Co-Doped Rare-Earth (La, Pr) and Co-Al Substituted M-Type Strontium Hexaferrite: Structural, Magnetic, and Mossbauer Spectroscopy Study

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Abstract

The present study investigates the influence of La3+ and Pr3+ doping on the structural, magnetic properties, and hyperfine fields of Sr0.7RE0.3Fe12−2xCoxAlxO19 (RE: La3+ and Pr3+, x = 0.0 - 0.8) hexaferrite compounds prepared via auto-combustion technique. The XRD analysis shows a linear decrease in a and c lattice and unit cell volume contraction with the content x. The room temperature magnetic study shows that for the Pr3+ doped Sr0.7Pr0.3Fe12−2xCoxAlxO19 (Pr3+-SrM), the magnetization value monotonically decreases while for La3+ doped Sr0.7La0.3Fe12−2xCoxAlxO19 (La3+-SrM) magnetization value shows a noticeable increase in magnetization value with x. The coercivity of the Pr3+-SrM compound was observed to decrease while that of the La3+-SrM compound showed a marked 40% increase at x = 0.2 (~5829 Oe) in comparison to undoped SrFe12O19 (~3918 Oe). A difference in Curie temperature was also observed, with Tc ~ 525˚C at x = 0.4 for Pr3+-SrM and Tc = 505˚C for x = 0.4 for La3+-SrM compound. The observed differences in magnetic properties have been explained on the basis of the site occupancy of Co2+ and Al3+ in the presence of rare-earth ions. The presence of non-magnetic rare-earth ion, La3+, improved saturation magnetization, and coercivity and deemed suitable replacement for Sr2+. The hyperfine parameters namely quadrupole shift showed a decrease with the La3+ or Pr3+ doping independent of (Co2+-Al3+) ions doping. Overall, the Mossbauer analysis suggests that the (Co2+-Al3+) impurities prefer occupancy at 2a site.
Keywords
Doped Hexaferrite, M-Type Hexaferrite, X-Ray Diffraction, Mossbauer Spectroscopy

1. Introduction

The M-type hexaferrite, Strontium hexaferrite, is an excellent candidate for technological applications because of its high uniaxial magneto-crystalline anisotropy, large magnetization, high permeability, low conductive losses, excellent chemical stability, corrosion resistance and excellent high-frequency response [1] [2] [3]. Strontium hexaferrite has been widely used as materials for industrial applications, such as in microwave devices, small motors, electromagnetic wave absorber, and ferroxdures [4] [5]. Besides this, the popularity of strontium hexaferrite is also due to its economic success, which is its low price per unit available magnetic energy and its wide availability. So far, efforts have been made to further improve electrical, dielectric and magnetic properties of strontium hexaferrite by means of doping, heat treatment, ion substitution, and processing conditions [6] [7] [8] [9] [10].

In M-type hexaferrite, the structure is comprised of 64 ions per hexagonal unit cell on 11 distinct basis sites. The 24 Fe3+ iron atoms of a unit cell occupy five different interstitial sites: three octahedral sites (2a, 12k, and 4f2), one tetrahedral site (4f1) and one trigonal bi-pyramidal site (2b). The coupling of these sites by superexchange interaction via O2− gives rise to a ferrimagnetic structure. The sites 12k, 2a, and 2b are sites with spin up while sites 4f2 and 4f1 are sites with the down-spin [10]. This provides an ample opportunity to tune the magnetic properties of M-type hexaferrite compound by carefully engineering site occupancy in favor of increasing net magnetization of the compound. In view of this, attempts are made with either partial substitution of Sr2+ or Fe3+ sites. For example, substitution with non-magnetic ions such as Al3+ [11] [12], Zn3+ [13], Ga3+ [14] and Cd3+ [15] [16] and magnetic ions such as Co2+ [17] and Cr3+ [18] at Fe sites, or with the partial substitution of Sr2+ site by RE3+ such as La3+ [19] [20], Nd3+ [21], Sm3+ [22] [23] and Pr3+ [24] ions, and substitution of Sr2+/Fe3+ together with Pr-Zn [25], La-Cu [26], and La-Zn [27]. The majority of these studies have attributed changes in the magnetic behavior of doped SrM either to the site-occupancy, which perturbs exchange interaction between Fe3+-O2−Fe3+, anisotropy changes occurring at 2b sites due to perturbation in electric field gradient or extrinsic features such as particle size.

