

Single-crystalline M-type Sr Hexaferrites studied by ^{57}Fe Mössbauer spectroscopy

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Abstract The ^{57}Fe Mössbauer spectra of the single crystalline and the finely ground $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ ($x = 0 : y = 0, x = 0.192 : y = 0.152$ and $x = 0.456 : y = 0.225$) samples have been measured to investigate the La-Co substitution effects. All observed spectra at 150 K were well fitted using the five subspectra which correspond to the five crystallographical nonequivalent Fe sites in the M-type hexaferrite, indicating that the valence changes to Fe^{2+} ions in the Fe^{3+} ions were not observed in our $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ samples. In $\text{SrFe}_{12}\text{O}_{19}$, the relative absorption intensities in the five subspectra show the large anisotropies in the recoilless fractions at the five Fe sites whereas these anisotropies were not observed in $\text{Sr}_{0.544}\text{La}_{0.456}\text{Fe}_{11.775}\text{Co}_{0.225}\text{O}_{19}$. These results indicate the chemical compositional dependence on the anisotropies of the recoilless fractions at the five Fe sites. The substitution of a Co^{2+} ion for the Fe^{3+} ion changes the center shifts of the Fe^{3+} ions near the Co^{2+} ion by the perturbation of the Fe-O-Co hybridizations. Therefore, the Co^{2+} ions occupy the $4f_1$ and the $4f_2$ sites due to the chemical compositional dependences of the refined magnetic hyperfine field and center shifts of the Fe^{3+} ions.

Keywords Hexaferrite · Hard magnetic materials · Mössbauer spectroscopy

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1 Introduction

M-type $\text{SrFe}_{12}\text{O}_{19}$ with the space group $P6_3/mmc$ is a ferrimagnetic material with the relatively high Curie temperature $T_C = 750$ K [1] and has a large magnetocrystalline anisotropy. In these hexaferrites, the La-Co substitution increases the magnetocrystalline anisotropy at room temperature [2, 3] and then improves the coercivity in the La-Co substituted M-type Sr hexaferrites. Accordingly, the La-Co substituted M-type Sr hexaferrites have many important permanent magnet applications. However, the intrinsic magnetic properties of $\text{SrFe}_{12}\text{O}_{19}$ and La-Co substituted ones remain open questions despite a lot of investigations. It is important to study the magnetic properties of La-Co substituted M-type hexaferrites using high quality single phase samples to understand fundamental effects of the La-Co substitution. Since there are the five nonequivalent Fe sites in the M-type hexaferrite, the determination of the substitutions of Co ions for the Fe ions is difficult despite a lot of efforts [4–8].

Le Breton *et al.* [6] investigated the La-Co substituted M-type Sr hexaferrites using ^{57}Fe Mössbauer spectroscopy to determine substituted Fe sites. They decided that the Co ions occupy the Fe ($4f_2$, $2a$ and maybe $2b$) sites from the La-Co concentration dependences of the absorption intensities in the five extracted Fe subspectra. In their discussion, however, they implicitly assumed that the ratio of the recoilless fractions between the five Fe sites is independent of the La-Co concentration. Meanwhile, Lechevallier *et al.* [8] also investigated the La-Co substituted M-type Sr hexaferrites using ^{57}Fe Mössbauer spectroscopy. They concluded that the Co ions occupy the octahedral Fe ($4f_2$ and $2a$) sites from the La-Co concentration dependences of the magnetic hyperfine fields of the five Fe sites. They assumed that the Fe^{3+} ions in the vicinity of a Co^{2+} ion were affected by perturbations of the superexchange $\text{Fe}^{3+}-\text{O}^{2-}-\text{Co}^{2+}$ interactions. However, these observed Mössbauer spectra using the La-Co substituted M-type Sr hexaferrite powder samples include a paramagnetic subspectrum and a magnetic subspectrum from impurity phases. Thus, the observed spectra were more complex than those obtained from the single phase samples.

In the La-Ni substituted M-type Sr hexaferrites, the Ni ions possibly occupy the Fe ($4f_1$, $4f_2$ and $2a$) sites which were determined from the La-Ni concentration dependences of the refined center shifts of the Fe sites [9]. We have measured ^{57}Fe Mössbauer spectra of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ using high purity single crystalline samples to investigate chemical compositional dependences of anisotropies in the recoilless fractions at the five Fe sites and reexamined the Fe sites substituted by the Co^{2+} ions in the La-Co substituted M-type Sr hexaferrites by using as well discussed in La-Ni substituted M-type Sr hexaferrites [9].

