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A strong magneto-optical activity in rare-earth La^{3+} substituted M-type strontium ferrites

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M-type strontium ferrites with substitution of Sr^{2+} by rare-earth La^{3+} were prepared by conventional ceramic technology. The structure, magnetic properties, and magneto-optical Kerr activity of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$) were investigated by x-ray diffraction (XRD), vibrating sample magnetometer (VSM), and magneto-optical ellipsometry, respectively. X-ray diffraction showed that the samples sintered at 1290 °C for 3 h were single M-type hexagonal ferrites. The magnetic properties were remarkably changed due to the valence change of Fe ions induced by the substitution of La ions. Most significantly, an important magneto-optical activity was induced in the La^{3+} substituted M-type strontium ferrites around 3 eV. © 2011 American Institute of Physics. [doi:10.1063/1.3587181]

I. INTRODUCTION

M-type strontium hexaferrites are the most important ceramic permanent magnets and have attracted a great deal of interest. Their high magnetic coercive force, saturation magnetization, and remanence enable them to be used in different applications such as microwave devices, magnetic recording media, and high frequency electromagnetic devices.^{1–4} Strontium hexaferrites have been prepared by diverse techniques such as the hydrothermal process,⁵ the self-propagating high-temperature synthesis,⁶ the polymerizable complex method,⁷ the microwave-assisted calcination route,⁸ the sol-gel method,⁹ and the ceramic process.¹⁰ In view of the large volume of the market, a considerable amount of work has been done to improve the performance of strontium hexaferrites by various methods such as doping,¹¹ heat-treatment,¹² ion substitution,¹³ etc. Most of the works were focused on the phases, microstructures, magnetic properties, microwave absorption properties, or thermoelectric power.^{14–16}

The magneto-optical Kerr effect is important in magneto-optical recording technology.¹⁷ A strong interest has been focused on this subject in the past couple of decades as it is used for optical readout of magnetically stored information in erasable video and audio disks.¹⁸ Other applications of the magneto-optical Kerr effect, such as microscopy for domain observation,¹⁹ magnetic characterization,²⁰ and magneto-optics, make it a very sensitive and nondestructive technique to investigate magnetism at the atomic scale as its origin relies on the spin-orbit coupling.^{21,22} For applications in high-density erasable magneto-optical memory devices, a large value of the Kerr rotation is required. The rare-earth

elements in magneto-optical materials play an important role in the magneto-optical Kerr effect. Meanwhile, our previous works have shown that by introducing rare-earth La^{3+} and transition Co^{2+} , the magnetic properties of M-type strontium hexaferrites can be improved.^{9,10} However, no information is available on the magneto-optical Kerr effect studies of rare-earth La^{3+} substituted strontium hexaferrites in the literature. In this paper, the influence of the amount of substituted La^{3+} on both the magneto-optical Kerr effect and the magnetic properties were systematically studied.

II. EXPERIMENTAL

The raw materials used in this study were SrCO_3 (99.0% purity), La_2O_3 (99.0%), and Fe_2O_3 (99.94%). $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ferrites were prepared by the conventional ceramic process, where x varies from 0 to 0.20 in 0.05 increments. The process consists of four main steps: (i) mixing the raw materials together, dry-milling the powder mixtures, presintering at 1000 °C for 2 h in a muffle, then cooling in the muffle down to room temperature, (ii) dry-milling the presintered samples, pressing into disk-shaped compacts of $12\text{Ø} \times 1\text{--}2$ mm h, (iii) sintering the pressed compacts in a muffle at 1290 °C for 3 h with a heating rate of 300 °C/h in air atmosphere, and cooling in the muffle down to room temperature, and (iv) finally, one side optical polishing of each disk-shaped compact for the investigation of the magneto-optical activity.

