Mössbauer spectroscopy studies of phase evolution in $\text{SrFe}_{12}\text{O}_{19}/\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ composites

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A composite system composed of $\text{SrFe}_{12}\text{O}_{19}$ (SFO) and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (LCMO) was prepared by a two-stage sol-gel/hydrothermal synthesis technique. Starting conditions were varied to obtain products with 1:1 and 1:2 molar ratios of SFO:LCMO. The morphology and composition of the composites were characterized by SEM and room-temperature Mössbauer spectroscopy, revealing the growth of nanocrystalline $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ particles ($d \leq 150$ nm) on the surface of $\text{SrFe}_{12}\text{O}_{19}$ platelets. Mössbauer spectra not only confirm the presence of well-formed M-type hexagonal ferrite in the composite materials, but also demonstrate the formation of a new, intermediate phase $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}(\text{Fe})\text{O}_3$ at the interface between SFO and LCMO. The signature of the intermediate Fe-containing phase increases with the starting molar content of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, as a greater fraction of the $\text{SrFe}_{12}\text{O}_{19}$ surface is covered by $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, increasing the total interfacial area. The trends in coercivity in the series of samples between 10 K and 300 K are reported and discussed in terms of sample morphology.

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1. Introduction

The hexagonal ferrites, first discovered in the 1950's continue to attract interest due to immense technological importance in a number of fields including permanent magnets, data storage, and high-frequency device components [1]. Despite the simplicity of its crystal structure compared to other members of the hexaferrite family, M-type hexagonal ferrites ($\text{AFe}_{12}\text{O}_{19}$, A = Ba, Sr, Pb) account for many of these traditional applications and show potential in emerging areas including multiferroics [2,3]. The structure of the M-type hexaferrites consists of alternating spinel ($\text{Fe}_6\text{O}_8^{2+}$) and hexagonal ($\text{AFe}_6\text{O}_{11}^{2-}$) layers [4]. Fe^{3+} ions are distributed in the interstitial spaces of the close-packed layers, with three octahedral sites, one tetrahedral site, and one bipyramidal site. The contribution from the spin of the five-coordinate bipyramidal Fe atom gives rise to large anisotropy in the uniaxial ferrites. $\text{SrFe}_{12}\text{O}_{19}$ (SFO) is a ferrimagnet below 460 °C that combines high saturation magnetization (>90 emu/g) and large anisotropy $K_1 = 3.5 \times 10^6 \text{ erg cm}^{-3}$ [1] yielding a room temperature hard magnetic behavior that makes SFO a widely exploited material in various composite systems requiring a hard magnetic phase [5-7]. Recently, SFO has been paired with magnetically soft phases $\alpha\text{Fe}_2\text{O}_3$ and Co-P to improve microwave absorption properties in nanowires and powders [8,9] and FeCo, resulting in exchange-coupled core/shell nanofibers with enhanced magnetic properties [10]. Perovskite-structured manganites $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$ (RE: rare earth, AE: alkaline earth) are well-known for strong coupling between structural, magnetic, and electronic degrees of freedom underlying unique phenomena such as colossal magnetoresistance (CMR), spin-polarized conduction, and complex phase diagrams [11]. The hard magnetic properties of the hexaferrites and the wide range of tunability in the ground state of the manganites lead to an intriguing possibility for all-oxide devices with novel functionalities. However, very few reports exist on manganite/hexaferrite composite systems [12-14].

Recently, we synthesized novel $\text{SrFe}_{12}\text{O}_{19}/\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (SFO/LCMO) composites via a two stage combined citrate precursor sol-gel and hydrothermal method, resulting in micron-sized

hexagonal platelets of SFO with LCMO nanocrystallites formed at the surface [14]. The composite samples showed a reduction in saturation magnetization and coercivity when compared with pure SFO. However, low temperature hysteresis loops recorded at 10 K after a field cooling process revealed the absence of exchange bias in the SFO/LCMO composite, ruling out the possibility of significant interfacial magnetic coupling between SFO and LCMO. Increasingly, emergent properties are observed at interfaces involving oxides, including chemically distinct intermediary phases [15-18]. To gain insight into the chemical properties at the boundary between SFO and LCMO in the composite system, we utilize Mössbauer spectroscopy.

