



Improvement in magnetic properties of La substituted BaFe₁₂O₁₉ particles prepared with an unusually low Fe/Ba molar ratio

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ABSTRACT

In this study, effect of lanthanum substitution on the phase composition, lattice parameters and magnetic properties of barium hexaferrite has been studied in samples synthesized in ammonium nitrate melt. Samples, prepared with different lanthanum amount and having various initial Fe/(Ba+La) ratios in between 12 and 2 $\{(Ba_{1-x}La_x) \cdot n Fe_2O_3, \text{ where } 0 \leq x \leq 1 \text{ and } 1 \leq n \leq 6\}$, are sintered at temperatures from 800 to 1200 °C. The lattice parameters, both *a* and *c*, decreases with increasing La amount which results in a decrease of the unit cell volume. The scanning electron microscope micrographs show that the pure and La-substituted sample with *x*=0.3, both calcinated at 1000 °C, have grain sizes smaller than 1 μm. The coercivities of the La-substituted samples increase with increasing La amount and reaches to a maximum value of 5.73 kOe, when *x*=0.3. Sintering at higher temperatures (above 1000 °C) decreases the coercivity, resembling a transition from single to multi-domain behavior of the particles, while saturation magnetization of the samples continues to increase due to the increasing grain size. Magnetization measurements of the samples prepared with different Fe/(Ba+La) molar ratios, *n*'s, revealed that the specific saturation magnetization slightly increases with decreasing *n*, while coercivities fluctuates around 5.5 kOe. However, a sharp increase in the saturation magnetization has been observed in the sample having *n*=1 and washed in HCl. It was measured as 59.2 emu/g at 15 kOe, which is higher than that of the pure sample (57.5 emu/g). Thus, the magnetic parameters are optimized in the sample Ba_{0.7}La_{0.3}Fe₁₂O₁₉ so as to maximize both coercivity and specific saturation magnetization in the HCl-washed sample synthesized by starting with an unusually low Fe/(Ba+La) molar ratio of 2 (or *n*=1).

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1. Introduction

Barium hexaferrites (BaFe₁₂O₁₉) have been extensively used as permanent magnets, microwave devices and magnetic recording media due to their attractive physical properties such as reliable magnetization, high coercive force, large magneto crystalline anisotropy and relatively high Curie temperature, as well as excellent chemical stability and corrosion resistivity. The magnetic properties of the hexaferrites used in electronic and recording industries depend crucially on the size, shape, purity and magnetic stability of the barium ferrite particles. These particles should have single-domain structure, pure phase, high coercivity and relatively high saturation magnetization. In other words, magnetic properties of these materials depend mostly on their grain size and phase purity which are very much affected by the synthesis techniques. There are many preparation methods to synthesize barium ferrite, including the traditional ceramic sintering route, which is usually carried out above 1200 °C,

the micro-emulsion [1], hydro-thermal reaction [2], glass crystallization [3], salt-melt technique [4], the sol-gel technique [5], the co-precipitation method [6], the microwave plasma technique [7], oxidation in nitric acid method [8], and ammonium nitrate melt (ANM) technique [9].

The magnetic properties of BaFe₁₂O₁₉ can be improved by the elemental substitutions to Ba²⁺- or Fe³⁺-sites, or both [10–14]. For Ba ions, metal ions having much larger ionic radii compared with the Fe ion radius such as La, can be used for enhancing the hard magnetic properties [15–17]. As shown in earlier research, La³⁺ ions totally can substitute all Ba ions of the hexaferrite, suggesting change in Fe³⁺ ions to Fe²⁺ ions on 2a crystallographic sites, in which the strong Fe²⁺ ion anisotropy attributes to increase magneto crystalline anisotropy or coercive field [10]. The La³⁺ ions may contribute to a change of new magnetic interactions, thus can improve the magnetic properties. When La is partially substituted to Ba- or Sr-sites in M-type hexaferrites, it was reported in the literature that saturation magnetization generally increases first and then decreases as La amount increases [10,11,13,15]. In these works, samples are calcinated at quite high temperatures around 1300 °C which leads to the

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formation of large grains (i.e., $> 1 \mu\text{m}$) with high magnetization, about 70–75 emu/g. Despite the considerable increase in coercivity, it remains around 2 kOe in BaM [10,11,14] and 3–4 kOe depending on the sintering temperature in SrM [15]. Contrary results were also reported in Ref. [18], which shows that saturation magnetization remains almost the same and there is only slight increase in coercivity (5%) as La amount increases in SrM samples. It should be noted that, in many of the references mentioned above, substituted La amount is limited to a small ranges. For instance, in Ref. [10], it varies between $x=0.00$ and 0.20 in $\text{Ba}_{1-x}(\text{La or Pr})_x\text{Fe}_{12}\text{O}_{19}$ samples and the same range is studied for $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ in Ref. [15], and up to $x=0.3$ in Ref. [11]. Very recently, Seifert et al. [19] studied the effect of La substitution in SrM samples in the range till all Sr ions are replaced by La ones. In this paper, magnetization measurements were performed at low temperatures, 5 K, and revealed that saturation magnetization decreases with increasing La concentration. In the literature, substitutions of La together with another cation to Ba/Sr and Fe-sites of M-type hexaferrites have also been reported [12,13,20,21]. Among these, La–Co substitutions to SrM, for example, cause remarkable increase in coercivity from 3.5 to 6.7 kOe and quite high saturation magnetization up to 65 emu/g [21]. La–Zn substitutions to BaM sharply decrease coercivity from 5.5 to 2 kOe with increasing doping concentration while the magnetization first increases to 80 emu/g and then decreases below 50 emu/g [13].