The powder x-ray diffraction (XRD) patterns were collected on a Bruker AXSD* Advanced Powder x-ray diffractometer by using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406$ nm). The patterns were recorded in the 2-theta (2θ) range from 20° to 80°. The magnetic parameters were measured using a Riken Denshi (BH-55 type) vibrating sample magnetometer (VSM) at room temperature with maximum applied magnetic field

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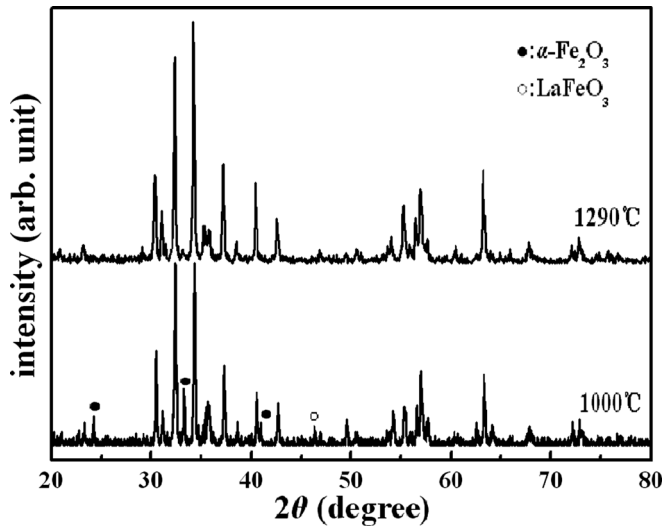


FIG. 1. X-ray diffraction patterns of $\text{Sr}_{0.8}\text{La}_{0.2}\text{Fe}_{12}\text{O}_{19}$ samples sintered at 1000°C for 2 h and at 1290°C for 3 h.

H of $800 \text{ kA}\cdot\text{m}^{-1}$. Magneto-optical ellipsometry measurements were carried out in the transverse Kerr configuration with a SOPRA GES E5 ellipsometer in the energy range 1.5–4.5 eV at an angle of incidence of 75° in order to maximize the effect under an in-plane magnetic field of $240 \text{ kA}\cdot\text{m}^{-1}$. The transverse Kerr effect taken from ellipsometry measurements was defined as $\text{TKE} = 100 \cdot (\tan^2\Psi_+ - \tan^2\Psi_-) / (\tan^2\Psi_+ + \tan^2\Psi_-)$, where $\tan\Psi$ is the module in the well-known ellipsometric ratio $\rho = \tan\Psi \cdot e^{i\Delta}$. The subindices + and – account for the values obtained under positive and negative applied fields.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the sample $\text{Sr}_{0.8}\text{La}_{0.2}\text{Fe}_{12}\text{O}_{19}$ sintered at 1000°C for 2 h and sintered at 1290°C for 3 h, respectively. As we can see, the desired M-type hexagonal structure (JCPDS 84-1531) was already formed at 1000°C . However, $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS 89-0599) phase and trace amounts of LaFeO_3 (JCPDS 75-0541) were also found by XRD simultaneously, indicating an incomplete reaction of the powders. These impurity phases disappeared as the sample $\text{Sr}_{0.8}\text{La}_{0.2}\text{Fe}_{12}\text{O}_{19}$ was sintered at 1290°C . Moreover with increasing sintering temperature, the relative intensity of the diffraction peaks became stronger and narrower, indicating a better structural quality of the materials. Compared to Sr^{2+} ions and Fe^{3+} ions, La^{3+} ions have lower mobility, and their diffusion is expected to be slower. It is therefore concluded that in order to eliminate the impurity phases that can deteriorate the magnetic properties and to form single phase La-substituted samples $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$, higher sintering temperatures and longer annealing time are required. In addition, we can obtain samples with a small coercivity ($<160 \text{ kA}\cdot\text{m}^{-1}$) by increasing the sintering temperature to a certain temperature range.