^{57}Fe Mössbauer spectroscopy is an important tool to extract information about the relationship between the structure and magnetic properties of materials, and provides evidence for changes due to substitution effects in magnetic materials. When substituted elements do not enter the structure of a material, Mössbauer contributions of Fe-containing extra phases are fitted and can be compared with X-ray diffraction analysis. When the substituted elements are incorporated into the parent structure, the corresponding changes in the Mössbauer spectra allow their position within the structure to be determined. Here, we report the Mössbauer spectra and magnetic properties of a series of chemically prepared ferrite-manganite hybrid $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ materials. Synthesis conditions are varied to observe the effect of starting molar ratio and calcination temperature on the morphology, phase composition, and magnetic properties of the SFO:LCMO bi-phasic system. Our results reveal the formation of an intermediary $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}(\text{Fe})\text{O}_3$ phase at the interface between SFO and LCMO. The presence of this Fe-containing manganite phase could explain our previous observation of the absence of exchange bias in the SFO/LCMO composites [14]. Our study also demonstrates the usefulness of Mössbauer spectroscopy technique for probing intermediate phases that are often formed at interfaces in bi-phasic composites and multilayer film systems [16] and their influences on the material properties.

2. Experimental details

Details of the synthesis of $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ composites have been reported elsewhere [14]. In brief, $\text{SrFe}_{12}\text{O}_{19}$ (SFO) particles were synthesized by a combined sol-gel and hydrothermal method. 1M solutions of metal nitrate (MN) precursors $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and citric acid (CA) dissolved in deionized water were combined in stoichiometric ratios with a CA:MN ratio of 3:1. The pH was adjusted to ~ 3 by the addition of ammonia while the solution was stirred at $75\text{--}80^\circ\text{C}$ for several hours. The solution was transferred to an autoclave and reacted at 160°C for 5 h. The resulting gel was dried at $80\text{--}100^\circ\text{C}$ overnight and pre-calcined at 250°C to form a porous black powder before a final 2 h calcination step at 1050°C to achieve SFO powders with good crystallinity. Pure SFO with no $\alpha\text{-Fe}_2\text{O}_3$ minority phase is obtained for calcination temperatures above 750°C [14]. $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (LCMO) is obtained by a similar sol-gel/hydrothermal method with $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ used as starting materials.

To form the SFO:LCMO composite samples, as-synthesized SFO powder was dispersed in ethanol, sonicated for 10 min then separated by centrifugation and added to a previously prepared solution of LCMO starting materials and CA dissolved in deionized water. The relative quantities of SFO powder and LCMO precursor solution were adjusted to prepare SFO:LCMO with molar ratios of 1:1 and 1:2 in the final products. The mixtures were subjected to the aging and heat treatment steps outlined above with calcination temperatures of 850°C or 1050°C , yielding composite materials with an LCMO layer on the surface of the SFO particles. Scanning electron microscopy (SEM) was used to characterize the grain size and morphology of the materials. Magnetic properties were measured with a Quantum Design Physical Property Measurement System (PPMS) using a vibrating sample magnetometer (VSM) attachment between 10 K and 300 K with applied magnetic fields of up to 50 kOe.

^{57}Fe Mössbauer effect measurements were taken at room temperature in transmission geometry with a conventional constant acceleration spectrometer operating in triangular wave mode and a ^{57}Co

