

## Solvothermal Synthesis and Magnetic Properties of La-Substituted Barium Ferrite

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A series of La-substituted barium ferrite ( $\text{Ba}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ,  $0 \leq x \leq 0.2$ ) have been prepared through a solvothermal route and routine high-temperature calcination. Compared with some existing techniques, this solvothermal method shows some advantages in simplicity and low cost, and the obtained products exhibit high-purity crystalline phase, small particle size, and strong magnetic properties.

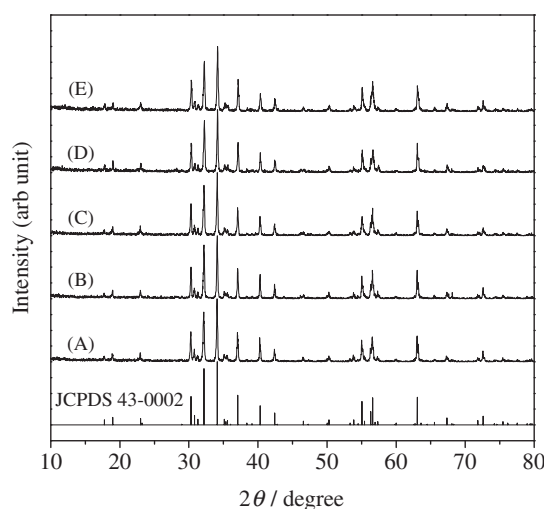
M-type barium ferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) with space group  $P6_3/mmc$  has been widely used as permanent magnets, magnetic recording media, and microwave devices due to its appealing chemical and physical properties such as high saturation magnetization, large coercivity, good chemical stability, and corrosion resistance.<sup>1–3</sup> In order to fulfill its applications in different fields, heteroatom-substitution has been considered as a common strategy to modulate material properties in the past decades.<sup>4–6</sup> The unique electric and magnetic properties of rare earth ions are widely utilized,<sup>7,8</sup> and it was reported that the replacement of  $\text{Ba}^{2+}$  by  $\text{La}^{3+}$  would make  $\text{Fe}^{3+}$  change into  $\text{Fe}^{2+}$  at 2a sites and induce an increase in magnetocrystalline anisotropy by strong ion anisotropy of  $\text{Fe}^{2+}$ ; thus, La-substituted  $\text{BaFe}_{12}\text{O}_{19}$  has received more and more attention in recent years.<sup>4,9–16</sup>

It is well known that technological applications require  $\text{BaFe}_{12}\text{O}_{19}$  particles to be a single magnetic domain, with good chemical homogeneity and narrow particle size distribution, which is inaccessible by conventional ceramic routes; thus, several unconventional techniques such as citric acid-assisted sol–gel,<sup>10–14</sup> coprecipitation/molten salt,<sup>4</sup> ammonium nitrate melt,<sup>15</sup> and reverse-microemulsion techniques,<sup>16</sup> have been applied to prepare fine La-substituted  $\text{BaFe}_{12}\text{O}_{19}$  particles. However, compared with conventional ceramic methods, a gap to real industrial applications still exists as these routes always possess relatively complex preparative processes and rigorous conditions, even excessive consumption of organic solvent, surfactants, and Ba species. Therefore, a simple method for fine La-substituted  $\text{BaFe}_{12}\text{O}_{19}$  particles is still desirable.

Recently, we developed a solvothermal route for  $\text{BaFe}_{12}\text{O}_{19}$  nanoparticles,<sup>17</sup> and the resultant products showed high-purity crystalline phase, small particle size, improved magnetic properties, and characteristic of single magnetic domains. By considering the advantages and results of a solvothermal system for pure barium ferrite, we attempted to synthesize La-substituted  $\text{BaFe}_{12}\text{O}_{19}$  in this letter. The effects of  $\text{La}^{3+}$  content on lattice parameters, microstructure, and magnetic properties were also investigated. In a typical synthesis of La-substituted  $\text{BaFe}_{12}\text{O}_{19}$ , 1.0 g of triblock copolymer P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) was dissolved in 30 mL of ethylene glycol, followed by addition of 2.02 g (5 mmol) of iron(III) nitrate [ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ] and required amounts of barium nitrate [ $\text{Ba}(\text{NO}_3)_2$ ] and lanthanum nitrate [ $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ], fixing the molar ratio of  $(\text{Ba} + \text{La})/\text{Fe}$

