

Synthesis and magnetic properties of the $\text{SiO}_2\text{--BaFe}_{12}\text{O}_{19}$ glass–ceramic composites

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Abstract

Samples of the magnetic glass–ceramics $\text{SiO}_2\text{--BaFe}_{12}\text{O}_{19}$ were obtained from mixtures of $\text{Fe}_2\text{O}_3\text{--BaSO}_4\text{--SiO}_2\text{--Na}_2\text{CO}_3\text{--CaCO}_3$ following a two-step route. The samples were characterized using XRD analysis and scanning electron microscopy, and their room temperature magnetization hysteresis loops were measured. It was found that the magnetic phase was completely developed in the precursor $\text{BaFe}_{12}\text{O}_{19}$ material when it was calcinated above 1000 °C. The size of the particles of the $\text{BaFe}_{12}\text{O}_{19}$ phase depends on the thermal treatment conditions and on the SiO_2 concentration. The magnetic data showed that the high value of the coercive magnetic field is preserved despite the fact that both the remanent and the saturation magnetizations diminish substantially.

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1. Introduction

Composites containing dispersed particles of hard magnetic hexaferrites in a glass matrix are important materials for developing compact glass ceramic and glass coated magnetic particles, with applications in material science [1–7] and biotechnology [8]. Glass coated magnetic particles are being investigated, for instance, for delivering drugs to specific body locations in new health treatment procedures. Traditionally, glass ceramics are prepared by the glass crystallization method [3], following a borate glass route. However, there are still difficulties in obtaining glass ceramic with well-controlled particle size, especially with a high content of ferrites, attracting considerable interest from the material science community. The chemical composition of the glass precursor influences the physical and chemical properties of the composite. Therefore, the inves-

tigation of new composite glass materials with controlled particles size distribution and aspect ratio are quite desirable.

In this paper, a new route is reported that allows the production of barium hexaferrite particles using a new glassmaking technology process, and to incorporate them into a soda lime silicate glass matrix. The samples were structurally characterized and the magnetic hysteresis loops were measured. It was found that the grain size distribution varies with the content of the glass while the magnetic coercive field of the ferrite remains nearly unchanged in the glass–ceramic composites.

2. Experimental procedure

The samples were obtained using a two-step synthesis. In the first step, barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) was produced starting from a mixture of Fe_2O_3 , BaSO_4 and the glassmaking Na_2CO_3 , keeping the proportional ratio of 6:1:1, respectively. The mixture was hand milled and

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calcinated at 1000 °C for 8 h in air. The resulting powder was washed with a HCl solution to remove any residual salts left in the first step process. In the second step, two glass ceramic samples with glass concentrations of 25 wt% and 50 wt% were obtained by mixing the barium hexaferrite with the silicate glass precursor in a suitable proportion of SiO₂, Na₂CO₃ and CaCO₄. The final mixture was heat treated at 1100 °C for 3 h. The bulk samples were then powdered and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and magnetization measurements were performed. The XRD patterns were obtained using CuK α radiation. The magnetization measurements were carried out using a vibrating sample magnetometer (VSM), varying the applied magnetic field up to 1.5 T.

3. Results

The XRD patterns for the barium hexaferrite (BaHex) obtained in the first synthesis step and for two glass ceramics with glass concentrations of 25 wt% (Vid25) and 50 wt% (Vid50) are shown in Fig. 1. The Rietveld analysis of the XRD pattern of barium hexaferrite (Fig. 1(a)) showed that the particles are single-phase BaFe₁₂O₁₉ ferrite, with a hexagonal crystalline structure belonging to the P63/mmc symmetry group. Barium hexaferrite single-phase particles were also observed in the Vid25 glass ceramic samples using the XRD analysis (Fig. 1(b)). The structural parameters and the quantitative ratios of the phases are presented in Table 1. The presence of small amounts of an iron oxide

Table 1
Weight percent wt% and lattice parameters *a* and *c*

Sample	Phase	wt%	<i>a</i> (Å)	<i>c</i> (Å)
BaHex	BaHex	97.0	5.906	23.276
	Hematite	3.0	5.009	13.85
	Glass	–	–	–
Vid25	BaHex	62.0	5.984	23.223
	Hematite	6.5	5.039	13.759
	Glass	31.5	–	–
Vid50	BaHex	18.0	5.893	23.217
	Hematite	24.0	5.039	13.762
	Glass	58.0	–	–

phase (hematite, α -Fe₂O₃) in the hexaferrite (3 wt%) and Vid25 (6.5 wt%) samples were identified, while in the Vid50 sample the amount was about 24 wt%.

