Crystalline and Electronic Structures and Magnetic and Electrical Properties of La-Doped $\text{Ca}_2\text{Fe}_2\text{O}_5$ Compounds

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Brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$ has been observed to exhibit many outstanding properties that are applicable to ecotechnology. However, very little work on doped $\text{Ca}_2\text{Fe}_2\text{O}_5$ compounds has been carried out to widen their application scope. We present herein a detailed study of the crystalline/geometric and electronic structures and magnetic and electrical properties of $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_5$ ($x = 0$ to 1) prepared by conventional solid-state reaction. X-ray diffraction patterns indicated that the compounds with $x = 0$ to 0.05 exhibited brownmillerite-type single phase. La doping with higher content ($x \geq 0.1$) stimulated additive formation of Grenier- ($\text{LaCa}_2\text{Fe}_3\text{O}_8$) and perovskite-type (LaFeO_3) phases. Extended x-ray absorption fine structure spectroscopy at the Fe K-edge and electron spin resonance spectroscopy revealed presence of Fe^{3+} in the parent $\text{Ca}_2\text{Fe}_2\text{O}_5$ ($x = 0$) and both Fe^{3+} and Fe^{4+} in the doped compounds ($x \geq 0.05$). The Fe^{4+} content tended to increase with increasing x . This stimulates ferromagnetic exchange interactions between Fe^{3+} and Fe^{4+} ions and directly influences the magnetic properties of $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_5$. Electrical resistivity (ρ) measurements in the temperature range of $T = 20$ K to 400 K revealed that all the compounds exhibit insulator behavior; the $\rho(T)$ data for $x \geq 0.1$ could be described based on the adiabatic small polaron hopping model.

Key words: Brownmillerite-type oxides, crystal structure, magnetic properties, electrical properties

INTRODUCTION

In recent years, $\text{Ca}_2\text{Fe}_2\text{O}_{5+\delta}$ with $\delta = 0$ has attracted intensive interest from research groups, because of its novel properties applicable to ecotechnology, such as its suitability for reliable resistive-switching memory,¹ electrochemical energy conversion devices (i.e., solid-oxide fuel cells and metal air batteries),² gas sensors,³ chemical looping H_2 production,⁴ and reversible CO_2 capture for air purification.⁵ At room temperature, it has brownmillerite-type orthorhombic structure in space group $Pcmn$ with lattice constants $a = 5.425$ Å, $b = 14.769$ Å,

and $c = 5.598$ Å.^{6,7} This structure can be described as alternating layers of corner-sharing FeO_6 octahedra and FeO_4 tetrahedra. The Fe^{3+} spins are nearly directed along the c axis, leading to G -type antiferromagnetic (AFM) order and weak ferromagnetism in $\text{Ca}_2\text{Fe}_2\text{O}_5$.^{3,8}

Detailed investigation of its thermal expansion has revealed that this compound exhibits several transitions,^{8–10} including an antiferromagnetic–paramagnetic (AFM–PM) transition at $T_N \approx 725$ K (the Néel temperature), transformation of the original $Pcmn$ structure to a body-centered structure at ~ 970 K, an incommensurate modulated transition caused by lattice expansion in the **a** and **c** directions at ~ 1180 K, and significant lattice contraction along the **b** direction at ~ 1308 K.¹⁰ These transitions can change the oxygen content (δ), and

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result in two symmetry types with left and right FeO_4 tetrahedral chains along the c axis in the same layer.^{9,10}

In terms of its electrical properties, $\text{Ca}_2\text{Fe}_2\text{O}_5$ is an insulator and considered as a model system for understanding oxygen-ion-related conductivity. A large change in the oxygen content of $\text{Ca}_2\text{Fe}_2\text{O}_{5+\delta}$ with $\delta = 1$ results in formation of the end system CaFeO_3 (with perovskite-type structure of ABO_3),^{11,12} and a metal-insulator transition at ~ 290 K.¹³ The electrical conductivity of $\text{Ca}_2\text{Fe}_2\text{O}_5$ has been found to be enhanced by N doping² or (Mg, Al) codoping.¹⁴ More recently, Dhankhar and coworkers found anomalous magnetoresistance below the T_N of $\text{Ca}_2\text{Fe}_2\text{O}_5$, and a memory effect when measuring the resistivity under an external magnetic field.¹⁵

Though promising applications of this material system have already been demonstrated, very little work on rare-earth-doped $\text{Ca}_2\text{Fe}_2\text{O}_5$ materials has been carried out.^{2,14,16} Additionally, systematic studies of the structural/geometric, electronic, magnetic, and electrical properties have not yet been conducted. Assessment of their applicability for use in electronic devices is also still lacking. In this work, we prepared La-doped $\text{Ca}_2\text{Fe}_2\text{O}_5$ compounds, then studied their crystal/geometric and electronic structures and magnetic and electrical properties. We suggest that La doping creates more holes (i.e., more Fe^{4+} ions), because of La^{3+} substitution for Ca^{2+} in $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_5$. Our studies show that La doping causes structural phase separation and a change in the concentrations of Fe^{3+} and Fe^{4+} ions. This influences the strength of the ferromagnetic (FM) exchange interactions between Fe^{3+} and Fe^{4+} ions as well as the electrical conductivity of the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_5$ compounds.