at 1:10 (According to previous work, a certain barium surplus is quite beneficial to yield barium ferrite particles with high-purity crystalline phase and improved magnetic properties.<sup>18,19</sup>) After complete dissolution, 1 g of NaOH was added, and the mixture was continuously stirred for 6 h. Then, the mixture was transferred into a stainless-steel autoclave for crystallization at 230 °C for 24 h. The resultant precipitate was collected by centrifugation, washed with distilled water, and dried at 50 °C. These products were calcined at 400 °C for 4 h and then 950 °C for 6 h. The final products were denoted as La-BF<sub>x</sub>, where x referred to the molar ratio of La/(La + Ba). Powder X-ray diffraction (XRD) data were recorded on a Rigaku D/MAXRC X-ray diffractometer with  $\text{CuK}\alpha$  radiation source (45.0 kV, 50.0 mA). Scanning electron microscope (SEM) images were obtained on the S-4800 (Hitachi). The magnetic properties were measured at 300 K by using a vibrating sample magnetometer (VSM, Lake Shore 7307).

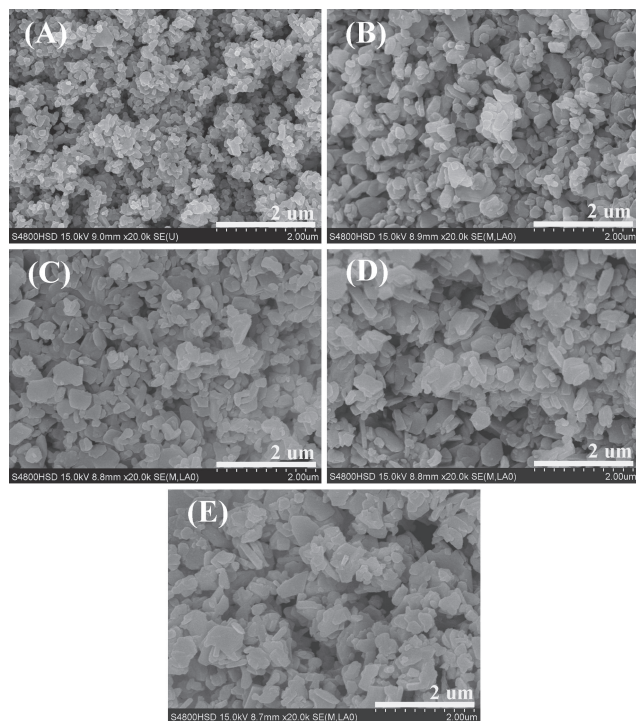
Figure 1 shows the XRD patterns of La-substituted  $\text{BaFe}_{12}\text{O}_{19}$  with different La contents. It is clear that all samples exhibit typical peaks that can be indexed to the standard pattern of M-type  $\text{BaFe}_{12}\text{O}_{19}$  crystals (JCPDS 43-0002), and no common intermediate phases such as  $\text{BaFe}_2\text{O}_4$ ,  $\text{LaFeO}_3$ ,  $\text{La}_2\text{O}_3$ , and  $\alpha\text{-Fe}_2\text{O}_3$  are detectable, indicating that the solvothermal route also works for high-purity La-substituted barium ferrite. In the magnification of the  $2\theta$  range of 28–36° (Supporting Information (SI); Figure S1),<sup>25</sup> one can see that there are slight shifts for several characteristic peaks of  $\text{BaFe}_{12}\text{O}_{19}$  with increasing La contents, implying the successful substitution of  $\text{Ba}^{2+}$  sites by  $\text{La}^{3+}$ . Based on the results of XRD,



**Figure 1.** XRD patterns of BF (A), La-BF<sub>0.05</sub> (B), La-BF<sub>0.10</sub> (C), La-BF<sub>0.15</sub> (D), and La-BF<sub>0.20</sub> (E). The local enlargement in the  $2\theta$  range of 28–36° is shown in Supporting Information (Figure S1<sup>25</sup>).

