Structural and magnetic properties of $\text{Er}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ garnets

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Abstract

Gallium substituted erbium iron garnets ($\text{Er}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$) prepared by solid state reaction method using ball milling and sintering at 1300 °C were all single-phase compounds with Ia3d symmetry. The lattice parameter and cell volume decreased slightly, whereas the x-ray density increased linearly with the increase of Ga concentration. XRD analysis, Mössbauer spectroscopy, and the magnetic data, all provided evidence of Ga$^{3+}$ substitution for Fe$^{3+}$ at tetrahedral sites in the composition range up to $x = 0.6$, and a small partial substitution at octahedral sites in the sample with $x = 0.8$. The saturation magnetization decreased almost linearly in accordance with a simple magnetic dilution model in the concentration range up to 0.6, and deviated slightly from this behavior at $x = 0.8$ due to partial substitution at octahedral sites. The low temperature thermomagnetic measurements on the unsubstituted sample revealed a compensation temperature at $-186$ °C, whereas the sample with $x = 0.8$ exhibited a minimum at a significantly higher temperature of $-51$ °C, with significant broadening.

1. Introduction

The discovery of yttrium–iron garnet (YIG), independently by two research groups in 1956 [1, 2], have signaled the evolution of a new era in the development of at least two new technologies, namely, passive components for microwave devices, and magnetic-bubble-domain digital memories [3, 4]. Since then, a large body of research work was devoted to the synthesis and characterization of YIG ($\text{Y}_3\text{Fe}_5\text{O}_{12}$) with a variety of substitution for Y$^{3+}$ ions by other rare-earth ($\text{R}^{3+}$) ions, and Fe$^{3+}$ ions by other nonmagnetic or magnetic ions, leading to new developments of materials for new technologies [5–10].

The garnet structure is characterized by cubic symmetry with space group Ia3d. In this crystal structure, three types of interstitial sites are available for the metallic ions, namely, the octahedral ($a$) sites, the tetrahedral ($d$) site, and the dodecahedral ($c$) site. The site selectivity of metallic ions depends on the size of the ion, and electronic configuration. The tetrahedral ($d$) site with the smallest metal–oxygen bond length of $\sim 1.87$ Å can accommodate a limited number of small metal ions, generally with spherically symmetrical charge configuration. The larger octahedral ($a$) site with a typical metal–oxygen bond length of $\sim 2.01$ Å can accommodate a larger variety of metallic substituents, including some of the small rare-earth ions [3]. On the other hand, the larger rare-earth ions normally occupy the largest dodecahedral ($c$) site with typical metal–oxygen bond length of $\sim 2.40$ Å. Accordingly, all three $\text{R}^{3+}$ ions are found in the dodecahedral sites, whereas the Fe$^{3+}$ ions are distributed with two ions in the octahedral sites and three in the tetrahedral sites in accordance with the formula ($\text{R}^{3+}_{1},[\text{Fe}^{3+}_{3}\text{O}_{12}]_{\text{a}}$)

Supercritical interactions between magnetic ions via intervening oxygen ions are responsible for magnetic ordering, and the appearance of magnetic sublattices in garnets [11–14]. In YIG, the Y$^{3+}$ ion does not have a magnetic moment, and the magnetic properties of the compound are completely determined by superexchange interactions between Fe$^{3+}$ ions at octahedral and tetrahedral sites, giving rise to only two magnetic sublattices (A...
and D, respectively) with a net magnetic moment of 5 μB per molecule at 0 K. However, in rare-earth iron garnet where the R³⁺ ions possess a net magnetic moment, three magnetic sublattices are present, A, D, and C (the rare-earth magnetic sublattice). The metal–O²⁻– bond lengths and metal–O²⁻–metal bond angles are in favor of the a-d superexchange interaction between Fe³⁺ ions, which is by far the strongest interaction in the garnet structure, leading to antiferromagnetic coupling between the A and D sublattices, and antiferromagnetic coupling of the rare-earth (C) sublattice with the net moment of Fe³⁺ [3]. For R³⁺ being a rare earth ion from the series Gd³⁺ through Yb³⁺, the rare earth sublattice magnetization at low temperatures is higher than the net magnetization of the Fe³⁺, and the magnetization of the rare earth iron garnet is given by:

\[ M(T) = M_c(T) - [M_a(T) - M_d(T)] \] (1)

Since the strength of the c–d interaction is an order of magnitude smaller than the a–d interaction, and the c-a interaction is even smaller, the effects of \( M_c \) on \( M_a \) and \( M_d \) were neglected in equation (1) [3]. As the temperature increases, the magnetization of the rare-earth drops faster than that of iron, and the net magnetization of the compound goes through zero (at the compensation point, generally below room temperature), and then reverses and starts rising again as the net magnetization \( [M_d(T) - M_a(T)] \) becomes greater than that of the C sublattice [3].