EXPERIMENTAL PROCEDURES

Polycrystalline $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_5$ compounds ($x = 0$ to 1) were fabricated by conventional solid-state reaction in air. Commercial powders of CaO , La_2O_3 , and Fe_2O_3 with purity of 99.9% were used as precursors. These powders were combined in stoichiometric amounts according to the nominal formula $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_5$, then well mixed by using an agate pestle and mortar. The mixtures were then pressed into pellets and preannealed at 1373 K for 12 h. After several intermediate applications of the grinding and preannealing processes at temperatures below 1523 K, the final pellets were annealed once more at 1573 K for 24 h. The crystal structure of the resulting products was checked by x-ray diffractometer (Rigaku, MiniFlex) equipped with Cu K_α radiation source (wavelength $\lambda = 1.5406$ Å). Notably, before taking x-ray diffraction (XRD) patterns, a small amount (~ 5 wt.%) of standard Si powder was mixed with all compounds, to minimize errors caused by position calibration of the incident x-ray beam. The electronic structure associated

with the Fe absorbing atom ($E_0 = 7112$ eV)¹⁷ in $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_5$ was studied by using x-ray absorption fine structure (XAFS) spectroscopy (Pohang Accelerator Laboratory, South Korea). Data in the x-ray absorption near-edge structure (XANES) region were collected in steps of 0.2 eV to 0.5 eV. The XAFS data were analyzed using the IFEFFIT software package. For reference, we also recorded XAFS spectra of Fe_3O_4 (with a mixture of Fe^{2+} and Fe^{3+}) and Fe_2O_3 (Fe^{3+}), corresponding to E_0 values of about 7121 eV and 7123 eV, respectively. Electron spin resonance (ESR) spectra were recorded from the powder compounds using a JEOL-TE300 spectrometer operating in the X-band frequency range at $f \approx 9.45$ GHz. Magnetization (M) versus magnetic field measurements were performed by vibrating-sample magnetometry (VSM), varying the magnetic field (H) from 0 kOe to 10 kOe. The electrical resistivity was measured in the temperature range of $T = 20$ K to 400 K by four-probe technique in van der Pauw configuration.

RESULTS AND DISCUSSION

Crystalline, Local Geometric, and Electronic Structures

Figure 1 shows the powder XRD patterns of all the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_5$ compounds, with fixed scan step of 0.01° . The XRD features reveal structural changes of $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_5$ as x was increased. This can be seen from the enlarged view of the diffraction peaks at around 31° to 35° in Fig. 2. Detailed analysis revealed that the compounds with $x = 0$ and 0.05 completely crystallized with orthorhombic brownmillerite structure (in space group $Pcmn$), corresponding to the Miller-indexed peaks.

Fig. 1. Room-temperature XRD patterns of all $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds prepared by solid-state reaction. The Miller-indexed peaks belong to the $Pnma$ brownmillerite phase (dotted lines). Additional peaks without Miller indices are assigned to Grenier- and/or perovskite-type phases.

However, for $x \geq 0.1$, additional peaks started to appear and the brownmillerite peaks gradually disappeared. By comparison with the reference compounds (Fig. 2), we believe that the additive peaks are related to development of Grenier- $(\text{LaCa}_2\text{Fe}_3\text{O}_8)$ and/or perovskite-type (LaFeO_3) phases caused by the increase in oxygen content; Fig. 3 shows the 3D crystal geometry of three phase structures for comparison. This means that the general formula of our compounds must be rewritten as $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$. In fact, $\text{Ca}_2\text{Fe}_2\text{O}_5$ and LaFeO_3 have been found to be two end members of $\text{LaCa}_2\text{Fe}_3\text{O}_8$ (i.e., the $\text{LaCa}_2\text{Fe}_3\text{O}_8$ structure is intermediate between the $\text{Ca}_2\text{Fe}_2\text{O}_5$ and LaFeO_3 structures), and the following process would happen during sample fabrication^{7,18,19}:

where $a = b + c$, z , and z' are variables. Coexistence of brownmillerite, Grenier, and/or perovskite phases in the compounds with $0.1 \leq x \leq 1$ leads to complex variation of the XRD patterns. Note that a small amount of Ca could partially substitute for La in perovskite LaFeO_3 , resulting in $\text{La}_{1-y}\text{Ca}_y\text{FeO}_3$ -type compounds, peak shifts, and secondary XRD peaks.