Doping of non-magnetic Al3+ in SrFe12−xAlxO19 has been reported to bring a considerable enhancement in the coercivity along with a reduction in saturation magnetization [11] [28] [29]. Thus with the Al3+ substitution, in spite of a large increase in the coercivity, the compound attains abysmal magnetization value. A strategy could be designed to keep both coercivity and magnetization value high.
In the present work, an attempt is made to co-doped Co$^{2+}$-Al$^{3+}$ in the SrFe$_{12}$O$_{19}$ compound. Magnetic ion Co$^{2+}$ (~3.7 $\mu_B$) is chosen to maintain high magnetization value, while Al$^{3+}$ doping is expected to maintain high coercivity value in SrFe$_{12}$O$_{19}$. Furthermore, Lechevallier et al. reported that the only light rare-earth enters the structure, which a solubility that is related to the shape of the charge distribution of the 4f electrons to its surroundings in the crystal structure. Thus, only those rare-earth ions have easy accommodation at the Sr$^{2+}$ site, whose surroundings favor an oblate electronic distribution. This makes Pr and Nd (with oblate 4f charge distribution, negative Stevens constant) ideal candidate to occupy the Sr$^{2+}$ site [25]. Furthermore, Co$^{2+}$ ions were reported to modify the surroundings of the Sr$^{2+}$ site, improving the introduction of rare-earth ions with oblate electronic distributions, in fact, the presence of Co$^{2+}$ increases the solubility of Pr$^{3+}$ [25]. Also, RE$^{3+}$-Co$^{2+}$-Al$^{3+}$, co-substitution naturally maintains the charge neutrality condition in the compound. With the substitution of RE$^{3+}$ for the Sr$^{2+}$, the extra positive charge is compensated by the substitution of Co$^{2+}$ at the Fe$^{3+}$ site. In the absence of Co$^{2+}$, one of the Fe$^{3+}$ has to convert to Fe$^{2+}$, which has a deleterious effect on the magnetization. With this strategy in mind, the present study investigates, the influence of the 1) rare-earth substitution, Pr$^{3+}$, and La$^{3+}$, at the Sr$^{2+}$ site and 2) Co$^{2+}$-Al$^{3+}$ substitution at Fe$^{3+}$ sites on the overall magnetic properties of the Sr$_{0.7}$RE$_{0.3}$Fe$_{12-2x}$CoxAl$_x$O$_{19}$ compound.

2. Experimental

The series of Sr$_{0.7}$RE$_{0.3}$Fe$_{12-2x}$CoxAl$_x$O$_{19}$ (RE: La$^{3+}$ and Pr$^{3+}$, x = 0, 0.2, 0.4, 0.6 and 0.8) compounds were prepared by auto-combustion method [11]. Nitrate salts of Fe(NO$_3$)$_3$·9H$_2$O (Sigma Aldrich, 99%), Sr(NO$_3$)$_2$ (Sigma Aldrich, 99%), Al(NO$_3$)$_3$·9H$_2$O (Sigma Aldrich, 99%), RE(NO$_3$)$_3$·9H$_2$O (Sigma Aldrich, 99%) and C$_6$H$_8$O$_7$ (Sigma Aldrich, 99%) were selected for the synthesis Sr$_{0.7}$RE$_{0.3}$Fe$_{12-2x}$CoxAl$_x$O$_{19}$ compounds. The stoichiometric amount of nitrates salts and citric acid were mixed in 25 ml of deionized water under constant stirring on a hot plate at 80°C for about 30 minutes. Aqueous ammonia was added dropwise in the homogeneous mixture until the pH value of the solution reached 6.5. The intermediate precipitate was heated at 100°C on a hot plate under stirring until the viscous brown gel is formed. The temperature is suddenly increased to 300°C to turn it into magnetic powder. Powders were calcined in air at 1000°C for twelve hours. The precursor used in the preparation of 1 g of sample is listed in Table 1.

The crystal structure and phase purity of the obtained samples were identified by analyzing x-ray diffraction (XRD) pattern collected via Bruker D8 Advance X-ray diffractometer using Cu K$_\alpha$ radiation source ($\lambda$ ~ 0.154056 nm). Vibrating sample magnetometer (VSM) was used to collect hysteresis loops of the samples at room temperature in the maximum field of 1.2 T. Curie temperature, $T_C$, were measured using Thermogravimetric analyzer, TGA, (DuPont 910) equipped with a permanent magnet. Room temperature $^{57}$Fe Mossbauer spectroscopy was
Table 1. Stoichiometry weight of SrFe₁₂O₁₉, Sr₀.₇La₀.₃Fe₁₂₋₂ₓCoₓAlₓO₁₉ and Sr₀.₇Pr₀.₃Fe₁₂₋₂ₓCoₓAlₓO₁₉.

| Mass (g) | Sr(NO₃)₂ | La(NO₃)₂·6H₂O | Fe(NO₃)₂·9H₂O | Co(NO₃)₂·6H₂O | Al(NO₃)₂·9H₂O | Citric acid |
|----------|----------|----------------|---------------|----------------|----------------|-------------|
| SrFe₁₂O₁₉ | 0.199    | 0.000          | 4.567         | 0.000          | 0.000          | 2.573       |
| Sr₀.₇La₀.₃Fe₁₂₋₂ₓCoₓAlₓO₁₉ | | | | | | |
| x = 0.0  | 0.176    | 0.361          | 4.038         | 0.000          | 0.000          | 2.275       |
| x = 0.2  | 0.175    | 0.359          | 3.951         | 0.048          | 0.062          | 2.264       |
| x = 0.4  | 0.175    | 0.357          | 3.865         | 0.096          | 0.124          | 2.253       |
| x = 0.6  | 0.174    | 0.355          | 3.780         | 0.143          | 0.185          | 2.241       |
| x = 0.8  | 0.173    | 0.354          | 3.695         | 0.190          | 0.245          | 2.230       |
| Sr₀.₇Pr₀.₃Fe₁₂₋₂ₓCoₓAlₓO₁₉ | | | | | | |
| x = 0.0  | 0.137    | 0.125          | 4.499         | 0.000          | 0.000          | 2.535       |
| x = 0.2  | 0.137    | 0.124          | 4.400         | 0.054          | 0.069          | 2.521       |
| x = 0.4  | 0.136    | 0.123          | 4.301         | 0.107          | 0.138          | 2.507       |
| x = 0.6  | 0.135    | 0.123          | 4.204         | 0.159          | 0.205          | 2.493       |
| x = 0.8  | 0.134    | 0.122          | 4.107         | 0.211          | 0.272          | 2.480       |

employed to derive hyperfine parameters. The Mossbauer spectrometer (SEE Co. Minneapolis, MN USA) was calibrated against α-Fe foil. The Mossbauer spectra were analyzed using WMoss software (SEE Co. Minneapolis, MN USA).