The XRD patterns corresponding to the samples $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ($x=0, 0.05, 0.10, 0.15, 0.20$) sintered at 1290°C for 3 h are shown in Fig. 2. The positions of the diffraction peaks of each sample are in good agreement with

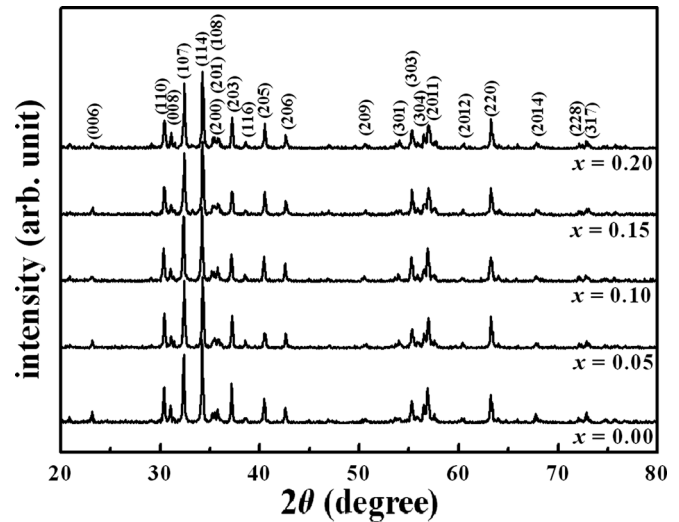


FIG. 2. X-ray diffraction patterns of samples $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ sintered at 1290°C for 3 h. The indicated diffraction indices correspond to the M-type hexagonal ferrite.

the reported JCPDS 84-1531 data. Therefore all the samples are single M-type hexagonal ferrites, and no other impurity was detected in the XRD patterns.

The variation of the lattice parameters a and c as a function of composition for $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ is shown in Table I. The lattice parameter c decreases monotonically with increasing x . It is in agreement with the results of Ref. 15. The lattice parameter a initially remains constant, up to a substitution of $x=0.15$, then decreases. Because the radius of La^{3+} (1.22 \AA) is smaller than Sr^{2+} (1.32 \AA) and radius of Fe^{2+} (0.80 \AA) is larger than Fe^{3+} (0.67 \AA), the slight changes of the lattice parameter may have been caused by the La^{3+} substitution for Sr^{2+} and valence change of Fe ions.

For a deeper insight into the nature of the samples, the hysteresis loops of samples $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ($x=0, 0.05, 0.10, 0.15, 0.20$) in the powder form were taken by VSM at room temperature. With the La ionic addition, σ_s and H_{cJ} of all the samples are different. For example, the saturation magnetization of $\text{SrFe}_{12}\text{O}_{19}$ is $65.4 \text{ A}\cdot\text{m}^2\cdot\text{kg}^{-1}$ and its coercivity is $105.7 \text{ kA}\cdot\text{m}^{-1}$ in Fig. 3(b) under the applied field $800 \text{ kA}\cdot\text{m}^{-1}$. It is expected that the coercivity of all the samples in the insert part of Fig. 3 need less than the applied field ($240 \text{ kA}\cdot\text{m}^{-1}$) of the magneto-optical measure.

Figure 4 illustrates the relationship between the magnetic properties of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ and the substituted amount x . It is found that the suitable amount of La^{3+} substitution may remarkably influence the saturation magnetization σ_s and intrinsic coercivity H_{cJ} . Our results are very similar to La substituted barium hexaferrites $\text{Ba}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ with the same range of substitution reported by S. Ounnunkad.²³ In the hexagonal $\text{SrFe}_{12}\text{O}_{19}$ ferrite, the Fe^{3+}

TABLE I. Lattice parameters a and c as a function of composition.

x	0.00	0.05	0.10	0.15	0.20
a (\AA)	5.886	5.889	5.888	5.880	5.880
c (\AA)	23.031	23.016	23.009	23.002	23.002