2 Experimental details

The single-crystalline samples of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ ($x = 0 : y = 0, x = 0.192 : y = 0.152$ and $x = 0.456 : y = 0.225$) were grown by the Na_2O flux method [10]. The La and Co concentrations in our La-Co substituted M-type Sr hexaferrites single crystals were determined using the wavelength-dispersive X-ray spectrometry. The ^{57}Fe Mössbauer experiments were performed at 150 K using a conventional constant-acceleration type spectrometer with a ^{57}Co in Rh source. The velocity scale was calibrated with a standard α -Fe foil. The absorbers of the single-crystalline $\text{SrFe}_{12}\text{O}_{19}$ and $\text{Sr}_{0.544}\text{La}_{0.456}\text{Fe}_{11.775}\text{Co}_{0.225}\text{O}_{19}$ samples were composed of the several plate-like crystals which were approximately 50 μm in thickness with the hexagonal c -axis. The absorbers of $\text{SrFe}_{12}\text{O}_{19}$ and

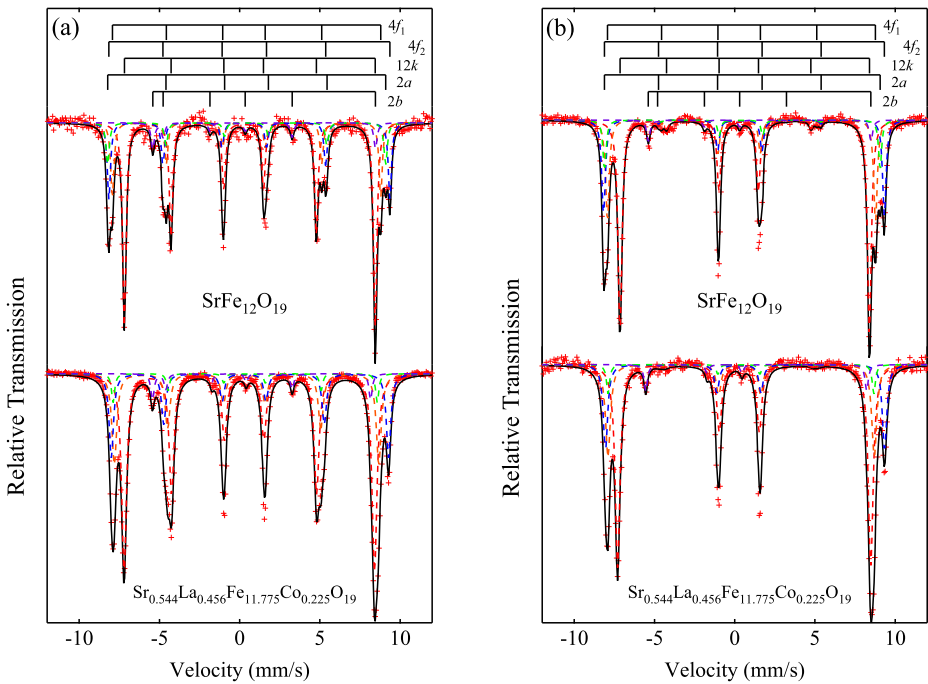


Fig. 1 Typical Mössbauer spectra of the (a) finely ground samples and (b) single crystalline samples, $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ at 150 K. The crosses, the solid lines represent the measured data and the fits calculated using the five subspectra, respectively. The broken lines represent the extracted subspectra of the five Fe sites

$\text{Sr}_{0.544}\text{La}_{0.456}\text{Fe}_{11.775}\text{Co}_{0.225}\text{O}_{19}$ were 87 and 50 mm² in area, respectively. The hexagonal *c*-axes of these absorbers were aligned along the direction of the incident γ -ray. The finely ground samples of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ ($x = 0 : y = 0, x = 0.192 : y = 0.152$ and $x = 0.456 : y = 0.225$) were prepared from the single crystalline samples to measure the ⁵⁷Fe Mössbauer spectra at 150 K.