source in a Rhodium matrix. The speed scale of the Doppler modulator and isomer shift calibration were performed using 10 μm thick $\alpha\text{-Fe}$ foil lines as a standard. The sample thickness is adjusted so that the Fe content is $\sim 10 \text{ mg/cm}^2$. The Mössbauer spectra (MS) were fitted using a least-squares method within specialized software [19] with the contributions of the M-type phase (five sextets corresponding to the five Fe^{3+} sites of the M-type crystal structure, i.e. the 12*k*, 4*f*1, 4*f*2, 2*a* and 2*b* sites) and, when necessary, with the contributions of the Fe-containing secondary phases. Hyperfine interaction parameters are denoted as follows: δ for isomer shift (mms^{-1}), Δ for quadrupolar shift (mms^{-1}) and H_{eff} for magnetic hyperfine field (T). Estimated errors for the hyperfine interaction parameters originate from the statistical errors given by the fitting program [19]. Preliminary fittings of the Mössbauer contribution of the M-type phase in the $\text{SrFe}_{12}\text{O}_{19}$ spectrum revealed that the relative intensity might deviate from the crystallographic occupancy. Such a deviation is generally observed in the M-type hexaferrites, and can be attributed to anisotropic *f*-factors, to stacking faults, or to the pronounced anisotropy of the 2*b* site.

3. Results

Figure 1 shows representative SEM images of SFO:LCMO composite samples with a molar ratio of 1:1 (Fig. 1a) and 1:2 (Fig. 1b). The hexagonal platelet-type morphology common in SFO [1,20,21] is evident in the composites, with an average size of $\sim 1\text{-}2 \mu\text{m}$. This is above the estimated single-domain limit in SFO of $\sim 0.5 - 1 \mu\text{m}$ [22]. The smaller rod-like shapes (lighter contrast) that appear in the SEM images are identified with the LCMO phase. LCMO nanocrystallites adhere to the surface of SFO, as the pre-formed platelets play the role of a substrate for the growth of LCMO during the second stage of the synthesis. Independent clusters of agglomerated LCMO particles are also visible. The calcination temperature of the composite has no observable effect on the morphology of the SFO phase. The LCMO phase is more sensitive to calcination temperature, with an ultrafine network of crystallites at 850°C (individual particle size below the resolution of our

instrument) giving way to more clearly defined individual particles at 1050°C with a diameter of ~ 150 nm.

As a confirmation of the phase purity of the SFO component, Fig. 2 shows the ^{57}Fe MS at 300 K for the SFO powder calcined at 1050°C for 2h. Generally speaking, this complex spectrum is composed of five sub-spectra corresponding to the five nonequivalent crystallographic sites of Fe in this hexagonal ferrite material. Unfortunately, there is considerable controversy regarding the five hyperfine fields in this material. We adopted the interpretation and the values suggested by [23-26]. The isomer shifts and the hyperfine fields obtained are in excellent agreement with the data already obtained in [23-26] and for the sake of brevity they have not been listed and discussed here. Thus, the spectrum in Fig. 2 fits reasonably well with that of standard $\text{SrFe}_{12}\text{O}_{19}$, confirming the expected phase. Fitted parameters of the MS for SFO are presented in Table 1. No additional lines belonging to another magnetically ordered or paramagnetic phase are observed in the spectrum. The hyperfine parameters of the sample are of the same order as those previously reported for SFO in [23-26], but deviate from data presented in [27].

The room temperature MS of composite SFO:LCMO samples with molar ratios of 1:1 and 1:2 and calcination temperatures of 850°C and 1050°C are shown in Fig. 3 and Fig. 4, respectively. The spectra of the composite powders show a contribution from an additional paramagnetic phase (doublet, with isomer shift $\delta \sim 0.33\text{mms}^{-1}$ and quadrupolar splitting $\Delta \sim 0.5\text{mms}^{-1}$) near a velocity of 0 mm/s. This doublet component could correspond to the $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}(\text{Fe})\text{O}_3$ phase, which is paramagnetic at room temperature [28-33]. The presence of both magnetically ordered and paramagnetic components at room temperature can be explained by the introduction of Fe ions into the structure of the manganite phase as it forms on the surface of the SFO platelets during calcination, resulting in an intermediate $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-\delta}\text{Fe}_\delta\text{O}_3$ (LCMFO) phase. It should be noted that the experimental MS of the paramagnetic phase is similar to those observed for manganites.