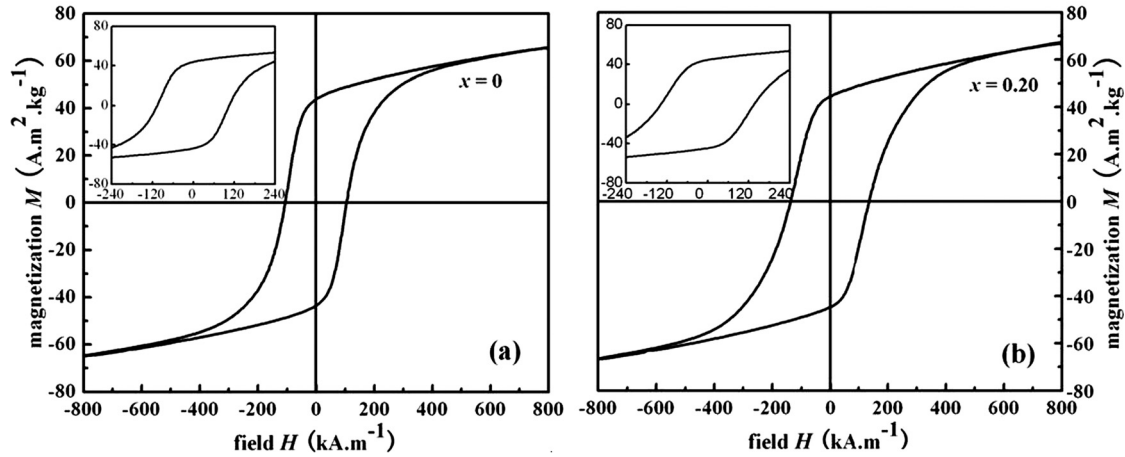


FIG. 3. Hysteresis loops of samples $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0, 0.20$) at room temperature. The samples were sintered at 129°C for 3 h.

ions are distributed over five different sites: three octahedral sites ($12k$, $4f_2$, and $2a$), one tetrahedral site ($4f_1$), and one bipyramidal site ($2b$). In the La-substituted samples, La^{3+} ions are expected to enter the Sr^{2+} sites because of their compatibility in radius. It leads to a valence change of Fe^{3+} to Fe^{2+} at $2a$ or $4f_2$ site to conserve the charge neutrality. The changes of the saturation magnetization σ_s and intrinsic coercivity H_{cj} shown in Fig. 4 are first decided by both a number of Fe^{3+} ions with spin-up orientation and the super-exchange interaction.²⁴

In order to determine the magneto-optical activity, two ellipsometry spectra were taken for each sample, one with a positive applied magnetic field and a second one with a negative applied magnetic field; $240 \text{ kA}\cdot\text{m}^{-1}$ in both cases as stated in the Sect. I. From the ellipsometric ratios taken at positive and negative applied fields, $\tan(\psi_+)$ and $\tan(\psi_-)$, the transverse Kerr effect is determined.²⁵ The magneto-optical activity of these samples is shown in Fig. 5. Provided that the magneto-optical response of the samples is proportional to the magnetization, the transverse ellipsometric Kerr effect was multiplied for each sample by a factor M_{800}/M_{240} ,

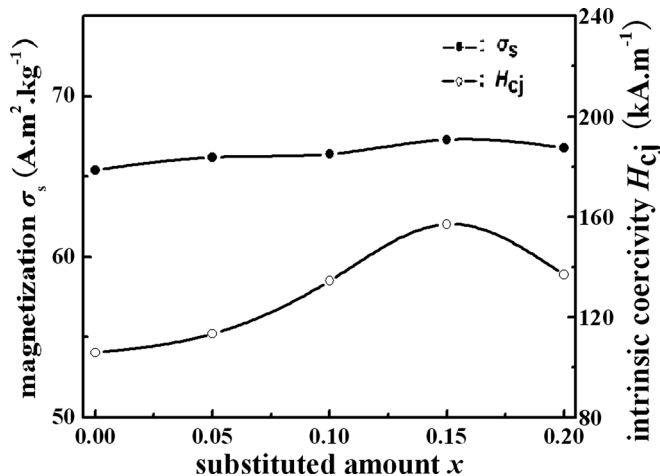


FIG. 4. The saturation magnetization σ_s and intrinsic coercivity H_{cj} depend on the substituted amount x for samples $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$). The samples were sintered at 1290°C for 3 h.