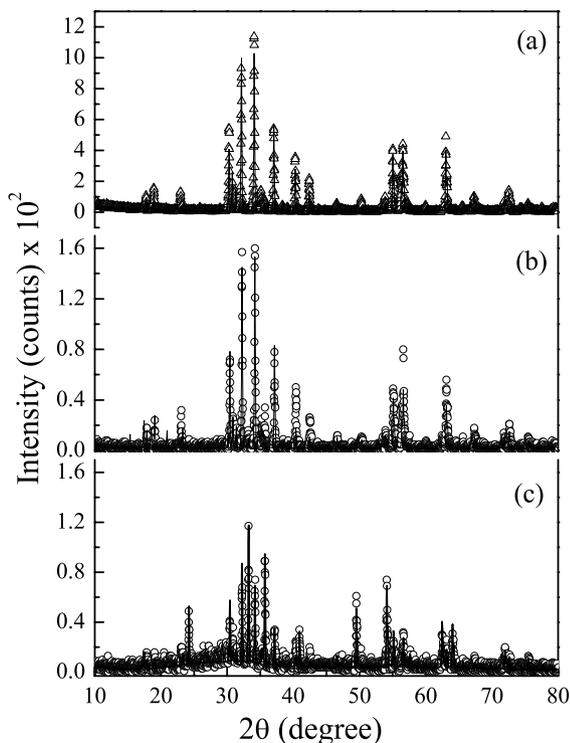


Fig. 1. X-ray diffractograms of barium hexaferrite (a) and barium hexaferrite composites with 25 wt% (b) and 50 wt% (c) glass matrices.

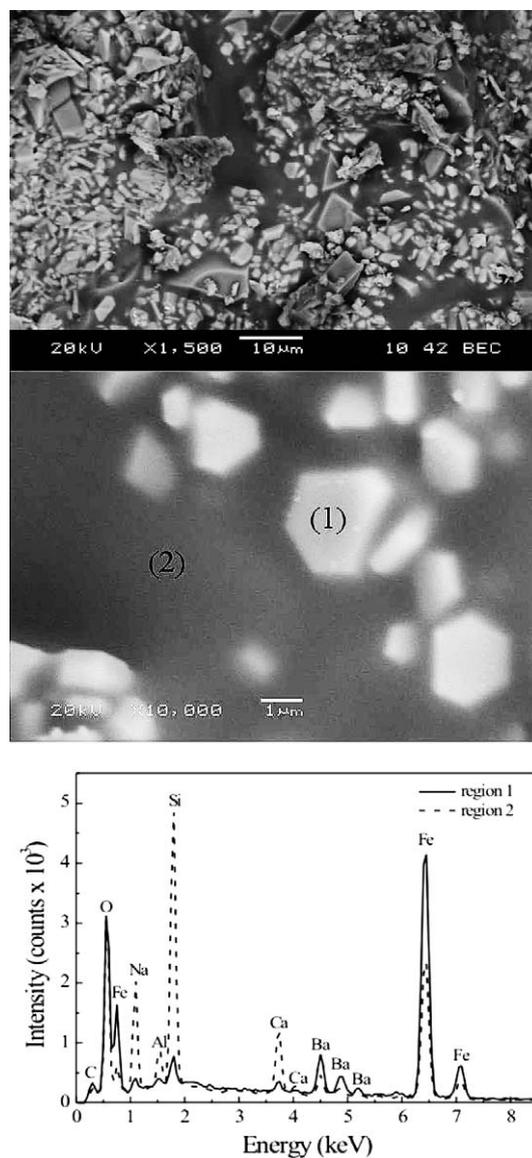


Fig. 2. SEM micrographs and EDS spectra of a barium hexaferrite composite with 25 wt% glass matrix.

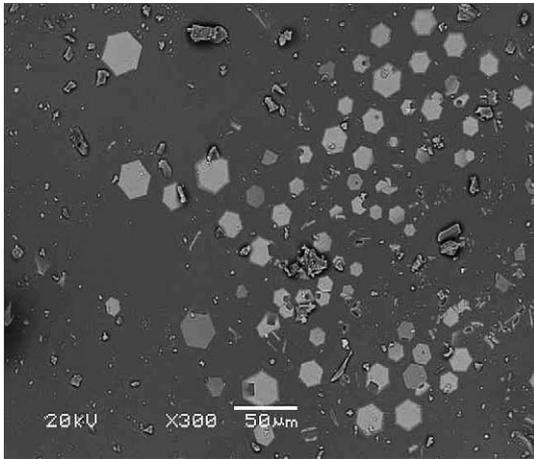


Fig. 3. SEM micrographs of a barium hexaferrite composite with 50 wt% glass matrix.