The stability of bubbles in garnet bubble films depends on the static magnetic parameters including the saturation magnetization and the magnetic anisotropy constant of the film [15]. However, the definition of these properties is required for satisfactory performance of a given device. Useful bubble films are usually rare-earth garnets with the iron sublattice diluted by non-magnetic ion substitution for iron. The magnetic dilution is used to reduce the saturation magnetization to useful values, while the rare-earth is used to increase the magnetic anisotropy constant and improve the dynamical properties. Accordingly, substantial theoretical and experimental work was devoted to investigate the effects of substitutions on the properties of garnets [15–22].

The non-magnetic ions used for magnetic dilution were mainly Al³⁺ and Ga³⁺ ions, which preferably substitute iron at tetrahedral sites [23, 24]. The site preference for these ions in Y₃Fe₅₋ₓAlₓO₁₂ and Y₃Fe₅₋ₓGaₓO₁₂, however, was shown to depend on the concentration \( x \) of the substituents, where the fraction of Al³⁺ ions [25, 26], or Ga³⁺ ions [27, 28] at tetrahedral sites decreased smoothly, demonstrating a progressively increasing tendency to occupy octahedral sites with the increase of \( x \). However, the fraction of Ga³⁺ ions at tetrahedral sites was higher than that of Al³⁺ ions up to \( x = 2.8 \). The practical values of \( x \) used for garnet bubbles extended up to \( 1.0 \), where the fraction of Ga³⁺ ions at tetrahedral sites is 90% (and even higher in single crystal [28]), whereas the fraction of Al³⁺ is slightly higher than 80%. In addition, the magnetic data of Al-substituted YIG indicated that the distribution of Al³⁺ ions at tetrahedral and octahedral sites is also dependent on the heat treatment [29].

Room temperature Mössbauer spectroscopy provided clear evidence of tetrahedral site preference of Al³⁺ ions in Al-substituted yttrium iron garnet [30] and holmium iron garnet [31]. However, evidence of Al³⁺ substitution for Fe³⁺ at octahedral sites in yttrium and yttrium–gadolinium iron garnets was provided by others [32–34]. The site selectivity of nonmagnetic ions plays a crucial role in determining the magnetic properties of the garnet, and the reported variations indicate sensitivity to the synthesis route, heat treatment, and the concentration of nonmagnetic ion.

Garnets with different rare-earth ion substitutions for Y³⁺ ions, and/or substitution of Fe³⁺ by magnetic or nonmagnetic ions were prepared using different techniques, including sol-gel method [30, 35, 36], co-precipitation method [37], and ball milling [32–34, 38, 39]. Although careful structural and magnetic studies were performed on erbium iron garnet single crystal and polycrystalline samples [2, 40, 41], up to our knowledge, no attempt was made to synthesize and characterize erbium iron garnet with partial substitution of Fe³⁺ ions by Ga³⁺ ions. The present study is concerned with the preparation and investigation of the structural and magnetic properties of Er₃Fe₅₋ₓGaₓO₁₂ (0 ≤ \( x \) ≤ 0.8) synthesized by solid state reaction. The site selectivity of Ga³⁺ ions in the garnet structure was examined using structural refinement of the x-ray diffraction data as well as Mössbauer spectroscopy and magnetic data, and the effect of Ga-substitution on the magnetic properties of the prepared garnets was investigated.

2. Experimental procedures

Er₃Fe₅₋ₓGaₓO₁₂ (\( x = 0.0, 0.2, 0.4, 0.6 \) and 0.8) garnets were prepared by ball milling stoichiometric proportions of high purity Er₂O₃, Fe₂O₃ and Ga₂O₃ starting powders, and sintering at temperatures sufficient to induce solid state reaction. The ball milling was carried out for 4 h using hardened stainless-steel bowls and milling balls, with a ball-to-powder mass ratio of 8:1, and rotational speed of 250 rpm. The powder mixture was then pelletized and sintered at 1300°C for 2 h. X-ray diffraction (XRD) patterns were collected using Philips PW 1720 x-ray diffractometer with Cu-Kα radiation (\( λ = 1.5405 \) Å). The samples were scanned over the angular range
$15^\circ < 2\theta < 75^\circ$ with 0.02° scanning step and speed of 1° min$^{-1}$. The XRD patterns were analyzed using X’pert HighScore 2.0.1 software for phase identification, and Rietveld refinement of the crystal structure was performed using FullProf suite 2000 software.