**Table 1.** Lattice constants and cell volume of various samples

Sample	$a/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$
BF	5.8977	23.1973	698.75
La-BF <sub>0.05</sub>	5.8977	23.1629	697.71
La-BF <sub>0.10</sub>	5.8942	23.1766	697.30
La-BF <sub>0.15</sub>	5.8908	23.1528	695.78
La-BF <sub>0.20</sub>	5.8876	23.1587	695.20

**Figure 2.** SEM images of BF (A), La-BF<sub>0.05</sub> (B), La-BF<sub>0.10</sub> (C), La-BF<sub>0.15</sub> (D), and La-BF<sub>0.20</sub> (E).

lattice constants  $a$  and  $c$  and cell volume can be calculated according to eqs 1 and 2, where  $h$ ,  $k$ , and  $l$  are Miller indices,  $d$  is interplanar distance [here planes (110), (107), (114), (217), (20 11), and (220) are used]. As shown in Table 1, although the values of  $a$  and  $c$  and cell volume vary in a small range and display occasional abnormalities, they present an overall decline, which can be attributed to smaller ionic radius of La<sup>3+</sup> (0.106 nm) than that of Ba<sup>2+</sup> (0.135 nm), leading to the shrinkage of unit cell.

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + l^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

$$V = \frac{\sqrt{3}}{2} a^2 c \quad (2)$$

Figure 2 shows the SEM images of La-substituted BaFe<sub>12</sub>O<sub>19</sub> with different La contents (larger magnification can be obtained in SI).<sup>25</sup> As observed, all samples are composed of well-dispersed irregular nanoparticles in the single domain limit (<1 μm),<sup>15</sup> and their particle sizes are significantly smaller than those from sol-gel method and coprecipitation/molten salt method<sup>4,13,14</sup> and comparable to that from ammonium nitrate

**Table 2.** Magnetic properties of various samples

Sample	$M_r/\text{emu g}^{-1}$	$M_s/\text{emu g}^{-1}$	$H_c/\text{Oe}$
BF	35.3	68.9	4798
La-BF <sub>0.05</sub>	35.4	67.0	4667
La-BF <sub>0.10</sub>	34.3	65.0	4331
La-BF <sub>0.15</sub>	35.1	65.8	4153
La-BF <sub>0.20</sub>	34.1	65.7	3814

melt technique,<sup>15</sup> indicating that the solvothermal route is a feasible method for nanoscaled La-substituted BaFe<sub>12</sub>O<sub>19</sub>. It is worth noting that there is an increasing tendency in particle size with increasing La content. As mentioned above, the replacement of Ba<sup>2+</sup> by La<sup>3+</sup> can result in the conversion from Fe<sup>3+</sup> to Fe<sup>2+</sup> at 2a sites in order to establish the charge balance.<sup>9</sup> However, the reduced valence of Fe<sup>3+</sup> will induce negatively electric characteristic at 2a sites, which can attract extra positive ions,<sup>20</sup> especially Fe<sup>3+</sup> ions, in other unit cell by a pulling force, thus promoting the growth rate of BaFe<sub>12</sub>O<sub>19</sub> particles during the heat-treatment process. As more La<sup>3+</sup> ions are introduced, more such electric attraction can be generated, and larger sized BaFe<sub>12</sub>O<sub>19</sub> particles will be produced due to the faster growth rate. This phenomenon can be also observed in other La-substituted BaFe<sub>12</sub>O<sub>19</sub>.<sup>15</sup>