where M_{800} is the saturation magnetization of the samples (the magnetization measured at $800 \text{ kA}\cdot\text{m}^{-1}$) and M_{240} is the magnetization measured at $240 \text{ kA}\cdot\text{m}^{-1}$, that is, the magnetization of the sample under the applied field during the transverse ellipsometric Kerr measurements. When the hexaferrite is not doped [Fig. 5(a)], its magneto-optical activity is very poor. When the substitution is low, $x = 0.05$, the magneto-optical activity is still not relevant [Fig. 5(b)]. It has been shown in previous works that the magneto-optical activity of the M-type Sr and Ba hexaferrites is very low²⁶ and due to the Fe^{3+} ions. The almost zero activity observed in this work at low La^{3+} concentrations can, therefore, be both attributed to the moderately low magnetic fields applied and to the low intrinsic magneto-optic activity. A small magneto-optical activity appears for $x = 0.10$ [Fig. 5(c)]. Two signatures are observed; one centered around 2 eV, whereas the second one is centered around 3 eV. When the La concentration is increased to 0.15 [Fig. 5(d)], there still exists a minor magneto-optical activity around 2 eV, but the activity at 3 eV is clearly increased, and the peak gets better defined. This is an indication that the activity detected at low energy is intrinsic of the hexaferrite, in agreement with Ref. 26, whereas the activity at higher energies is induced by the doping. The reason why this activity had not been observed at the lower contents of La doping may be attributed to the small changes in the magnetization obtained with the $240 \text{ kA}\cdot\text{m}^{-1}$ of applied magnetic field in the low La content samples (Fig. 3). This is indeed confirmed when the La doping is increased to $x = 0.20$ [Fig. 5(e)]. In this case, the magneto-optical activity rises to almost 1% around 3 eV. The low energy magneto-optical activity is kept low, reinforcing the idea that it is due only to the Fe^{3+} ions from the undoped hexaferrite. In Ref. 27, Co^{2+} is substituted for Fe^{3+} ; this leads to a decrease in the polar Kerr effect around 380 nm that is then attributed to fewer Fe^{3+} ions or more specifically actually to a decrease in the amount of Fe atoms rather than to a chemical reduction. In the present work, in which La^{3+} is substituted for Sr^{2+} , only a minor amount of Fe atoms reduce, but there is no decrease in the total amount of Fe atoms in contrast to Ref. 27. This explains why the magneto-optical behavior evolves in different ways in Ref. 27 and in