The spectra in Fig. 3 and Fig. 4 were fitted with the contributions of the M-type phase (5 sextets, one for each Fe³⁺ site) and the contributions of the paramagnetic secondary LCMFO phases. The hyperfine interaction parameters of the five Fe ion sublattices derived from MS are shown in Table 2. The relative magnitudes of the hyperfine fields H_{hf} , are in agreement with [23-26], evolving as follows: $H_{hf}(2b) < H_{hf}(12k) < H_{hf}(4f1) < H_{hf}(2a) < H_{hf}(4f2)$. Isomer shifts are in the range 0.10–0.40 mm/s relative to metallic α -Fe indicating that the ionic states of Fe ions on the five sites are ferric Fe³⁺. The sequence of relative isomer shifts values found is $\delta(4f1) < \delta(2b) < \delta(4f2) < \delta(12k) < \delta(2a)$. The quadrupole shift of site 2b is very large because of the strongly distorted environment.

The room temperature magnetic hysteresis loops for pure SFO and the composite samples calcined at 1050°C are shown in Fig. 5. The ordering temperature of SFO is over 700 K, so that at 300 K it shows a hard magnetic behavior. Compared to SFO, the addition of LCMO causes a reduction in both the magnetization and the coercivity. The reduction of magnetization becomes more pronounced as the molar ratio of LCMO increases, which is expected due to its paramagnetic contribution at 300 K. The coercivity in the composite with an SFO:LCMO molar ratio of 1:2 (3.1 kOe) is somewhat larger than the SFO:LCMO 1:1 sample (2.8 kOe). Weak ferromagnetic behavior with $T_C \sim 250$ K has been observed previously in nanocrystalline La_{0.5}Ca_{0.5}MnO₃ powders prepared using the same synthesis route described above [14]. From the inset of Fig. 5 it can be seen that the temperature dependence of magnetization in the composite sample shows no significant features below 300 K, indicating that the SFO phase dominates the magnetic response of the composite materials.

Hysteresis loops were measured for the series of samples at various temperatures between 10 K and 300 K. The temperature variation of the coercivity is displayed in Fig. 6. The magnetocrystalline anisotropy in hard ferrites arises primarily from spin-orbit coupling, with $K_1 \gg K_2, K_3$ and an easy direction of the magnetization along the c-axis in the M-type compounds. In BaFe₁₂O₁₉, the saturation magnetization M_S decreases more strongly with temperature than does K_1 ,

leading to an anisotropy $2K_1/M_S$ that first increases with temperature up to ~ 500 K before decreasing [34]. The maximum attainable coercivity can thus be expected to follow a similar trend. An increase in coercivity with temperature below 300 K has been borne out experimentally in both $\text{BaFe}_{12}\text{O}_{19}$ [35] and $\text{SrFe}_{12}\text{O}_{19}$ [36]. Our results showing $dH_C/dT > 0$ in Fig. 6 are consistent with these previous reports. Across the temperature interval investigated, H_C is considerably larger in SFO than in the composite materials, ranging from 2.8 kOe at 10 K to 3.9 kOe at 300 K. At 10 K, similar coercive fields are measured in the SFO:LCMO samples with a 1:1 ratio (2.15 kOe) and with a 1:2 ratio (2.30 kOe). The 1:2 ratio composites in general show the larger coercivities, however $H_C(T)$ rises more quickly with temperature in the samples treated at 1050°C , so that the coercivity of SFO:LCMO 1:1 1050°C surpasses that of SFO:LCMO 1:2 850°C at 300 K.

4. Discussion

Lotgering and van Diepen [37,38] suggested that the substitution of La^{3+} for Sr^{2+} in the SrM ferrite structure leads to the presence of Fe^{2+} instead of Fe^{3+} to compensate for the excess of positive charge. This change in the valence state of Fe occurs in the $2a$ site [39]. In this scenario, better fittings of the MS should be obtained by assuming the presence of a small amount of Fe^{2+} on the $2a$ site [40]. However, it is noteworthy that results of mathematical analysis of the experimental spectra presented in Fig. 2 and Fig.3 show that no Fe^{2+} component was detected in the spectra, i.e. Sr^{2+} ions in the $\text{SrFe}_{12}\text{O}_{19}$ structure are not replaced by La^{3+} ions when a composite is formed with LCMO. On the other hand a small amount of Fe is incorporated on the B-site of the manganite structure, forming the secondary LCMFO phase. From Table 2 and Table 3, the relative contribution to the MS spectra from paramagnetic LCMFO (doublet) is 7.9 % (850°C) and 7.8 % (1050°C) in samples with a 1:1 molar ratio and 17.5% (850°C) and 18.2% (1050°C) in samples with a 1:2 molar ratio. The presence of more LCMFO in the final composite when LCMO is in excess during synthesis is a result of greater coverage of the SFO surface by adhered LCMO particles, which can be observed in the SEM images in Fig. 1. In contrast to the molar ratio of the starting materials, the calcination temperature