3 Experimental results and discussion

Figure 1 shows the typical Mössbauer spectra observed at 150 K using the finely ground samples and the single crystalline samples of $\text{SrFe}_{12}\text{O}_{19}$ and $\text{Sr}_{0.544}\text{La}_{0.456}\text{Fe}_{11.775}\text{Co}_{0.225}\text{O}_{19}$. The spectra observed using the three finely ground samples were analyzed using the model proposed by Evans, *et al.* [9, 11] and assuming that the magnetic hyperfine interactions are much larger than the electric quadrupole interactions within an axial symmetry approximation in the five Fe sites. In $\text{SrFe}_{12}\text{O}_{19}$, the initial magnetic hyperfine fields H_{hf} of the five Fe sites at 150 K were evaluated using the temperature dependences on H_{hf} of the five Fe sites of $\text{BaFe}_{12}\text{O}_{19}$ [12] and of $\text{SrFe}_{12}\text{O}_{19}$ [13]. As shown in the upper panel of Fig. 1a, the spectrum of $\text{SrFe}_{12}\text{O}_{19}$ was well fitted within these assumptions. The spectra of the finely ground samples of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ ($x = 0.192 : y = 0.152$ and $x = 0.456 : y = 0.225$) were also well fitted with the five subspectra using a similar model to that of $\text{SrFe}_{12}\text{O}_{19}$ as seen in the

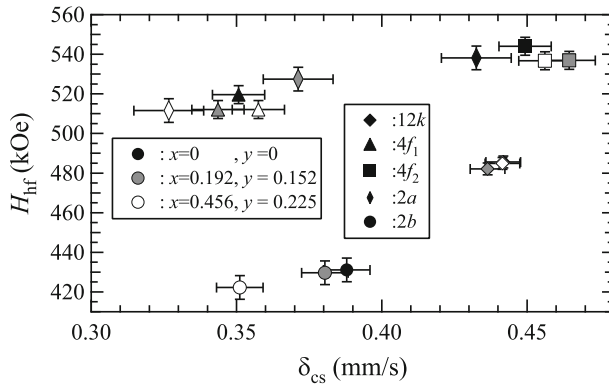


Fig. 2 The refined H_{hf} of the five Fe sites as a function of the refined δ_{cs}

lower panel in Fig. 1a. Although the valence changes from the Fe^{3+} to the Fe^{2+} ions in some Fe ions at the 2a site were observed in the M-type $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ [4, 7], these valence changes were not observed in our $Sr_{1-x}La_xFe_{12-y}Co_yO_{19}$ ($x = 0.192 : y = 0.152$ and $x = 0.456 : y = 0.225$) samples in our experimental accuracy.

As shown in Fig. 1b, the spectra of the single crystalline $SrFe_{12}O_{19}$ and $Sr_{0.544}La_{0.456}Fe_{11.775}Co_{0.225}O_{19}$ samples were well fitted using the same hyperfine parameters as those obtained by the finely ground ones, respectively, within experimental accuracy. Since the absorption components around ± 5 mm/s of each subspectrum correspond to the $\Delta m = 0$ condition in the ^{57}Fe Mössbauer transitions, these absorption components almost disappear in the spectra measured in single crystalline $SrFe_{12}O_{19}$ and $Sr_{0.544}La_{0.456}Fe_{11.775}Co_{0.225}O_{19}$ samples, as seen in Fig. 1b, indicating the directions of H_{hf} at the five Fe sites are parallel to the hexagonal c -axes in $SrFe_{12}O_{19}$ and $Sr_{0.544}La_{0.456}Fe_{11.775}Co_{0.225}O_{19}$ within the experimental accuracy.

In $SrFe_{12}O_{19}$, the relative intensities between the five extracted subspectra in the single crystalline $SrFe_{12}O_{19}$ sample are different from those of the finely ground one. The difference in the intensity ratios between the single crystalline and finely ground samples indicates that there are large anisotropies of the recoilless fractions at the five Fe sites. This result in $SrFe_{12}O_{19}$ is consistent with the previous results [9, 14]. However, as seen in the lower panel in Fig. 1b, the relative intensities between the five extracted subspectra of the single crystalline $Sr_{0.544}La_{0.456}Fe_{11.775}Co_{0.225}O_{19}$ samples are similar to those in the finely ground ones. These results reveal that the anisotropies of the recoilless fractions depend on the chemical composition in the M-type $Sr_{1-x}La_xFe_{12-y}Co_yO_{19}$. Therefore, Co occupation sites are not determined by the chemical compositional dependences of the intensities ratio between the five extracted subspectra. It is necessary to determine the Co occupation sites in the changes of the hyperfine interaction parameters with the chemical composition in the M-type $Sr_{1-x}La_xFe_{12-y}Co_yO_{19}$, as well discussed in La-Ni substituted M-type ferrite [9].