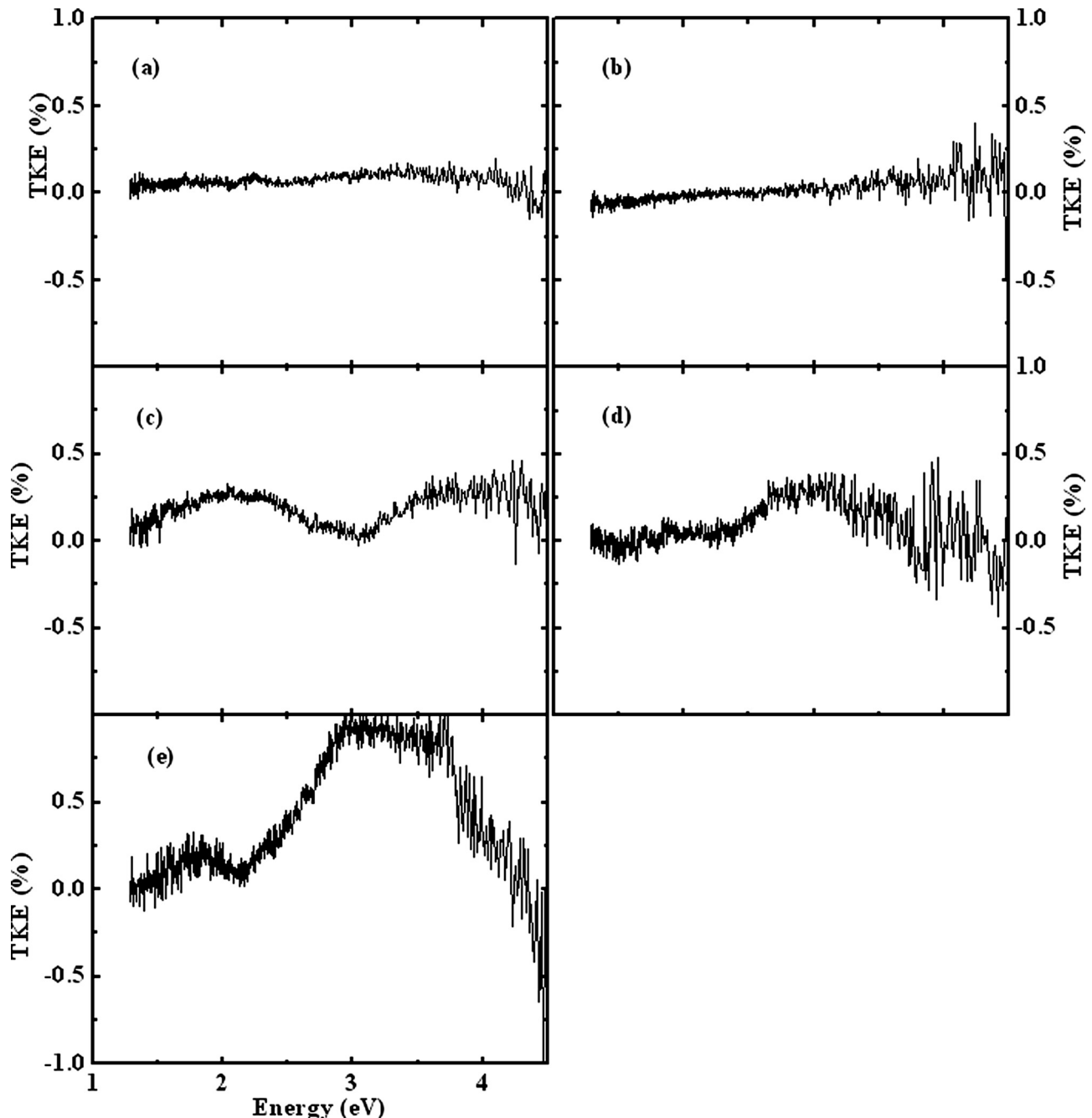


FIG. 5. Magneto-optical activity for samples $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ with $x = 0$ (a); 0.05 (b); 0.10 (c); 0.15 (d); 0.20 (e).

the present work. These results indicate and rare earth doping of M-type hexaferrites is an interesting route to induce a strong magneto-optical activity in these systems.

IV. CONCLUSIONS

Single-phase M-type strontium ferrites with substitution of Sr^{2+} by rare-earth La^{3+} , according to the formula $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$), were prepared by the conventional ceramic technology. X-ray diffraction showed that a high treatment temperature and a long annealing time were required to form single phase $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$. The magnetic properties were remarkably changed due to the valence change of Fe ions induced by the

substitution of La ions. Most importantly, a large magneto-optical Kerr activity was induced in the La^{3+} substituted M-type strontium ferrites, opening a route to fabricate hexaferrite based magneto-optical sensors.