Room temperature Mössbauer spectra of the samples were collected over 1024 channels using a standard constant acceleration spectrometer with $^{57}$Co source dispersed in rhodium matrix. Fitting software based on least-squares analysis was used to fit the spectra, and the centroid of $\alpha$-iron was used as the origin of the velocity scale. The magnetic measurements were performed using Vibrating Sample Magnetometer (VSM MicroMag 3900, Princeton Measurements Cooperation), operating at a maximum applied magnetic field of 10 kOe, and Quantum Design 9T- PPMS EverCool-II magnetometer.

3. Results and discussion

3.1. Structural and microstructural characteristics

X’ Pert HighScore analysis of the XRD patterns of $\text{Er}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ garnets indicated that all samples consisted of a single garnet phase with Ia3d symmetry, consistent with the standard pattern (ICDD: 01-081-0131) for $\text{Er}_3\text{Fe}_5\text{O}_{12}$ (ErIG). The results of Rietveld refinement of the XRD patterns of all $\text{Er}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ samples are shown in figure 1, where the experimental data are shown as red circles. The figure indicated excellent agreement between the experimental data and the theoretical refined pattern (represented by a continuous black line), where the residual difference between the experimental and theoretical data (represented by the continuous blue line below the pattern) is a straight horizontal line with small ripples only around the main structural peak positions. Also, the vertical (green) bars below the XRD patterns (representing Bragg peak positions) coincided with the Bragg peak positions of the standard pattern of ErIG.

The refined lattice constant $a = 12.346$ Å for the sample with $x = 0.0$ is in good agreement with the value of 12.347 Å obtained by Geller et al [42]. A small decrease of the lattice constant with the increase of Ga substitution (down to 12.337 Å for the sample with $x = 0.8$) was observed, which is also in agreement with the decreasing behavior of the lattice constant of $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ with the increase of Ga content [27]. This decrease is manifested by the shift of the diffraction peaks as illustrated by figure 2, and can be associated with the smaller ionic radius of Ga$^{3+}$ (0.47 Å) compared to the ionic radius of Fe$^{3+}$ (0.49 Å) at tetrahedral sites [43]. Even though the refined cell volume demonstrated a similar decreasing behavior with the increase of $x$, the x-ray density increased almost linearly as shown in figure 3. Accordingly, the effect of decreasing volume (being $\sim 0.07\%$ over the entire range of substitution) is negligible compared to the effect of the linearly increasing molecular mass with the increase of $x$. 

![Figure 1. Rietveld Refinement for the XRD patterns of $\text{Er}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ samples.](image)
Rietveld analysis also provides further microstructural information, which can be derived from the crystallographic information output file (CIF). The unit cell of the crystal structure, as well as the oxygen polyhedra around the metal ions, were constructed from the data in the CIF file using Diamond software (figures 4 and 5 for the samples with $x = 0.0$ and 0.8, respectively). The three crystallographic sites of the metal ions, namely, the 16a (octahedral) and the 24d (tetrahedral) sites of iron, and the 24c (dodecahedral) sites of the rare-earth, are shown in these figures. The constructions for the remaining Ga-substituted samples are not shown to avoid redundancy. The fractions of Fe$^{3+}$ ions and Ga$^{3+}$ ions at tetrahedral and octahedral sites in the investigated samples were also determined using the data in the CIF file. The results indicated that Ga$^{3+}$ ions substituted Fe$^{3+}$ ions at tetrahedral (d) sites, with no appreciable substitution at octahedral sites up to $x = 0.6$. Analysis of the structural data of the sample with $x = 0.8$, however, indicated that the fraction of the Ga$^{3+}$ ions at tetrahedral sites is 96.9%. This result is in agreement with previously reported Ga$^{3+}$ site selectivity in Ga-substituted YIG, where 93% of Ga$^{3+}$ ions were found to occupy tetrahedral sites at $x \sim 0.5$, dropping down to 90% at $x = 1.0$ [27]. The small difference between the observed site occupancy of Ga$^{3+}$ in ErIG and that in YIG could be due to the difference in the type of rare-earth metal at dodecahedral sites, different preparation conditions and heat treatment, or to experimental uncertainty.