Synthesis of single domain hexaferrites having high saturation magnetization together with high coercivity is of great importance from both scientific and industrial point of view. To achieve this, synthetic parameters like calcination temperature, (Ba or Sr):Fe ratio, doping level, HCl treatment, etc. should be optimized. The optimal (Ba or Sr):Fe ratio is important to avoid formation of impurity phases like hematite ($\alpha\text{-Fe}_2\text{O}_3$). Besides, to eliminate the non-magnetic barium monoferrite phase (BaFe_2O_4), the annealed powders can be washed with hydrochloric acid (HCl) [22].

In this work, we aimed to synthesize single domain La-substituted BaM hexaferrite nanoparticles with high magnetization and high coercivity by optimizing the preparation conditions. Up to best of our knowledge, there is no systematic approach in the literature to investigate the effect of La substitution to BaM by considering all the environmental variables mentioned above. For this reason, we decided to make further investigation on this subject. As a first stage of the optimization studies, we have preferred to use ANM technique [9] rather than the solid state reaction route to synthesize

$\text{Ba}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ($0.0 \leq x \leq 1.0$). Having determined the best calcination temperature and optimum La content to have single domain particles, several powders were prepared with different Fe/(Ba+La) ratio to maximize both saturation magnetization and the coercivity. Finally, HCl treatment was applied to remove barium monoferrite phase which increases with decreasing Fe/(Ba+La) ratio.

2. Experimental

Appropriate amounts of BaCO_3 , Fe_2O_3 and La_2O_3 powders of high purity were weighed and mixed to prepare $(\text{Ba}_{1-x}\text{La}_x) \cdot n\text{Fe}_2\text{O}_3$ ($0.0 \leq x \leq 1.0$ and $1 \leq n \leq 6$) samples having various Fe/(Ba+La) ratios between 2 and 12. The mixed powder was put into the melted ammonium nitrate. The solution was mixed on a hot plate with magnetic stirrer until the liquid phases disappear. Before grinding in an agate mortar for 15 min, small amount of isopropyl alcohol was added to make wet grinding. The precursor was calcinated at 450°C for 5 h to remove possible organic compounds. Then, it was again ground for 15 min with isopropyl alcohol and dried, pelletized under the pressure of 200 MPa. In our previous publication, it was shown that pelletizing before calcinations may improve the hard phase fraction and thus the magnetization of the material [23]. The pressed disk-shaped pellets (diameter 16 mm, and thickness 3 mm) were sintered at $800\text{--}1200^\circ\text{C}$ for 2 h in air and cooled in the furnace. Finally, another grinding process took place for 15 min to obtain the samples in powder form which were washed with HCl and measured in VSM.

Structural analysis was done by Rigaku–Miniflex diffractometer ($\text{Cu-K}\alpha$) utilizing the ICDD qualitative analysis software and by scanning electron microscope (JEOL 6335F, Field Emission Gun). The lattice parameters were calculated using the least-squares computer program, DICVOL 04. The magnetic properties of the samples were examined at room temperature using the vibrating sample magnetometer (LDJ, Electronics Inc., Model 9600) with maximum field up to 15 kOe.

3. Results and discussion

3.1. Structural characterization

The X-ray diffraction patterns of $(\text{Ba}_{1-x}\text{La}_x) \cdot n\text{Fe}_2\text{O}_3$ ($x=0$, 0–1.0 with $n=6$) hexaferrite powders sintered at 1000°C for 2 h

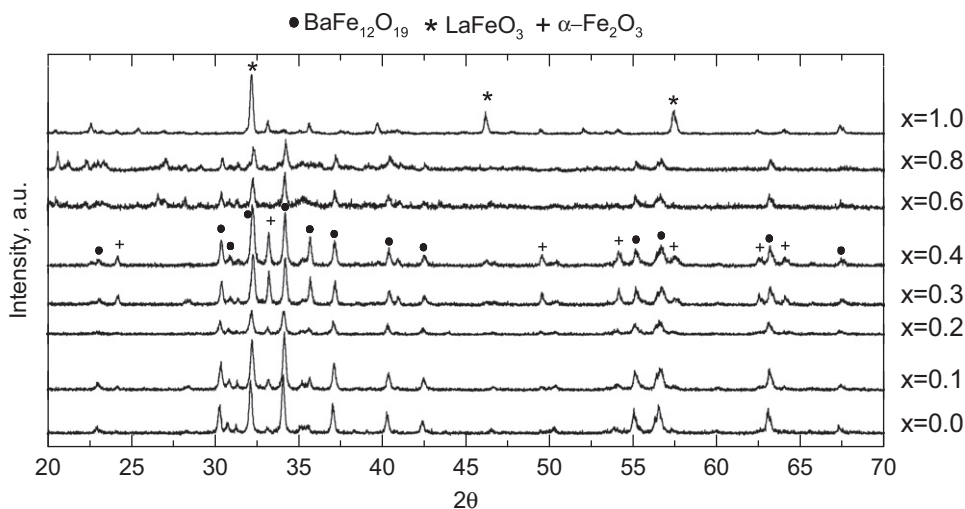


Fig. 1. XRD patterns of the pure and La-substituted samples, $\text{Ba}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$, x increases from bottom to top as 0.0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0.

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