3. Results and Discussions

The room temperature XRD pattern of Sr₀.₇RE₀.₃Fe₁₂₋₂ₓCoₓAlₓO₁₉ (RE: La³⁺ and Pr³⁺, x = 0.0, 0.2, 0.4, 0.6, and 0.8) is shown in Figure 1. XRD patterns of the substituted compounds indicated the presence of a magnetoplumbite structure (ICCD 080-1198) corresponding to the hexagonal P63/mmc symmetry phase group without any secondary phase. The lattice parameters of the compound were calculated from their inter-planar spacing $d_{hkl}$ corresponding to the major peaks (107), (114), and (008) using equation [30]:

$$d_{hkl} = \left( \frac{4(h^2 + hk + k^2)}{3a^2} \right)^{\frac{1}{2}}$$  \hspace{1cm} (1)

where $h$, $k$, and $l$ are Miller indices. The calculated lattice parameters $a$ and $c$ of the hexaferrites are shown in Table 2. The plot for $a$ and $c$ as a function of doping content is shown in Figure 2. A linear decrease in the lattice parameters $a$ and $c$ with the doping content was observed. The linear decrease in the lattice parameter may occur due to the substitution of Al³⁺ (ionic radii, $r \sim 0.51$ Å) and
Figure 1. X-ray diffraction pattern of (a) Sr$_{0.7}$La$_{0.3}$Fe$_{12-2x}$Co$_x$Al$_x$O$_{19}$ and (b) Sr$_{0.7}$Pr$_{0.3}$Fe$_{12-2x}$Co$_x$Al$_x$O$_{19}$ obtained using Cu Kα radiation.

Figure 2. Lattice parameters of Sr$_{0.7}$La$_{0.3}$Fe$_{12-2x}$Co$_x$Al$_x$O$_{19}$ and Sr$_{0.7}$Pr$_{0.3}$Fe$_{12-2x}$Co$_x$Al$_x$O$_{19}$ as a function of content, x, derived from X-ray diffraction pattern.
Table 2. Lattice parameters of SrFe_{12}O_{19}, Sr_{0.7}La_{0.3}Fe_{12-2x}Co_{x}Al_{x}O_{19} and Sr_{0.7}Pr_{0.3}Fe_{12-2x}Co_{x}Al_{x}O_{19} as obtained from XRD pattern using Equation (1) and crystalline size using Equation (2).

|                  | a (Å) | c (Å) | V (Å³) | c/a | Crystallite size (nm) |
|------------------|-------|-------|--------|-----|----------------------|
| SrFe_{12}O_{19}  |       |       |        |     |                      |
| Sr_{0.7}La_{0.3}Fe_{12-2x}Co_{x}Al_{x}O_{19} | x = 0.0 | 5.856 | 22.936 | 688.498 | 3.919 | 58.345 |
|                  | x = 0.2 | 5.869 | 22.995 | 686.086 | 3.913 | 65.900 |
|                  | x = 0.4 | 5.867 | 22.943 | 684.758 | 3.911 | 61.670 |
|                  | x = 0.6 | 5.860 | 22.964 | 682.798 | 3.910 | 59.465 |
|                  | x = 0.8 | 5.869 | 23.012 | 681.155 | 3.908 | 56.070 |
| Sr_{0.7}Pr_{0.3}Fe_{12-2x}Co_{x}Al_{x}O_{19} | x = 0.0 | 5.873 | 23.034 | 687.308 | 3.914 | 60.825 |
|                  | x = 0.2 | 5.923 | 23.076 | 687.038 | 3.914 | 76.640 |
|                  | x = 0.4 | 5.915 | 23.047 | 684.448 | 3.913 | 65.985 |
|                  | x = 0.6 | 5.911 | 23.027 | 683.225 | 3.914 | 67.210 |
|                  | x = 0.8 | 5.904 | 23.035 | 681.995 | 3.911 | 65.000 |

Co^{2+} (r ~ 0.72 Å) for Fe^{3+} (r ~ 0.64 Å) and smaller La^{3+} (r ~ 1.172 Å) and Pr^{3+} (r ~ 1.13 Å) for the Sr^{2+} (r ~ 1.32 Å) ions [31]. According to Wagner [32], an examination of c/a parameter ratio may be used to quantify the structure type, as the M-type (magnetoplumbite) structure can be assumed if the ratio is observed to be in the range 3.917 and 3.963. As per Table 2, the c/a ratios of as-prepared samples are in the range of 3.908 to 3.919, assuring that the as-prepared samples have maintained the M-type structure.