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- ¹S. A. Oliver, S. D. Yoon, I. Kozulin, M. L. Chen, and C. Vittoria, *Appl. Phys. Lett.* **76**, 3612 (2000).
- ²A. Vijayalakshmi and N. S. Gajbhiye, *J. Appl. Phys.* **83**, 400 (1998).
- ³N. K. Reddy and V. N. Mulay, *Mater. Chem. Phys.* **76**, 75 (2002).
- ⁴P. Hernández-Gómez, P. G. Bercoff, O. Alejos, C. Torres, J. M. Muñoz, C. de Francisco, J. I. Iniguez, and H. R. Bertorello, *Phys. B* **320**, 267 (2002).
- ⁵M. Jean, V. Nachbaur, J. Bran, and J. Le Breton, *J. Alloy Compd.* **496**, 306 (2010).
- ⁶L. Qiao, L. You, J. Zheng, L. Jiang, and J. Sheng, *J. Magn. Magn. Mater.* **318**, 74 (2007).
- ⁷T. Kikuchi, T. Nakamura, T. Yamasaki, M. Nakanishi, T. Fujii, J. Takada, and Y. Ikeda, *J. Magn. Magn. Mater.* **322**, 2381 (2010).
- ⁸Z. Wang, L. Zhong, J. Lv, H. Qian, Y. Zheng, Y. Fang, M. Jin, and J. Xu, *J. Magn. Magn. Mater.* **322**, 2782 (2010).
- ⁹X. S. Liu, W. Zhong, S. Yang, Z. Yu, B. X. Gu, and Y. W. Du, *Phys. Status Solidi A* **193**, 314 (2002).
- ¹⁰X. S. Liu, P. Hernández-Gómez, Y. X. Deng, K. Huang, X. B. Xu, S. X. Qiu, and D. Zhou, *J. Magn. Magn. Mater.* **321**, 2421 (2009).
- ¹¹Z. Pang, X. Zhang, B. Ding, D. Bao, and B. Han, *J. Alloy Compd.* **492**, 691 (2010).
- ¹²N. Rezlescu, C. Doroftei, E. Rezlescu, and P. D. Popa, *J. Alloy Compd.* **451**, 492 (2008).
- ¹³N. Langhof and M. Göbbels, *J. Solid State Chem.* **182**, 2725 (2009).
- ¹⁴M. W. Pieper, A. Morel, and F. Kools, *J. Magn. Magn. Mater.* **242–245**, 1408 (2002).
- ¹⁵D. Seifert, J. Töpfer, F. Langenhorst, J. Le Breton, H. Chiron, and L. Lechevallier, *J. Magn. Magn. Mater.* **321**, 4045 (2009).
- ¹⁶D. H. Choi, S. W. Lee, I. Shim, and C. S. Kim, *J. Magn. Magn. Mater.* **304**, e243 (2006).
- ¹⁷R. Gerber, R. Atkinson, and Z. iSimisa, *J. Magn. Magn. Mater.* **175**, 79 (1997).
- ¹⁸K. H. J. Buschow, P. G. Van Engen, and R. Jongebreur, *J. Magn. Magn. Mater.* **38**, 1 (1983).
- ¹⁹F. Schmidt, W. Rave, and A. Hubert, *IEEE Trans. Magn.* **21**, 1596 (1985).
- ²⁰Y. K. Kato, R. C. Myers, A. C. Gossard, and D. D. Awschalom, *Science* **306**, 1910 (2004).
- ²¹A. V. Kimel, A. Kirilyuk, P. A. Usachev, R. V. Pisarev, A. M. Balbashov, and T. Rasing, *Nature* **435**, 655 (2005); Y. K. Kato, R. C. Myers, A. C. Gossard, and D. D. Awschalom, *Science* **306**, 1910 (2004).
- ²²S. A. Crooker, D. G. Rickel, A. V. Balatsky, and D. L. Smith, *Nature* **431**, 49 (2004).
- ²³S. Ounnunkad, *Solid State Commun.* **138**, 472 (2006).
- ²⁴X. S. Liu, W. Zhong, S. Yang, Z. Yu, B. X. Gu, and Y. W. Du, *J. Magn. Magn. Mater.* **238**, 207 (2002).
- ²⁵L. Fernandez-Garcia, M. Suárez, and J. L. Menéndez, *Funct. Mater. Lett.* **3**, 237 (2011).
- ²⁶P. Papakonstantinou, R. Atkinson, M. O'Neill, I. W. Salter, and R. Gerber, *IEEE Trans. Magn.* **31**, 3283 (1995).
- ²⁷R. Atkinson, P. Papakonstantinou, I.W. Salter, and R. Gerber, *J. Magn. Magn. Mater.* **138**, (1994) 222–231.