The substitution of Fe$^{3+}$ ions by Ga$^{3+}$ ions did not show significant variations of the bond lengths and bond angles in the garnet structure. However, the structural analysis indicated that the Ga substitution results in a
small decrease of the Fe$^{3+}$(a)–O$^{2−}$ and Fe$^{3+}$(d)–O$^{2−}$ bond lengths, and a small increase of Fe$^{3+}$(a)–O$^{2−}$–Fe$^{3+}$(d) bond angle. For comparison, the parameters of the two extreme samples (with $x = 0.0$ and 0.8) are shown in Table 1. The observed bond lengths and bond angles for the sample with $x = 0.0$ are in good agreement with the parameters of YIG [3, 19], even though the ionic radius of Er$^{3+}$ at dodecahedral sites (1.004 Å) is somewhat smaller than that of Y$^{3+}$ (1.019 Å) [43].
The crystallite size was determined from the broadening of the XRD reflection at $2\theta = 55.8^\circ$ using Scherrer’s relation. The results did not show systematic variations with the increase of Ga concentration, where the crystallite size was $77 \pm 5$ nm for all samples. The variations of the crystallite size and other structural and microstructural parameters with the increase of $x$ indicated that the substitution of Ga$^{3+}$ for Fe$^{3+}$ does not have an appreciable effect on the crystallinity of Er$_3$Fe$_{5-x}$Ga$_x$O$_{12}$.

3.2. Mössbauer spectroscopy

Mössbauer spectroscopy of solid materials is an effective tool to investigate hyperfine interactions, atomic distribution in the lattice, and the effects of local chemical environments around the Fe nucleus [44, 45]. Recently, Mössbauer spectroscopy on gadolinium erbium iron garnets was reported, providing the hyperfine parameters for the unsubstituted ErIG [39]. In the present study, Mössbauer spectra of the Ga$^{3+}$ substituted samples with $x = 0.4$ and 0.8 (figure 6), were investigated to examine the conclusions concerning the distribution of Ga$^{3+}$ ions within the garnet lattice based on the structural analysis. The sample with $x = 0.4$ was selected to represent the substitution range of $x = 0.2–0.6$, since the structural analysis revealed that the distribution of metallic ions did not change in this range.

The spectrum of the sample with $x = 0.4$ was best fitted with three sextet components, two of which were attributed to octahedral sites having different orientations of the electric field gradient with respect to the hyperfine field, and one to tetrahedral sites [46–48]. The general features, as well as the center shift (CS) and relative intensities (I) of the three components of this spectrum are in agreement with those of the ErIG sample [39], whereas the widths ($W$) of the spectral lines are significantly higher, and the hyperfine fields ($B_{hf}$) are significantly lower (see results in table 2). Due to the significant line broadening ($W = 0.46–0.60$ mm s$^{-1}$) and large overlap between the three components, the relative intensities of the components cannot be reliable in drawing a conclusion regarding the site selectivity of Ga$^{3+}$ ions in the garnet lattice. However, the substitution of magnetic Fe$^{3+}$ by non-magnetic Ga$^{3+}$ ions induces variations of the local chemical environments around the Fe nucleus, leading to the observed significant line broadening. Also, the magnetic dilution results in weakening of the A–D sublattice coupling, leading to the observed significant decrease of the hyperfine fields. At this substitution level, the single component associated with Fe$^{3+}$ ions at tetrahedral sites could be an indication that the distribution of metal ions at neighboring octahedral sites is not different from that for the sample with $x = 0.0$, and thus could indicate that Ga$^{3+}$ substituted Fe$^{3+}$ at tetrahedral sites, with effects limited to line broadening and reduction of the hyperfine fields. The spectrum of the sample with $x = 0.8$, however, was more complicated, with stronger overlapping between the sub-spectral components. The spectrum could not be fitted well with three components, and was best fitted with five components, three of which were attributed to octahedral sites, and two to tetrahedral sites (fitting parameters are shown in table 2). The evolution of a third octahedral component could be associated with the increased variations of the local chemical environments around octahedral sites, the lower hyperfine field being associated with Fe$^{3+}$ at octahedral sites coupled to tetrahedral sites more heavily populated by Ga$^{3+}$ ions. The significant increase of the center shift for the low-field component is an indication of higher Ga concentration around the corresponding octahedral site, which is consistent with the observed increase of the center shift of the component associated with Fe surrounded by Al...
The splitting of the single tetrahedral component into two, however, is an indication of the presence of at least two different octahedral sites coupled to tetrahedral sites, which is an evidence of Ga$^{3+}$ partial substitution at octahedral sites. The hyperfine field for the high-field component is within experimental uncertainty of the original component (376 kOe versus 381 kOe), so that this component can be associated with unperturbed tetrahedral sites. The second component, however, has significantly lower hyperfine field (341 kOe), and can therefore be associated with tetrahedral sites sharing a corner with octahedral sites containing Ga$^{3+}$ ions.