The crystallite size of as-synthesized particles was calculated using Scherrer’s equation [33]:

\[
D(hkl) = k \lambda / (\beta \cos \theta)
\]  

(2)

where \(k\) denotes the Scherrer constant (\(k = 0.9\)), \(\lambda\) is the wavelength of x-ray source (\(\lambda = 0.154056\) nm), \(\beta\) is the full-width-half-maximum of a diffraction peak and \(\theta\) is the diffraction angle. As listed in Table 2, the crystallite size of as-synthesized samples is in the range of 54 to 77 nm. In the comparison of the pure SrFe_{12}O_{19} sample with a crystallite size of 80.7 nm, the doped compounds show reduced crystallite size. Grain refinement is usually observed in rare-earth and doped oxide compounds [34]. This grain refinement is reported to result from the 1) increased microstrain and defect density with substitution content and 2) diffusion of substituent element to the grain boundaries, the migration that restrains the grain growth by lowering down the grain growth mobility. If the retarding force generated is more than the driving force for the grain growth due to dopants, the movement of the grain boundary is impeded [35].

DOI: 10.4236/msa.2020.117.033
The room temperature hysteresis loops, $M$ vs. $H$, of $\text{Sr}_{0.7}\text{RE}_{0.3}\text{Fe}_{12-2x}\text{Co}_x\text{Al}_x\text{O}_{19}$ are shown in Figure 3. The magnetic parameters viz. saturation magnetization, $M_s$, remanence, $M_r$, and coercivity, $H_c$ were extracted from the hysteresis loops and are listed in Table 3. The $M$ vs. $H$ curves show hard ferrites behaviors with high coercivity. The magnetic properties have been changed significantly upon RE$^{3+}$ and Co$^{2+}$-Al$^{3+}$ substitution in $\text{Sr}_{0.7}\text{RE}_{0.3}\text{Fe}_{12-2x}\text{Co}_x\text{Al}_x\text{O}_{19}$ as compared to undoped ferrite $\text{SrFe}_{12}\text{O}_{19}$. The $M_s$ value of Pr$^{3+}$-SrM is observed to have a maximum value of 86 emu/g for $x = 0.2$ but decreases with Co$^{2+}$-Al$^{3+}$ content and achieves a minimum value of 65 emu/g for $x = 0.8$. However, in the case of La$^{3+}$-SrM, the $M_s$ increases with $x$ and attains a maximum value of 87 emu/g at $x = 0.8$. As compared to pure $\text{SrFe}_{12}\text{O}_{19}$, La$^{3+}$-SrM displays a noticeable 20% enhancement while Pr$^{3+}$-SrM shows a 10% reduction in the $M_s$ value. The variation of $M_r$ and $M_s$ as a function of $x$ content is shown in Figure 4. The value of $M_r$ follows a trend similar to that of $M_s$. As explained in the Mossbauer section, for series of compounds shows the marked preference of Co$^{2+}$-Al$^{3+}$ for the 2$a$ site, a site with the spin-up moment. Despite the substitution of Co$^{2+}$-Al$^{3+}$ at the 2$a$ site with the up-spin moment, the magnetization of La$^{3+}$-SrM displayed a marked increase in the magnetization value with the substitution. A possible explanation for this observation is that the substitution of non-magnetic La$^{3+}$ at the Sr$^{2+}$ 1) could enhance hyperfine fields at 12$k$ site due to strengthening in the Fe$^{3+}$-$\text{O}^{2-}$-Fe$^{3+}$ superexchange interaction giving higher net magnetization. This increase in the hyperfine field of 12$k$ site is evident from the Mossabuer analysis, and 2) may increase the spin canting at the near-neighbor 4$f^2$ site (Sr$^{2+}$-$4f^2$ ~ 0.366 nm), which results in a positive contribution to the overall magnetic moment. However, the possibility of Co$^{2+}$ occupying a 4$f^2$ site cannot be ignored, which increases the net positive moment per unit cell of the compound [36] [37]
Table 3. Magnetic parameters of SrFe₁₂O₁₉, Sr₀.₇La₀.₃Fe₁₂−₂ₓCoxAlₓO₁₉ and Sr₀.₇Pr₀.₃Fe₁₂−₂ₓCoxAlₓO₁₉ measured using VSM. Curie temperature, Tc, of samples was measured using TGA.

|                | Ms (emu/g) | Mr (emu/g) | Mr/Ms | Hc (Oe) | Tc (˚C) |
|----------------|------------|------------|-------|---------|---------|
| SrFe₁₂O₁₉      | 72.35      | 44.71      | 0.61  | 3918    | 458.60  |
| Sr₀.₇La₀.₃Fe₁₂−₂ₓCoxAlₓO₁₉ | x = 0.0  | 58.44      | 40.14 | 0.69    | 4318    | 477.80  |
|                 | x = 0.2   | 69.22      | 43.62 | 0.63    | 5829    | 427.13  |
|                 | x = 0.4   | 79.67      | 51.50 | 0.65    | 5031    | 506.00  |
|                 | x = 0.6   | 78.00      | 49.97 | 0.63    | 4498    | 492.38  |
|                 | x = 0.8   | 86.64      | 51.91 | 0.60    | 4761    | 455.75  |
| Sr₀.₇Pr₀.₃Fe₁₂−₂ₓCoxAlₓO₁₉ | x = 0.0  | 83.40      | 50.88 | 0.61    | 4651    | 456.63  |
|                 | x = 0.2   | 86.09      | 52.81 | 0.61    | 4090    | 428.75  |
|                 | x = 0.4   | 74.10      | 48.05 | 0.65    | 4130    | 523.56  |
|                 | x = 0.6   | 62.20      | 39.97 | 0.64    | 3659    | 505.30  |
|                 | x = 0.8   | 65.40      | 41.52 | 0.63    | 3379    | 489.19  |

Figure 4. Room temperature Ms and Mr of Sr₀.₇La₀.₃Fe₁₂−₂ₓCoxAlₓO₁₉ and Sr₀.₇Pr₀.₃Fe₁₂−₂ₓCoxAlₓO₁₉ measured at 1.2 T field as a function of content, x.