The field-dependent magnetization results at room temperature on a vibrating sample magnetometer with a maximum applied field of 20 kOe for various samples are presented in Table 2, and the corresponding magnetic hysteresis loops are shown in SI (Figure S3).<sup>25</sup> Compared with pure BaFe<sub>12</sub>O<sub>19</sub>, La-BF<sub>x</sub> herein shows a slight decrease in saturation magnetization ( $M_s$ ) and a mild decrease in coercivity ( $H_c$ ) throughout the whole interval of study, but which are still comparable or even superior to those of to date reported La-substituted barium ferrite by other routes<sup>4,12–14</sup> and are well suited for the applications in magnetic recording.<sup>21</sup> According to previous literature,<sup>12,15</sup> partial replacement of Ba<sup>2+</sup> by La<sup>3+</sup> accompanied with changing Fe<sup>3+</sup> (high spin) valence state to Fe<sup>2+</sup> (low spin) state on 2a site will produce a magnetic dilution. Meanwhile, the appearance of Fe<sup>2+</sup> can weaken the Fe<sup>3+</sup>–O–Fe<sup>3+</sup> superexchange interaction and form a noncollinear arrangement of the spins in Fe<sup>3+</sup>–O–Fe<sup>3+</sup> group (spin canting). Both of them will be responsible for the decrease in  $M_s$ . On the other hand, it should be mentioned that La-BF<sub>x</sub> from solvothermal route fails to show an improvement in  $H_c$  with increasing La contents, although it is widely accepted that the introduction of rare earth ions in BaFe<sub>12</sub>O<sub>19</sub> crystals will induce an increase in magnetocrystalline anisotropy. The major reason is that another important parameter relating to  $H_c$  is the particle size, where increasing particle size will inevitably bring drastic decrease in  $H_c$ .<sup>22,23</sup> In our case, the particle sizes of La-BF<sub>x</sub> obviously increase with increasing La content, but the decrease in  $H_c$  is relatively mild, indicating the existence of La helps to relieve the decrease in  $H_c$ , which again verifies the successful substitution of Ba<sup>2+</sup> by La<sup>3+</sup>. The decreased  $H_c$  with increasing La content can be also observed in other studies about La-substituted barium ferrite.<sup>10,11,14</sup>

Generally, preparation of BaFe<sub>12</sub>O<sub>19</sub> substituted by rare earth ions is more difficult than that of pure BaFe<sub>12</sub>O<sub>19</sub>, because of its more complex chemical composition and crystallization process including distribution, migration, and implantation of

heteroatoms. To date, only a few methods can be applied for the preparation of La-substituted  $\text{BaFe}_{12}\text{O}_{19}$ .<sup>4,10–16</sup> Sol–gel method is a popular one, but gelation conditions should be accurately controlled, where the products are easily influenced by solution properties, pH value, citric acid concentration, evaporation rate, etc.;<sup>14,24</sup> besides, pre-elimination of nitrate is also very important,<sup>10,11</sup> otherwise it will induce self-propagation of gel and result in huge particle size (several microns).<sup>13,14</sup> Molten salt-assisted coprecipitation can be also used to prepare La-containing  $\text{BaFe}_{12}\text{O}_{19}$  with sub-micrometer particle size, but repeated desalination processes are quite complicated.<sup>4</sup> Although ammonium nitrate melt and reverse-microemulsion techniques have been proven to be effective for nanoscaled La-substituted  $\text{BaFe}_{12}\text{O}_{19}$  particles with good magnetic properties, excessive consumption of Ba and La species [initial ratio of  $\text{Fe}/(\text{Ba} + \text{La})$  reaches 2.0],<sup>15</sup> organic solvent, and surfactants, as well as necessary phase purification with HCl, limits further applications of these techniques.<sup>15,16</sup> In contrast, the solvothermal route in this paper only involves solvothermal treatment, routine calcination without additional processes, and excessive consumption of chemical resources and exhibits high versatility for both pure  $\text{BaFe}_{12}\text{O}_{19}$  and La-substituted  $\text{BaFe}_{12}\text{O}_{19}$  particles with high-purity phase, small particle size, and comparable magnetic properties, suggesting that it is a more suitable method for La-substituted  $\text{BaFe}_{12}\text{O}_{19}$  as compared with aforementioned techniques. More importantly, one can obtain about 0.46 g of  $\text{La-BF}_x$  powders in each typical process, which means that the yield of this method can reach ca. 97%. When the typical process of  $\text{La-BF}_{0.05}$  is scaled up to ten times with an autoclave (500 mL), the yield remains at ca. 97% and the obtained sample still shows high-purity phase and similar particle size (SI; Figures S4 and S5),<sup>25</sup> further demonstrating the promising application of this method for fine La-substituted barium ferrite.