### 3.3. Magnetic measurements

Figure 7 shows the hysteresis loops for Er$_3$Fe$_{5-x}$Ga$_x$O$_{12}$ garnets measured with a 100 Oe field step. The curves revealed soft magnetic nature of all erbium iron garnets. Since the samples did not reach magnetic saturation at the highest applied field, the saturation magnetization was determined from the intercept of the $M$ versus $1/H$ curves in the high field region [49]. The saturation magnetization of the unsubstituted sample (16.4 emu g$^{-1}$) is somewhat higher than the value of 14.2 emu g$^{-1}$ reported recently by Opuchovic et al for ErIG [50]. This could be due to the higher purity of our sample, and the difference in synthesis route and heat treatment. The saturation magnetization of the substituted samples decreased monotonically with the increase of Ga concentration as indicated by figure 8, reaching a value of 4.1 emu g$^{-1}$ at $x = 0.8$.

At room temperature, the net magnetization of the iron sublattices ($M_I - M_a$) is higher than the magnetization of the rare-earth sublattice ($M_a$), and the sample magnetization is determined by ($M_g - M_a - M_e$). The saturation magnetization of 16.4 emu g$^{-1}$ for the sample with $x = 0.0$ corresponds to a net magnetic moment of 2.86 $\mu_B$ per molecule, whereas the saturation magnetization of 4.1 emu g$^{-1}$ for the sample with $x = 0.8$ corresponds to 0.72 $\mu_B$ per molecule. The saturation magnetization decreased almost linearly with

### Table 2. Fitting parameters of Mössbauer spectra of the samples with $x = 0.4$ and 0.8.

| Site     | $B_{hf}$ (kOe) $\pm 5$ | $CS$ (mm s$^{-1}$) $\pm 0.02$ | $W$ (mm s$^{-1}$) | $I$ (%) |
|----------|-------------------------|--------------------------------|------------------|---------|
| Octahedral | 471                     | 0.36                           | 0.46             | 23      |
|          | 450                     | 0.37                           | 0.47             | 13      |
| Tetrahedral | 381                     | 0.15                           | 0.60             | 64      |
| Octahedral | 459                     | 0.33                           | 0.38             | 6       |
|          | 438                     | 0.36                           | 0.56             | 20      |
|          | 404                     | 0.50                           | 0.51             | 8       |
| Tetrahedral | 376                     | 0.16                           | 0.71             | 56      |
|          | 341                     | 0.14                           | 0.52             | 10      |

Figure 7. Hysteresis loops for Er$_3$Fe$_{5-x}$Ga$_x$O$_{12}$ garnets measured with a 100 Oe field step.
increasing $x$ up to 0.6, and deviated only slightly from linearity at $x = 0.8$. This behavior is consistent with magnetic dilution resulting from the substitution of Ga$^{3+}$ ions at tetrahedral sites. The magnetic dilution of the iron sublattices also results in a reduction of the strength of the $c$-$d$ exchange interaction responsible for the magnetization of the rare-earth sublattice, leading to spin canting, and a consequent reduction of the magnetic moment of the C-sublattice. Assuming Ga$^{3+}$ ionic substitution at tetrahedral sites, the saturation magnetization as a function of $x$ can be expressed by the relation:

$$M_s = \frac{2.86(1-x)\mu_B N_A}{973 + 13.88x}$$  \hspace{1cm} (2)$$

where the denominator represents the molecular mass, and the magnetic moment of the sample with $x = 0.0$ was taken as the experimental saturation magnetization of the sample. Figure 8 shows excellent agreement between the experimental and theoretical values up to $x = 0.6$. The discrepancy at $x = 0.8$ can be due to very small amounts of Ga$^{3+}$ ions substituting Fe$^{3+}$ ions at octahedral sites, resulting in the observed increase in the saturation magnetization. In this case, equation (2) does not apply, where the structural results indicated that $\sim 3.1\%$ of the Ga$^{3+}$ ions substituted Fe$^{3+}$ ions at octahedral sites, in which case the net moment of this sample is $(2.86 \times 0.25 \mu_B$ per molecule) rather than $(2.86 \times 0.20 \mu_B$ per molecule). Accordingly, the calculated saturation magnetization of this sample is 4.06 emu g$^{-1}$, which is in excellent agreement with the experimental value of 4.1 emu g$^{-1}$. Although high-level depletion of iron may result in an increasing importance of intra-sublattice interactions, leading to antiferromagnetic coupling in the (A) and (D) sublattices [3], and a drastic deterioration of the net magnetization, the linear decrease of the saturation magnetization indicated that such effects are not important in the substitution range of this study.

In order to investigate the effect of Ga-substitution on the coercivity ($H_c$) of the garnets, hysteresis loops were measured using a maximum applied field of 1 kOe and a 2 Oe field step (figure 9(a)). The expanded view of the hysteresis loops (figure 9(b)) indicated that the coercivity increased slightly with Ga-substitution up to $x = 0.4$, and then exhibited a sharper increase at higher Ga concentrations as revealed by figure 10. The coercivity of the sample with $x = 0.0$ was 5.8 Oe, and the highest coercivity was 19.2 Oe for the sample with $x = 0.8$.

The temperature dependent magnetization $M(T)$ of the samples was measured as a function of temperature in a constant applied field of 800 Oe, and the results are shown in figure 11. The thermomagnetic curves demonstrated non-linear decrease of magnetization with the increase in temperature, and a sharper decrease was observed as Curie temperature was approached. Curie temperature of each compound was estimated from the derivative curve $(dM/dT)$ as shown in figure 12. Curie temperature as a function of Ga$^{3+}$ concentration in Er$\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ (figure 13) demonstrated almost linear decrease with the increase of $x$. However, the observed small decrease of Fe$^{3+}$($a$)-O$^{2-}$ and Fe$^{3+}$($d$)-O$^{2-}$ bond lengths and small increase of Fe$^{3+}$($a$)-O$^{2-}$--Fe$^{3+}$($d$) bond angle (toward 180°) as a result of Ga substitution has an effect of increasing the strength of superexchange interactions, which should result in an increase of the Curie temperature. Therefore, we conclude that the behavior of the Curie temperature in Ga-substituted ErIG is dominated by the magnetic dilution rather than by structural effects. According to the statistical theory of Gilleo [51], this behavior can be associated with the
Figure 9. Hysteresis loops for Er$_3$Fe$_{5-x}$Ga$_x$O$_{12}$ samples (a) measured with a 2 Oe field step using a maximum field of 1kOe, and (b) an expanded view of the loops.

Figure 10. Coercive fields as a function of Ga concentration of Er$_3$Fe$_{5-x}$Ga$_x$O$_{12}$ garnets.
decrease of the number of $\text{Fe}^{\text{III}}_a - \text{O}^{2-} - \text{Fe}^{\text{III}}_d$ linkages per magnetic ion per formula unit, which results from the substitution of $\text{Fe}^{\text{III}}$ by $\text{Ga}^{\text{III}}$ ions.

The magnetization of the samples as a function of temperature, $M(T)$, was also measured under a constant applied field of 100 Oe in a temperature range below room temperature in order to investigate the effect of Ga-substitution on the temperature dependent magnetic behavior of ErIG. Figure 14 shows representative thermomagnetic curves for the samples with $x = 0.0$ and 0.8. The magnetization of the unsubstituted sample exhibited a sharp decrease to zero at the compensation temperature $T_{\text{comp}} = -186^\circ\text{C}$, which is in good agreement with the reported value for ErIG [40]. As a consequence of the temperature dependences of the rare-earth and iron sublattices, the magnetization of Er$_3$Fe$_5$O$_{12}$ below $T_{\text{comp}}$ is parallel to the magnetization of the Er$^{\text{III}}$ sublattice, which decreases faster than the magnetization of the Fe$^{\text{III}}$ sublattices as the temperature increases, resulting the vanishing of the magnetization of the sample at the compensation temperature. Above $T_{\text{comp}}$, the magnetization of the sample reverses to the direction of the net magnetization of the Fe$^{\text{III}}$ sublattices, since the temperature dependence of the moments of the magnetic sublattices leads to a greater net magnetization of the Fe$^{\text{III}}$ sublattices compared to the Er$^{\text{III}}$ sublattice. As a result, the magnetization of the sample starts increasing with the increase of temperature above $T_{\text{comp}}$. However, as a consequence of the competition with the overall
decrease of magnetization due thermal effects, the magnetization reaches a maximum, and then starts decreasing to zero at the Curie temperature as shown in figure 11.