[39]. On the other hand, the substitution of magnetic Pr³⁺ at the Sr²⁺ site may not allow spin-canting at the 4L₂ site, and with the replacement of Fe³⁺ at the 2a site, the overall magnetic moment decreases in the Pr³⁺-SrM compounds.

The variation of coercivity, Hc, of La³⁺-SrM and Pr³⁺-SrM compounds as a function of x content is shown in Figure 5. Consistently La³⁺-SrM samples display higher Hc values than Pr³⁺-SrM compounds for all x values. The Hc value of La³⁺-SrM displays a marked ~50% increase at x = 0.2 when compared to that of pure SrFe₁₂O (Hc ~ 3918 Oe). On the other hand, Hc value decreases linearly with increasing the x content for the Pr³⁺-SrM compound. Being an extrinsic
property, the coercivity depends on factors such as crystal structure, morphological features, elemental composition, and defects. In general, \( H_c \) can be expressed as,

\[
H_c = \left( \alpha \left( \frac{2K1}{\mu_0 M_s} \right) - N \left( M_r + M_s \right) \right) / \mu_0
\]

where \( \alpha \) is the microstructure factor which has a reciprocal dependence on the grain size, \( N \) is the demagnetization factor, \( 2K1/\mu_0 M_s \) is the \( Ha \) is the magnetocrystalline anisotropy field [39]. In the M-type hexaferrite, magnetocrystalline anisotropy mainly originates from Fe\(^{3+} \) ions at the 2\( b \) and 4\( f1 \) site [40] [41]. It has been reported that Al\(^{3+} \) ions have a preference for 4\( f2 \), 2\( a \), and 12\( k \) sites, [42] [43], and Co\(^{3+} \) ions mainly prefer 4\( f2 \) (mainly) and 2\( a \) sites [37] [38] [44]. In accordance with the Mossbauer analysis, discussed later, it is observed that in both series of samples studied herein, the Co\(^{3+} \)-Al\(^{3+} \) ions have a preference for the 2\( a \) site. Thus the intrinsic coercivity as per Equation (3), should increase for both series of samples due to the increase in the magnetocrystalline anisotropy, as the site 2\( b \) remains unaffected with the said substitution. However, from Figure 5, it is observed that the La\(^{3+} \)-SrM sample shows a maximum (5829 Oe) in coercivity value at \( x = 0.2 \), followed by a decrease with increasing \( x \) content in the sample. On the other hand, the \( H_c \) value of the Pr\(^{3+} \)-SrM sample shows a monotonous decrease with the \( x \) content in the sample. Also, the La\(^{3+} \)-SrM sample displays consistently higher coercive field value as compared to Pr\(^{3+} \)-SrM. In a comparative study on Sr(La/Pr)Fe\(_{12} \)O\(_{19} \) samples it was reported that the Pr\(^{3+} \) doped Sr(Pr)Fe\(_{12} \)O\(_{19} \) displayed higher coercivity than La\(^{3+} \) doped Sr(Pr)Fe\(_{12} \)O\(_{19} \) sample because of the higher magnetocrystalline anisotropy of the former. However, the contrary results in the present study can be explained by taking microstructure factor, \( \alpha \), in account in Equation (3) above. The La\(^{3+} \)-SrM samples have relatively smaller crystallite size as compared to Pr\(^{3+} \)-SrM; as a result, the microstructure factor, \( \alpha \), will have a higher value than that of Pr\(^{3+} \)-SrM sample. This will make the first term in the Equation (3) above greater than for La\(^{3+} \)-SrM as compared to that for Pr\(^{3+} \)-SrM. The observed decrease in coercivity with the substitution.
could be attributed to the fact that the second term in the Equation (3) decreases much rapidly as compared to the αHa term.

The Curie temperature, $T_c$, of Sr$_{0.7}$RE$_{0.3}$Fe$_{12-2x}$Co$_x$Al$_x$O$_{19}$ are shown in Figure 6. The maximum $T_c$ value for La$^{3+}$-SrM and Pr$^{3+}$-SrM was observed to be 505 and 525 K, respectively at $x = 0.40$. After attaining maximum value, the $T_c$ decreases gradually for $x > 0.40$. The overall decrease in $T_c$ after attaining maximum can be explained on the basis of three combined effects [45] [46], 1) substitution of Co$^{2+}$-Al$^{3+}$ ions for Fe$^{3+}$ ions reduce the Fe$^{3+}$ ions and hence leads to a reduction of Fe$^{3+}$-O$_{2^-}$-Fe$^{3+}$ number of superexchange interaction and strength and 2) lattice contraction with the substitution alters the bond length and angle of Fe$^{3+}$-O$_{2^-}$-Fe$^{3+}$ from its optimum interaction strength value. However, in the beginning, $T_c$ drops down for $x = 0.20$, where presumably Fe$^{3+}$ might be substituted more with non-magnetic Al$^{3+}$ and above combined effect become prevalent. However, the increasing magnetic Co$^{2+}$ ion content helps regain the strength of the superexchange interaction and hence increases the $T_c$ value for $x = 0.40$ [47].