(850°C vs 1050°C) has little effect on the amount of LCMFO present in the final products. From this, combined with our observation above that La^{3+} is not incorporated into the SFO crystal structure, we can conclude that interdiffusion of metal ions between SFO and LCMO during calcination is not a significant factor in the formation of the LCMFO phase. Rather, Fe ions at the surface layer of SFO are incorporated into the perovskite structure as it crystallizes. The formation of an intermediary LCMFO phase at the boundary between magnetically soft LCMO and magnetically hard SFO could explain our earlier observation of the absence of exchange bias in SFO:LCMO composites [14].

The reduced coercivity in the composite samples as compared to pure SFO (Fig. 5 and Fig. 6) can be seen as a consequence of the modification of the surface properties of SFO. In general coercivity is reduced when the number of defects capable of nucleating reversed domains increases. Such defects include surface irregularities with large demagnetizing fields and to a lesser extent physical and chemical defects with depressed local values of magnetocrystalline anisotropy [41]. In hard/soft magnetic systems the soft phase can be regarded as an extended defect, since domain walls are more readily nucleated in the soft region with small anisotropy and may propagate through the hard phase. LCMO particles grown on the surface of SFO serve both as a magnetically soft phase and a source of surface irregularities and defects, accounting for the globally lowered coercive fields in the composite samples. Since the coating of LCMO on SFO underlies the reduction of H_C , it is seemingly counterintuitive that when the composites prepared under different conditions are compared, samples with greater LCMO coverage exhibit the larger values of H_C . However, in the 1:2 molar ratio samples the manganite particles adhered to the SFO are in close contact with one another and partially sintered, producing areas with a more-or-less uniform LCMO coating layer. More regularity at the surface reduces the occurrence of the large demagnetizing fields expected in the vicinity of individual spheroids on the SFO surface, such as those identifiable in Fig. 1(a). On the other hand, the Mössbauer spectroscopy analysis indicates that the intermediary LCMFO phase increases with the starting molar content of LCMO in the composite samples. Since the LCMFO

phase is likely in a form of randomly magnetic spins, and the increased amount of this phase at the interface between SFO and LCMO could also result in greater values of H_C for the 1:2 molar ratio samples as compared to the 1:1 molar ratio samples (Fig. 6).

Finally, it is interesting to note in Fig. 6 that the coercivity in the samples treated at 1050°C rises more quickly with temperature than in the samples treated at 850°C, regardless of starting molar ratio. In addition to thermal activation, contributions to $H_C(T)$ in a magnetic material include the variation of anisotropy and saturation magnetization with temperature. Given that the value of magnetization as well as the sharpness of $M(T)$ in sol-gel derived manganite nanomaterials is quite sensitive to calcination temperature [42], the subtle differences in the shape of $H_C(T)$ in the SFO:LCMO composites is likely influenced by trends in $M_S(T)$ in the LCMO phase.

5. Conclusions

In summary, $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ composites were prepared by a combined sol-gel/hydrothermal synthesis technique subject to different starting molar ratios and calcination temperatures. $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ nanocrystallites ($d \leq 150$ nm) were observed to grow on the surface of μm -sized $\text{SrFe}_{12}\text{O}_{19}$ platelets. Room temperature Mössbauer investigations confirmed the presence of well-formed M-type hexagonal ferrite. In the composite samples, Mössbauer spectra show a contribution from an additional paramagnetic phase corresponding to $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}(\text{Fe})\text{O}_3$. The relative contribution of the intermediate phase increases with the starting molar content of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, consistent with greater coverage of the $\text{SrFe}_{12}\text{O}_{19}$ surface. The coercivity of the composite materials is lower than that of pure $\text{SrFe}_{12}\text{O}_{19}$ prepared under the same synthesis conditions. The relative values of coercivity in the series of samples can be understood by the presence and density of surface irregularities and nucleation sites in the vicinity of LCMO particles adhered to the SFO surface. The temperature dependence of coercivity in the composite samples follows the same trend as in SFO, with slightly more rapid growth in the samples calcined at the