The magnetization of the sample with $x = 0.8$ exhibited a slower rate of decrease with the increase of temperature compared to the unsubstituted sample, reaching a minimum value at $-51$ °C. This upward shift of the compensation temperature is consistent with the behavior of Al-substituted erbium iron garnet single crystals, where the compensation temperature was found to increase by $72$ °C at $x = 0.55$ with respect to the pure sample [52]. This is an indication that the range of temperature over which the magnetization of the rare-earth sublattice is higher than that of the iron sublattices was extended to higher temperatures, with obvious broadening of the minimum peak structure. This behavior is caused by the depletion of $\text{Fe}^{3+}$, which may induce significant changes in the magnetic structure and temperature dependence of the magnetization of the magnetic sublattices. Firstly, the depletion of $\text{Fe}^{3+}$ has the effect of reducing the net magnetization of the $\text{Fe}^{3+}$ sublattices, which makes the rare-earth magnetization dominant over a wider temperature range. Secondly, this depletion leads to a reduction of the strength of the $A-D$ superexchange interactions, resulting in spin canting and a faster decrease of the $\text{Fe}^{3+}$ magnetization with the increase of temperature, which also is expected to increase the temperature at which minimum magnetization occurs. Since the rare-earth sublattice is magnetized by coupling with the net magnetization of $\text{Fe}^{3+}$ sublattices, its net magnetization is also expected to be lowered relative to the

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**Figure 13.** Curie temperature as a function of Ga concentration in Er$_3$Fe$_{5-x}$Ga$_x$O$_{12}$ samples.

**Figure 14.** Magnetization as a function of temperature for Er$_3$Fe$_{5-x}$Ga$_x$O$_{12}$ ($x = 0.0$ and $0.8$) samples.
unsubstituted sample, and exhibit a higher degree of spin canting of the rare earth sublattice \cite{33}. However, since the rare-earth sublattice was not magnetically diluted, the effect of Ga-substitution is expected to influence the net magnetization of the Fe$^{3+}$ sublattices more significantly, leading to the observed effects in the temperature dependence of the magnetization of the substituted sample.

4. Conclusions

Single-phase Ga-substituted erbium iron garnets Er$_3$Fe$_{5-x}$Ga$_x$O$_{12}$ (0.0 $\leq x \leq$ 0.8) were prepared by ball milling and sintering at 1300 °C. XRD results, Mössbauer spectra, and the magnetic data were all consistent with the substitution of Ga$^{3+}$ ions for Fe$^{3+}$ ions at tetrahedral sites in the samples with $x$ up to 0.6, whereas evidence of partial substitution at octahedral sites in the sample with $x = 0.8$ was provided by the three techniques. The partial substitution of Ga$^{3+}$ at octahedral sites resulted in the splitting of the octahedral component in Mössbauer spectrum of the sample with $x = 0.8$ into two components. The saturation magnetization decreased linearly with increasing $x$ in accordance with a simple magnetic dilution model up to $x = 0.6$, and deviated slightly from the linear behavior at $x = 0.8$ due to partial substitution at octahedral sites. The lattice parameter and cell volume decreased slightly, whereas the x-ray density increased with increasing $x$. The Curie temperature also decreased almost linearly with the increase of Ga concentration, due to the progressive decrease of the strength of superexchange interactions resulting from the substitution of magnetic Fe$^{3+}$ by non-magnetic Ga$^{3+}$ ions. The thermomagnetic curves below room temperature indicated that the unsubstituted sample exhibited the usual compensation point of ErIG, while the sample with $x = 0.8$ exhibited a minimum at a higher temperature, with significant broadening of the peak profile. These results indicated that Ga substitution resulted in a significant change of the temperature dependence of the magnetic sublattices, in addition to the significant reduction of the overall magnetization above the compensation point.

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