In order to investigate the site occupancies of transition metal ions and resulting hyperfine parameters in the samples, Mossbauer spectra were collected at room temperature. Figure 7 shows the fitted Mossbauer spectra as a function of content $x$ in the as-synthesized samples. All spectra consist of five Lorentzian sextets originating from 12k, 4f1, 4f2, 2a, and 2b crystallographic sites of Fe$^{3+}$ ions. The spectra were fitted with the constrain that all the linewidths of the absorption lines were the same. The extracted Mossbauer parameters are listed in Table 4(a) and Table 4(b). The observed sequences of the magnetic hyperfine magnetic fields, HF (4f2 > 2a > 4f1 > 12k > 2b) and isomer shift, δ (the isomer shifts follow the sequence of 4f2 > 12k > 2a > 2b > 4f1) for both samples are in agreement with the reported results [47].

It is well known that the magnitude of the hyperfine magnetic field at the Fe$^{3+}$ site depends on the distribution of neighboring magnetic cations. The hyperfine field, $HF$, the parameter of the most intense 12k line effectively shows no variation...
Figure 7. Room temperature fitted Mössbauer spectra of (a) Sr$_{0.7}$La$_{0.3}$Fe$_{12-2x}$Co$_{x}$Al$_{x}$O$_{19}$ and (b) Sr$_{0.7}$Pr$_{0.3}$Fe$_{12-2x}$Co$_{x}$Al$_{x}$O$_{19}$ respectively.
Table 4. (a) Hyperfine parameters of Sr$_{0.7}$La$_{0.3}$Fe$_{12-2x}$Co$_x$Al$_x$O$_{19}$ extracted from fitting room temperature Mossbauer spectra; (b) Hyperfine parameters of Sr$_{0.7}$Pr$_{0.3}$Fe$_{12-2x}$Co$_x$Al$_x$O$_{19}$ extracted from fitting room temperature Mossbauer spectra.

(a)

| Sr$_{0.7}$La$_{0.3}$Fe$_{12-2x}$Co$_x$Al$_x$O$_{19}$ | x | HF (kOe) | QS (mm/s) | IS (mm/s) | Area (%) |
|-----------------------------------------------|---|----------|-----------|-----------|----------|
| SrFe$_2$O$_{19}$                              | 0.0 | 411.50   | 0.20      | 0.23      | 47.60    |
|                                               | 0.2 | 412.38   | 0.18      | 0.23      | 47.06    |
|                                               | 0.4 | 413.66   | 0.17      | 0.23      | 46.97    |
|                                               | 0.6 | 413.73   | 0.17      | 0.23      | 46.26    |
|                                               | 0.8 | 416.37   | 0.18      | 0.24      | 43.50    |
| SrFe$_{12-x}$O$_{19}$                         | 0.0 | 491.00   | 0.09      | 0.15      | 18.20    |
|                                               | 0.2 | 477.73   | 0.05      | 0.15      | 23.20    |
|                                               | 0.4 | 480.87   | 0.06      | 0.15      | 22.72    |
|                                               | 0.6 | 480.11   | 0.05      | 0.15      | 23.81    |
|                                               | 0.8 | 475.82   | 0.05      | 0.16      | 24.63    |
| SrFe$_{12-x}$O$_{19}$                         | 0.0 | 517.4    | 0.15      | 0.27      | 26.6     |
|                                               | 0.2 | 507.18   | 0.17      | 0.26      | 20.05    |
|                                               | 0.4 | 509.46   | 0.18      | 0.26      | 21.37    |
|                                               | 0.6 | 509.23   | 0.16      | 0.25      | 22.81    |
|                                               | 0.8 | 506.32   | 0.14      | 0.25      | 24.90    |
| SrFe$_{12-x}$O$_{19}$                         | 0.0 | 508.10   | 0.00      | 0.22      | 8.70     |
|                                               | 0.2 | 508.10   | 0.00      | 0.22      | 5.60     |
|                                               | 0.4 | 508.10   | 0.00      | 0.22      | 4.14     |
|                                               | 0.6 | 508.10   | 0.00      | 0.22      | 1.84     |
|                                               | 0.8 | 508.10   | 0.00      | 0.22      | -        |
| SrFe$_{12-x}$O$_{19}$                         | 0.0 | 409.10   | 1.12      | 0.19      | 7.00     |
|                                               | 0.2 | 407.55   | 0.98      | 0.10      | 6.92     |
|                                               | 0.4 | 407.49   | 1.01      | 0.12      | 6.84     |
|                                               | 0.6 | 408.37   | 0.97      | 0.10      | 7.10     |
|                                               | 0.8 | 407.23   | 0.99      | 0.11      | 7.12     |
|                                               | 0.8 | 406.20   | 0.99      | 0.11      | 6.98     |
| Sr$_{0.7}$Pr$_{0.3}$Fe$_{12-2x}$Co$_x$Al$_x$O$_{19}$ | x | HF (kOe) | QS (mm/s) | IS (mm/s) | Area (%) |
|---------------------------------------------|---|---------|----------|---------|---------|
| SrFe$_{12}$O$_{19}$                        | 0.0 | 413.4 | 0.20 | 0.24 | 46.70 |
|                                            | 0.2 | 414.4 | 0.17 | 0.23 | 47.30 |
|                                            | 0.4 | 413.4 | 0.16 | 0.23 | 46.20 |
|                                            | 0.6 | 414.0 | 0.18 | 0.23 | 44.60 |
|                                            | 0.8 | 412.3 | 0.19 | 0.22 | 42.50 |
| SrFe$_{12}$O$_{19}$                        | 0.0 | 489.8 | 0.09 | 0.15 | 18.30 |
|                                            | 0.2 | 485.0 | 0.06 | 0.16 | 21.10 |
|                                            | 0.4 | 482.4 | 0.06 | 0.16 | 22.30 |
|                                            | 0.6 | 482.8 | 0.04 | 0.16 | 23.60 |
|                                            | 0.8 | 481.3 | 0.05 | 0.15 | 22.50 |
| SrFe$_{12}$O$_{19}$                        | 0.0 | 516.0 | 0.15 | 0.27 | 18.10 |
|                                            | 0.2 | 511.6 | 0.18 | 0.27 | 18.70 |
|                                            | 0.4 | 510.2 | 0.18 | 0.26 | 20.40 |
|                                            | 0.6 | 510.7 | 0.15 | 0.26 | 22.60 |
|                                            | 0.8 | 509.6 | 0.13 | 0.26 | 24.50 |
| SrFe$_{12}$O$_{19}$                        | 0.0 | 508.1 | 0.00 | 0.22 | 8.70  |
|                                            | 0.2 | 508.1 | 0.00 | 0.22 | 8.80  |
|                                            | 0.4 | 508.1 | 0.00 | 0.22 | 5.90  |
|                                            | 0.6 | 508.1 | 0.00 | 0.22 | 3.20  |
|                                            | 0.8 | 508.1 | 0.00 | 0.22 | 1.30  |
| SrFe$_{12}$O$_{19}$                        | 0.0 | 408.4 | 1.10 | 0.17 | 8.10  |
|                                            | 0.2 | 411.0 | 1.02 | 0.11 | 7.00  |
|                                            | 0.4 | 408.9 | 0.99 | 0.12 | 7.80  |
|                                            | 0.6 | 409.4 | 0.99 | 0.12 | 7.80  |
|                                            | 0.8 | 405.0 | 1.01 | 0.12 | 7.00  |
with \( x \) in Pr\(^{3+}\)-SrM, while \( HF \) increases with \( x \) in the La\(^{3+}\)-SrM sample. The increase in \( HF \) value of La\(^{3+}\)-SrM is in agreement with the observed increase in the saturation magnetization, \( Ms \), with content \( x \). Other lines \( 4f1, 2a, \) and \( 4f2 \) show a monotonous decrease in \( HF \) with \( x \).