highest temperature. This observation may be attributed to sharper change in $M(T)$ for the LCMO phase.

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Table 1 Hyperfine **interaction** parameters (δ – isomer shift, Δ – quadrupole splitting, H_{eff} – average magnetic hyperfine field) obtained by fitting the room-temperature Mössbauer spectrum of $SrFe_{12}O_{19}$. Number of iron cations (per formula unit of $SrFe_{12}O_{19}$) located in available cation sublattices 12k (**black line**), 4f1 (**yellow line**), 4f2 (**green line**), 2a (**purple line**), 2b (**red line**) was calculated from the relative intensities of the corresponding subspectra.

Sample	$SrFe_{12}O_{19}$ 1050°C			
	δ (mm/s)	Δ (mm/s)	H_{eff} (T)	%
12k	0.351+/-0.001	-0.392+/-0.003	41.395+/-0.010	46.01
4f1	0.359+/-0.005	-0.296+/-0.010	51.730+/-0.025	11.23
4f2	0.267+/-0.012	-0.058+/-0.023	51.637+/-0.069	15.58
2a	0.243+/-0.005	-0.148+/-0.009	49.131+/-0.038	21.44
2b	0.228+/-0.019	-1.848+/-0.038	39.410+/-0.157	5.74

Table 2 Hyperfine **interaction** parameters obtained by fitting the room-temperature Mössbauer spectra of $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with the ratio 1:1 calcined at 850 °C and 1050 °C. Number of iron cations located in available cation sublattices 12k (**black line**), 4f1 (**yellow line**), 4f2 (**green line**), 2a (**purple line**), 2b (**red line**) was calculated from the relative intensities of the corresponding subspectra. Doublet – paramagnetic phase of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnFeO}_3$.

SrFe ₁₂ O ₁₉ /La _{0.5} Ca _{0.5} MnO ₃ 1:1 850 °C				
	δ (mm/s)	Δ (mm/s)	H _{eff} (T)	%
12k	0.354+/-0.001	-0.392+/-0.002	41.308+/-0.006	44.07
4f1	0.362+/-0.003	-0.317+/-0.006	51.571+/-0.017	9.15
4f2	0.329+/-0.006	0.009+/-0.012	- 51.136+/-0.021	15.00
2a	0.267+/-0.002	-0.175+/-0.005	48.948+/-0.024	18.34
2b	0.290+/-0.008	-2.186+/-0.016	40.734+/-0.057	5.59
Doublet	0.338+/-0.008	0.479+/-0.014	0	7.85

SrFe ₁₂ O ₁₉ /La _{0.5} Ca _{0.5} MnO ₃ 1:1 1050 °C				
	δ (mm/s)	Δ (mm/s)	H _{eff} (T)	%
4SL				
12k	0.355+/-0.001	-0.393+/-0.002	41.124+/-0.008	46.85
4f1	0.387+/-0.002	-0.364+/-0.004	50.977+/-0.012	8.03
4f2	0.356+/-0.006	-0.040+/-0.011	50.861+/-0.017	12.30
2a	0.280+/-0.002	-0.158+/-0.004	48.429+/-0.017	19.35
2b	0.282+/-0.006	-2.096+/-0.012	41.012+/-0.038	5.67
Doublet	0.338+/-0.004	0.515+/-0.008	0	7.80

Table 3 Hyperfine **interaction** parameters obtained by fitting the room-temperature Mössbauer spectra of $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with the ratio 1:2 calcined at 850 °C and 1050 °C. Number of iron cations located in available cation sublattices 12k (**black line**), 4f1 (**yellow line**), 4f2 (**green line**), 2a (**purple line**), 2b (**red line**) was calculated from the relative intensities of the corresponding subspectra. Doublet – paramagnetic phase of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnFeO}_3$.