The SEM for the Vid25 and for the Vid50 samples are shown in Figs. 2 and 3. The micrographs show that the shape of the barium hexaferrite particles are hexagonal platelet crystallites. For the Vid25 sample, the average particle diameters are smaller than 2 μm , while for the Vid50 they are substantially larger, getting close to 16 μm . The identification of the phases present in the samples was carried out by energy dispersive spectroscopy (EDS), as well. Typical EDS spectra obtained from a barium hexaferrite particle (1) and from the soda lime silicate glass (2) obtained for the Vid25 sample are shown in Fig. 2.

The magnetization hysteresis loops for the three samples are shown in Fig. 4. They yielded the values of the saturation

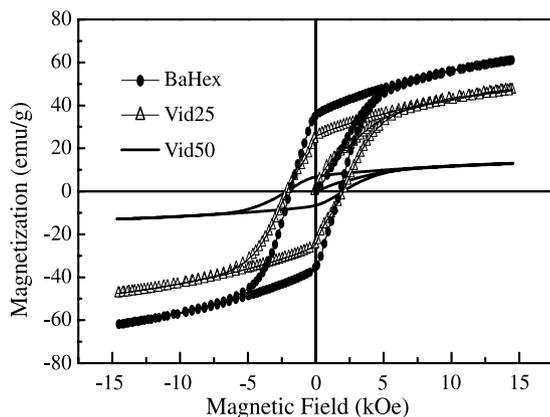


Fig. 4. Hysteresis curve of the samples: BaHex, Vid25, and Vid50, respectively.

Table 2

Magnetic parameters: saturation magnetization M_S , remanent magnetization M_r , and magnetic coercive field H_c

Sample	M_S (emu/g)	M_r (emu/g)	H_c (kOe)
BaHex	61.5 ± 0.5	35.3 ± 0.3	1.85 ± 0.02
Vid25	47.5 ± 0.7	25.0 ± 0.4	2.07 ± 0.03
Vid50	12.9 ± 0.2	6.7 ± 0.1	2.08 ± 0.04

The errors were estimated from the dispersion on the experimental data.

tion magnetization M_S , the remanent magnetization M_r and the magnetic coercive fields H_c . These data are summarized in Table 2.

4. Discussion

The above experimental results show that the values of M_S , M_r and H_c for pure barium hexaferrite are in good agreement with the values reported for commercial powders prepared by the conventional carbonate process. For the Vid25 sample, both M_S and M_r decrease by about 25% compared to the values obtained for the BaHex sample. This is close to what would be expected based on the substitution of the amount of BaHex particles by the glass matrix. For the Vid50 sample, however, the decrease in M_S and M_r was greater than 80%. This value is a somewhat higher variation than that expected from the substitution of the magnetic phase (ferrite) by the non-magnetic phase (glass) based on the nominal composition (50%). This occurs because the Vid50 sample, as shown in Table 1, has in its composition 18% of BaHex ferrite and 24% of hematite which is antiferromagnetic. The magnetic coercive field of the glass ceramic samples, on the other hand, remains practically unchanged. Indeed, H_c is slightly higher in the glass samples than it is in the BaHex sample. For the Vid25 sample, where the hematite content is very low, the H_c enhancement is probably due to the existence of a single-domain in most of the hexaferrite particles [9]. The single-domain particle size for barium hexaferrite is about 0.9 μm [10] and in the Vid25 sample the particle size varies in the range 0.5–2 μm (see Fig. 2). The presence of hematite in Vid50 leads to an additional mechanism for enhancing H_c in this sample. The presence of antiferromagnetic interactions from the hematite phase may be responsible for increasing the coercive field. This mechanism was indeed observed in ball milled strontium hexaferrite composites [11].

5. Conclusions

In summary, a new glass making process that allows the production of barium hexaferrite and glasses with barium hexaferrite particles embedded in them was reported. This process has both economic and technological appeal since it uses lower temperatures to prepare the samples and uses less expensive reagents to start them with. The size of the particles and the magnetic properties can be tuned by varying the sample composition. Furthermore, it was found that the high value of the magnetic coercive field of the barium hexaferrite remains nearly unchanged even when the magnetic phase is diluted with a high amount of a non-magnetic glass matrix.

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