The isomer shift plot as a function of \( x \) is shown in Figure 8. The isomer shift, \( \delta \), for both series of samples for all sites visibly remains invariant except for the \( 2b \) site. Also, the \( 2b \) site’s isomer shift value clearly reflects the influence of the

![Figure 8](image)

**Figure 8.** Room temperature hyperfine parameters of Sr\(_{0.7}\)La\(_{0.3}\)Fe\(_{12-2x}\)Co\(_{x}\)Al\(_{19}\) and Sr\(_{0.7}\)Pr\(_{0.3}\)Fe\(_{12-2x}\)Co\(_{x}\)Al\(_{19}\) obtained from Mossbauer spectral analysis.
rare-earth ion in the compound. In the presence of rare-earth ion, the isomer shift value of 2b drops significantly as compared to that of a pure SrFe$_{12}$O$_{19}$ compound. Isomer shift is a measure of 3d electron density at the nucleus of the Fe atom. The closest sites of Sr$^{2+}$ sites are 12k, 4f2, and 2b. The 2b sites are located in the same plane as Sr$^{2+}$ ions (at a distance of 0.340 nm), while the 4f2 and 12k sites are located in the adjacent planes at nearly the same distance from Sr$^{2+}$ viz. Sr$^{2+}$-12k ~ 0.365 nm and Sr$^{2+}$-4f2 ~ 0.366 nm [48] [49]. Pr [Xe] 4f$^{3}$ 6s$^{2}$ and La[Xe] 5d$^{1}$ 6s$^{2}$ with more electrons as compared to Sr (Kr[5s$^{2+}$]) has a negative effect on the isomer shift, that is increased substitution of Pr$^{3+}$ or La$^{3+}$ increases the net s-electron charge density at the 2b site.

The quadrupole shift, QS, values of 2b site show a similar ~10% drop in both Pr$^{3+}$ and La$^{3+}$ substituted samples. The quadrupole values for all sites remain invariant with x for both series of samples. It is known that QS is a measure of the asymmetry of a crystallographic site. Since the 2b sites are located in the same plane as Sr$^{2+}$, the substitution of the smaller Pr$^{3+}$ and La$^{3+}$ for Sr$^{2+}$ ions induces a deformation, which affects the electronic site symmetry of the nearby 2b site. Due to the substitution of smaller La$^{3+}$ and Pr$^{3+}$ ion for Sr$^{2+}$ ion, the lattice constant c contracts. Consequently, large Fe-O distances parallel to the c-axis decreases. As a result, the oxygen bipyramid of the 2b-site becomes more symmetric, which is in agreement with the observed reduction in the quadrupole shift value with content x. A similar decrease in 2b quadrupole splitting originating from the presence of La$^{3+}$ substitution has been reported in Sr$_{1-x}$La$_{x}$Fe$_{12-y}$CoyO$_{19}$ [39].

