field sweep and the measurements were taken for a wide range from 27 to 40 GHz. When $H_{\text{ext}}$ is parallel to the film, the FMR condition is given as follws:[6]

$$\frac{\omega}{\gamma} = \sqrt{(H_{\text{ext}} + H_A)(H_{\text{ext}} + H_A + 4\pi M_S)},$$

where $\omega=2\pi f$ and $\gamma=2\pi(g \times 1.4 \times 10^6)$ Hz/Oe. Figure 4 shows the variation of FMR derivative linewidth ($\Delta H$) as a function of frequency over a range of 27–40 GHz for the $x=0.3$ and 0.8 samples. Minimum linewidths of 800 and 1500 Oe were realized for the $x=0.3$ and 0.8 films, respectively. The broadening of the linewidth is also not linearly proportional to the frequency as shown in Fig. 4 which is usually observed for single crystals and epitaxial films. This is due to the large role of extrinsic loss mechanisms (for example, presence of porosity) that often do not have a linear relationship with frequency.[7] Hence, it is possible to produce in-plane oriented thick films at low cost using the present method. The linewidth can be further reduced by improving the in-plane orientation and density of the film. Experimental values of *g* (Lande spectroscopic splitting factor) were deduced from the relation between resonant frequencies versus resonance field for the screen printed films and were found to be 1.92 for $x=0.3$ and 2.01 for $x=0.8$. This is in good agreement with the value $g=2$ found for bulk samples.[8]

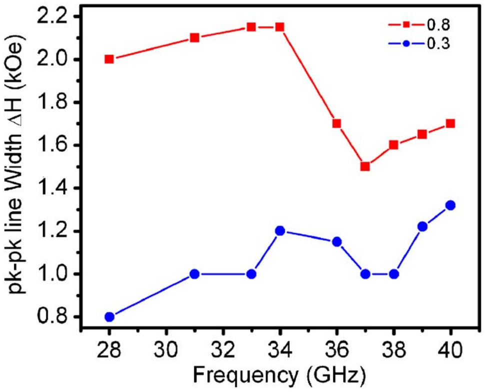

FIG. 4. (Color online) FMR linewidth ($\Delta H$) vs frequency for the in-plane oriented, screen printed annealed $BaFe_{11.7}Sc_{0.3}O_{19}$ and $BaFe_{11.2}Sc_{0.8}O_{19}$ films.

## IV. CONCLUSIONS

Large-scale chemical synthesis of phase pure Sc doped barium hexaferrite platelets was prepared by a modified coprecipitation method. The size of the platelets was controlled by the sintering temperature. The in-plane oriented, screen printed thick films show a squareness ratio of about 0.9 and a minimum linewidth of 800 Oe at 34 GHz for the $x=0.3$ and 1500 Oe at 37 GHz for the $x=0.8$ samples. The saturation magnetic moment decreases with increasing Sc ion substitution. The high squareness ratio, coercivity, and narrow FMR linewidth depend strongly on the sintering temperature and the resulting density of the film.

## ACKNOWLEDGMENTS

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