$\text{SrFe}_{12}\text{O}_{19}/\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ 1:2 850 °C				
7SL	δ (mm/s)	Δ (mm/s)	H_{eff} (T)	%
12k	0.352+/-0.003	-0.390+/-0.006	41.341+/-0.021	30.67
4f1	0.354+/-0.009	-0.309+/-0.018	51.638+/-0.058	6.00
4f2	0.361+/-0.006	0.152+/-0.011	51.235+/-0.029	25.05
2a	0.265+/-0.010	-0.165+/-0.019	49.204+/-0.085	17.11
2b	0.277+/-0.030	-2.175+/-0.056	40.729+/-0.237	3.70
<i>Doublet</i>	0.330+/-0.008	0.529+/-0.015	0	17.47

$\text{SrFe}_{12}\text{O}_{19}/\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ 1:2 1050 °C				
8SL	δ (mm/s)	Δ (mm/s)	H_{eff} (T)	%
12k	0.358+/-0.003	-0.374+/-0.005	41.056+/-0.024	43.97
4f1	0.366+/-0.005	-0.408+/-0.009	50.469+/-0.024	6.70
4f2	0.335+/-0.008	-0.022+/-0.016	50.734+/-0.038	12.28
2a	0.280+/-0.004	-0.129+/-0.008	47.930+/-0.038	14.80
2b	0.296+/-0.015	-1.980+/-0.030	40.597+/-0.102	4.06
<i>Doublet</i>	0.333+/-0.003	0.544+/-0.006	0	18.18

Figure captions

Fig. 1 SEM micrograph of (a) $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ composite with the ratio 1:1 calcined at 1050 °C and (b) $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ composite with the ratio 1:2 calcined at 850 °C.

Fig. 2 Room-temperature Mössbauer spectrum of $\text{SrFe}_{12}\text{O}_{19}$. (•) indicates the experimental points, lines represent calculated fitting. Contributions corresponding to the 12k (black line), 4f1 (yellow line), 4f2 (green line), 2a (purple line), 2b (red line) sublattices of $\text{SrFe}_{12}\text{O}_{19}$ are displayed. Difference between experimental spectrum and fitting result is shown in the lower part of the panel. The blue line is the curve resulted from the fitting and means the sum of these five components.

Fig. 3 Room-temperature Mössbauer spectra of $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with the ratio 1:1 annealed at (a) 850 °C and (b) 1050 °C. Contributions corresponding to the 12k (black line), 4f1 (yellow line), 4f2 (green line), 2a (purple line), 2b (red line) sublattices of $\text{SrFe}_{12}\text{O}_{19}$ are displayed with the doublet paramagnetic phase of $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}(\text{Fe})\text{O}_3$. Differences between experimental spectra and fitting results are shown in the lower portions of the panels. The blue line is the curve resulted from the fitting and means the sum of these five components.

Fig. 4 Room-temperature Mössbauer spectra of $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with the ratio 1:2 annealed at (a) 850 °C and (b) 1050 °C. Contributions corresponding to the 12k (black line), 4f1 (yellow line), 4f2 (green line), 2a (purple line), 2b (red line) sublattices of $\text{SrFe}_{12}\text{O}_{19}$ are displayed with the doublet paramagnetic phase of $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}(\text{Fe})\text{O}_3$. Differences between experimental spectra and fitting results are shown in the lower portions of the panels. The blue line is the curve resulted from the fitting and means the sum of these five components.

Fig. 5 Room-temperature magnetic hysteresis loops measured between +50 kOe and -50 kOe for $\text{SrFe}_{12}\text{O}_{19}$, $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ 1:1, and $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ 1:2 all calcined at 1050 °C. Inset: Field-cooled magnetization vs. temperature curves of $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ 1:1 with $H = 100$ Oe.

Fig. 6 Temperature dependence of coercive field H_C for $\text{SrFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}:\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ composite samples.

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