The refined quadrupole shifts ΔE_Q are almost independent of the La and Co concentration expect for that of the 2b site. The La concentration dependence of ΔE_Q of the 2b site is similar to that of La substituted M-type Sr hexaferrite [15]. As seen in Fig. 2, there are strong correlations between the refined H_{hf} and δ_{cs} . These correlations between H_{hf} and δ_{cs} indicate that the substitution of a Co^{2+} ion for the Fe^{3+} ion changes H_{hf} and δ_{cs} of the Fe^{3+} ion in its vicinity by the perturbation of the Fe-O-Co hybridizations. The number of the nearest Fe^{3+} and Sr^{2+} ions and the coordinating mean distances for the Fe

Table 1 Number of the nearest neighbors Fe^{3+} and Sr^{2+} ions and mean distances for the Fe sites in $\text{SrFe}_{12}\text{O}_{19}$ [8, 9]

Site	12 <i>k</i>	4 <i>f</i> ₁	4 <i>f</i> ₂	2 <i>a</i>	2 <i>b</i>	Sr
12 <i>k</i>	4 2.93 Å	3 3.52 Å	2 3.47 Å	1 3.03 Å	1 3.67 Å	1 3.67 Å
4 <i>f</i> ₁	9 3.52 Å	–	–	3 3.46 Å	–	–
4 <i>f</i> ₂	6 3.47 Å	–	1 2.82 Å	–	3 3.68 Å	3 3.68 Å
2 <i>a</i>	6 3.03 Å	6 3.46 Å	–	–	–	–
2 <i>b</i>	6 3.67 Å	–	6 3.68 Å	–	–	3 3.40 Å

sites in $\text{SrFe}_{12}\text{O}_{19}$ are summarized in Table 1 [8, 9]. The decreases of H_{hf} and δ_{cs} of the 2*a* and 2*b* sites with the Co concentration reveal that the Co^{2+} ions possibly substitute for the 12*k*, 4*f*₁ and 4*f*₂ sites. However, H_{hf} and δ_{cs} of the 12*k* are slightly affected by the Co concentration. These results indicate that the Co^{2+} ions does not occupy the 12*k* site in $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$. Therefore, the Co occupations in $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ are possibly the 4*f*₁ and 4*f*₂ sites, which is different from those reported in the La-Co substituted $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{Co}_x\text{O}_{19}$ previously by using Mössbauer spectroscopy [4, 6, 8]. Meanwhile, this result is the same as that obtained by NMR [7] and is different from those reported by Raman spectroscopy [4], neutron diffraction [5, 6].

4 Summary

The Mössbauer spectra were measured in the single crystalline $\text{SrFe}_{12}\text{O}_{19}$ and $\text{Sr}_{0.544}\text{La}_{0.456}\text{Fe}_{11.775}\text{Co}_{0.225}\text{O}_{19}$ samples, and the finely ground $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ ($x = 0 : y = 0, x = 0.192 : y = 0.152$ and $x = 0.456 : y = 0.225$) samples at 150 K to investigate the La-Co substitution effects and to determine the Fe sites substituted by the Co^{2+} ions. All observed spectra were well fitted using the five subspectra which correspond to the five nonequivalent Fe sites. This result indicates that the valence change from the Fe^{3+} to Fe^{2+} ions was not observed in our La-Co substituted samples in our experimental accuracy. The Mössbauer spectra of the single crystalline and finely ground $\text{SrFe}_{12}\text{O}_{19}$ samples indicate the anisotropies of the recoilless fractions at the five Fe sites whereas the Mössbauer spectrum of the single crystalline $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ samples was well fitted using same relative intensity ratio between the five extracted subspectra obtained by using the finely ground sample. These results indicate the chemical compositional dependence on the anisotropies of the recoilless fractions. The Mössbauer spectra of the single crystalline $\text{SrFe}_{12}\text{O}_{19}$ and $\text{Sr}_{0.544}\text{La}_{0.456}\text{Fe}_{11.775}\text{Co}_{0.225}\text{O}_{19}$ samples reveal that the directions of H_{hf} at the five Fe sites of those samples are parallel to the hexagonal *c*-axes. The refined δ_{cs} and H_{hf} at the 2*a* and the 2*b* sites were possible affected by the La-Co substitution. The Co occupation Fe sites were determined from the change of δ_{cs} and H_{hf} . In $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$, the Co^{2+} ions possibly substitute for the Fe (4*f*₁ and 4*f*₂) sites.

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