A close examination of the fitted spectra shows a decreasing trend of 2a absorption intensities with increasing x. Without Co$^{2+}$-Al$^{3+}$ co-doping, the intensity of 2a site lines in both Sr$_{0.7}$La$_{0.3}$Fe$_{12}$O$_{19}$ and Sr$_{0.7}$Pr$_{0.3}$Fe$_{12}$O$_{19}$ are nearly the same as that of undoped SrFe$_{12}$O$_{19}$. However, with the substitution of Co$^{2+}$-Al$^{3+}$, the 2a absorption area decreased linearly and finally disappeared at x = 0.6 and 1.0 for La$^{3+}$-SrM and Pr$^{3+}$-SrM sample, respectively. This suggests preferential occupation of Co$^{2+}$-Al$^{3+}$ for the 2a site. It has already been reported that Al$^{3+}$ ion prefers 12k and 2a site [50] while Co$^{2+}$ was reported to enter 4f2 site in Sr$_{1-x}$La$_{x}$Fe$_{12-x}$CoyO$_{19}$ [51]. There is only one 2a site in every one formula unit of M-type hexaferrite. Therefore, the fact that the 2a absorption line of Sr$_{0.7}$La$_{0.3}$Fe$_{12-2x}$Co$_{x}$Al$_{x}$O$_{19}$ disappeared completely at x = 0.6 means that all the Co$^{2+}$-Al$^{3+}$ dopants almost exclusively go into 2a site. In the case when x > 0.5, the excessive Co$^{2+}$-Al$^{3+}$ dopant should occupy the crystallographic sites other than the 2a site. On the other hand, in the case of Sr$_{0.7}$Pr$_{0.3}$Fe$_{12-2x}$Co$_{x}$Al$_{x}$O$_{19}$, 2a absorption intensity has decreased linearly and has completely diminished at x = 1.0, which indicates that all the 2a sites become full when x = 1.0. This suggests that only half of the Co$^{2+}$-Al$^{3+}$ dopant occupies the 2a site compared to the case of the La$^{3+}$-SrM sample. Then, the other half of the 2a site should be occupied by Fe$^{3+}$ ions through the range of x examined. In the case of Pr$^{3+}$ series samples, a slight decline in the absorption area.
for the most intense 12k site is observed, while in the La³⁺ containing samples, 12k areal almost remains constant. Thus it seems that the excessive Co²⁺-Al³⁺ dopant occupies the 2a site and 12k site in Sr₀.₇Pr₀.₃Fe₁₂₋₂xCoₓAlₓO₁₉. The above observation clearly indicates that the tendency of 12k site occupation by the Co²⁺-Al³⁺ dopant is affected by the species of rare-earth ions at the Sr²⁺ site. Where Co²⁺-Al³⁺ impurity mostly prefers 2a site and its preference for 12k site is enhanced in the presence of Pr³⁺ rather than La³⁺, once the 2a site is completely filled. This observation is interesting considering the fact that there are no 2a sites in the vicinity of Sr²⁺, and hence the substitution at Sr²⁺ with rare-earth ions is not expected to influence the site occupancy at the 2a site. Furthermore, the physical reason for the preferential site occupancy of Co²⁺-Al³⁺ in the presence of La³⁺ or Pr³⁺ is not clear at this stage. Mossbauer spectroscopy cannot discriminate against the site occupancies of both Co²⁺ and Al³⁺ ions separately. But one scenario is that Co²⁺ ions might not prefer the 2a site in the presence of Pr³⁺ ion, which needs further investigation.

4. Conclusion

The structural, magnetic, and Mossbauer spectrum study of the influence of rare-earth La³⁺ and Pr³⁺ on Sr₀.₇RE₀.₃Fe₁₂₋₂xCoₓAlₓO₁₉ (RE: La and Pr) hexaferrite compounds were investigated. Overall, dopant ion brings a unit cell contraction, which affects the Curie temperature and saturation magnetization of both series of samples. La³⁺-SrM samples show marked improvement in the magnetization value, while Pr³⁺-SrM samples show deterioration in Ms value with the Co²⁺-Al³⁺ substitution. This is suggestive of the fact that magnetic Pr³⁺, unlike non-magnetic La³⁺ (no 4f electrons), substitution for Sr²⁺ could be detrimental to the overall magnetization behavior of the SrFe₁₂O₁₉ compound. The Co²⁺-Al³⁺ substitution brings in grain refinement, more for the La³⁺-SrM than Pr³⁺-SrM, which has a considerable impact on the coercivity values of the compound. The Mossbauer spectral analysis revealed 2a as a preferred substitution for Co²⁺-Al³⁺ ions for both series of samples. Due to lattice contraction, the 2b site displayed a considerable reduction in its quadrupole shift value. The improved hyperfine field for the 12k site in the La³⁺-SrM series is attributed to the increase in its magnetization value with the substitution of Co²⁺-Al³⁺ ions for Fe³⁺. For the study, it is concluded that the substitution of rare-earth ions with 4f charge distribution for Sr²⁺ could be detrimental to the overall magnetic performance of the M-type hexaferrite materials.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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