In summary, the solvothermal route herein exhibits considerable versatility for both pure  $\text{BaFe}_{12}\text{O}_{19}$  and La-substituted  $\text{BaFe}_{12}\text{O}_{19}$  particles with high-purity phase, small particle size, and good magnetic properties. The introduction of  $\text{La}^{3+}$  can reduce lattice constants and cell volume and simultaneously increase the particle size. Under the competition between magnetocrystalline anisotropy and size effect, the coercivity of obtained products present a mild decrease, however, which are still comparable or even superior to those of to date reported La-substituted barium ferrite by other routes. By considering the advantages of solvothermal route in simplicity and efficiency, it will be promising to extend this method to other ferrites substituted by various rare earth ions.

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## References and Notes

- V. G. Harris, A. Geiler, Y. Chen, S. D. Yoon, M. Wu, A. Yang, Z. Chen, P. He, P. V. Parimi, X. Zuo, C. E. Patton, M. Abe, O. Acher, C. Vittoria, *J. Magn. Magn. Mater.* **2009**, *321*, 2035.
- A. Ghasemi, A. Hossienpour, A. Morisako, A. Saatchi, M. Salehi, *J. Magn. Magn. Mater.* **2006**, *302*, 429.
- U. Topal, H. Ozkan, H. Sozeri, *J. Magn. Magn. Mater.* **2004**, *284*, 416.
- Y. Liu, M. G. B. Drew, Y. Liu, J. Wang, M. Zhang, *J. Magn. Magn. Mater.* **2010**, *322*, 3342.
- U. Topal, *Mater. Sci. Eng., B* **2011**, *176*, 1531.
- S. Pignard, H. Vincent, E. Flavin, F. Boust, *J. Magn. Magn. Mater.* **2003**, *260*, 437.
- M. Küpferling, R. Grössinger, M. W. Pieper, G. Wiesinger, H. Michor, C. Ritter, F. Kubel, *Phys. Rev. B* **2006**, *73*, 144408.
- N. Chen, K. Yang, M. Gu, *J. Alloys Compd.* **2010**, *490*, 609.
- F. K. Lotgering, *J. Phys. Chem. Solids* **1974**, *35*, 1633.
- J. C. Corral-Huacuz, G. Mendoza-Suárez, *J. Magn. Magn. Mater.* **2002**, *242–245*, 430.
- Z. H. Hua, S. Z. Li, Z. D. Han, D. H. Wang, M. Lu, W. Zhong, B. X. Gu, Y. W. Du, *Mater. Sci. Eng., A* **2007**, *448*, 326.
- S. Ounnunkad, *Solid State Commun.* **2006**, *138*, 472.
- S. Ounnunkad, P. Winotai, S. Phanichphant, *J. Electroceram.* **2006**, *16*, 357.
- H.-g. Li, R.-q. Guo, P.-m. Sun, Y.-j. Li, Z.-w. Zhao, M.-s. Liu, P.-t. Su, *Trans. Nonferrous Met. Soc. China* **2001**, *11*, 447.
- H. Sözeri, I. Küçük, H. Özkan, *J. Magn. Magn. Mater.* **2011**, *323*, 1799.
- X. Gao, Y. Du, X. Liu, P. Xu, X. Han, *Mater. Res. Bull.* **2011**, *46*, 643.
- L. Du, Y. Du, Y. Li, J. Wang, C. Wang, X. Wang, P. Xu, X. Han, *J. Phys. Chem. C* **2010**, *114*, 19600.
- A. Mali, A. Ataie, *J. Alloys Compd.* **2005**, *399*, 245.
- P. Xu, X. Han, M. Wang, *J. Phys. Chem. C* **2007**, *111*, 5866.
- H. Qiu, G. Chen, R. Fan, C. Cheng, S. Hao, D. Chen, C. Yang, *Chem. Commun.* **2011**, *47*, 9648.
- X. Sui, M. Scherge, M. H. Kryder, J. E. Snyder, V. G. Harris, N. C. Koon, *J. Magn. Magn. Mater.* **1996**, *155*, 132.
- J. Dho, E. K. Lee, J. Y. Park, N. H. Hur, *J. Magn. Magn. Mater.* **2005**, *285*, 164.
- Y. Du, H. Gao, X. Liu, J. Wang, P. Xu, X. Han, *J. Mater. Sci.* **2010**, *45*, 2442.
- J. Liu, W. Zhang, C. Guo, Y. Zeng, *J. Alloys Compd.* **2009**, *479*, 863.
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