We additionally analyzed the brownmillerite phase in the compounds with $x = 0$ to 0.2, and determined the lattice parameters (a , b , c) and unit cell volume (V). The values of $a = 5.424$ Å, $b = 14.761$ Å, and $c = 5.589$ Å determined for $\text{Ca}_2\text{Fe}_2\text{O}_5$ ($x = 0$) in Table I are in good agreement with those previously reported.^{6,7} With increasing x from 0 to 0.1, these parameters slightly increased, owing to replacement of La^{3+} with larger ionic radius (1.16 Å) for Ca^{2+} with smaller radius (~ 1.0 Å). However, increase of x above 0.1 reduced the unit cell parameters, owing to formation of Grenier and perovskite phases. These results indicate that $x_c = 0.05$ is the concentration threshold for formation of brownmillerite $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ single-phase compounds. For other systems reported previously, such as $\text{Ba}_2(\text{In}_{1-x}\text{Ga}_x)_2\text{O}_5$,²⁰ $\text{Ba}_2(\text{In}_{1-x}\text{Al}_x)_2\text{O}_5$,²¹ and $\text{Ca}_2\text{FeAl}_{1-x}\text{Mg}_x\text{O}_5$,¹⁴ brownmillerite single phase was also found for $x < 0.2$. However, $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ -based brownmillerite compounds could be prepared with higher x values, with $x_c \approx 0.65$.²² Synthesis of brownmillerite compounds with all x values is very difficult and dependent on many experimental factors.

Variation of x and δ in $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ also changed the valence state of Fe, as revealed by XAFS spectroscopy. Figure 4 shows normalized Fe K-edge XANES spectra (upper panel) and their first derivative (lower panel) for the compounds with $x = 0, 0.1, 0.3, 0.5, 0.7$, and 1 at room temperature.

Fig. 2. Enlarged view of XRD patterns of $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ in the diffraction region of 31° to 35° , compared with those of reference oxides $\text{LaCa}_2\text{Fe}_3\text{O}_8$ and LaFeO_3 .

Fig. 3. Crystal geometry of (a) brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$, (b) Grenier $\text{LaCa}_2\text{Fe}_3\text{O}_8$, and (c) perovskite LaFeO_3 structures.

Table I. Experimental values of some parameters determined by studying the crystalline and electronic structures and electrical and magnetic properties of La-doped $\text{Ca}_2\text{Fe}_2\text{O}_5$ compounds. The structural parameters (a , b , c , and V) were only calculated for compounds that crystallized mainly in brownmillerite phase

Compound	a (Å)	b (Å)	c (Å)	V (Å ³)	E_{exp} (eV)	$R_{\text{Fe-O}}$ (Å)	E_a (eV)
$x = 0$	5.424	14.761	5.589	447.48	7123.1	1.910	—
$x = 0.05$	5.429	14.775	5.595	448.79	—	—	—
$x = 0.1$	5.433	14.785	5.593	449.27	7123.3	1.924	123.8
$x = 0.15$	5.427	14.780	5.592	448.54	—	—	—
$x = 0.2$	5.421	14.786	5.594	448.39	—	—	98.0
$x = 0.3$	—	—	—	—	7123.7	1.958	94.8
$x = 0.5$	—	—	—	—	7123.9	1.958	97.4
$x = 0.7$	—	—	—	—	7124.2	1.975	95.1
$x = 1$	—	—	—	—	7124.9	2.001	104.6

Fig. 4. Fe K-edge XANES spectra (upper panel) and their first derivative (lower panel) for typical $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds. Inset shows enlarged view of pre-edge peak P_1 .

Careful analysis of the XANES spectra reveals three points of interest as follows:

(1) The intensity of the pre-edge peak (labeled P_1) at around 7112 eV attributed to the $1s \rightarrow 3d$ dipole-forbidden transition of Fe ions^{23,24} is associated with the symmetry of the crystal field around the Fe absorbing atom. Tetrahedrally coordinated Fe ions give strong P_1 intensity, due to the mixture of p and d orbitals in the tetrahedral symmetry, for the case of brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$. Meanwhile, low P_1 intensity will be observed for octahedrally coordinated Fe ions, due to the quadrupole-allowed transition in the octahedral symmetry, for the case of perovskite LaFeO_3 .

(2) There is a shoulder (labeled P_2 in Fig. 4) at around 7119 eV, which is ascribed to the $1s \rightarrow 4p$

transition with simultaneous ligand-to-metal charge transfer.²⁴ Similar to the case of P_1 , the intensity of P_2 is also dependent on the crystal field symmetry. It is strong for brownmillerite-type structure with alternating sheets of FeO_4 and FeO_6 , and weak for other (i.e., Grenier and perovskite) phases. The intensity decreased and the peak shifted towards higher energy for P_1 and P_2 with increasing x (Fig. 4 and inset), demonstrating the brownmillerite-to-perovskite transformation through the Grenier phase.

(3) The midpoint of the absorption edge (labeled E_{exp}), corresponding to the maximum of the first derivative curve (Fig. 4, lower panel), correlates with the valence state of Fe atoms, being about 7123 eV for the parent $\text{Ca}_2\text{Fe}_2\text{O}_5$ ($x = 0$). This value is the same as the E_0 value of Fe^{3+} in Fe_2O_3 . However, with increasing x , E_{exp} tended to shift towards higher energy corresponding to Fe^{4+} , being about 7125 eV for $x = 1$, as presented in Table I.

The local geometric structure around Fe ions can be determined by plotting the Fourier-transformed (FT) spectra of the extended x-ray absorption fine structure (EXAFS) region. Specifically, the FT spectra of the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds (Fig. 5) showed a strong peak centered at about 1.5 Å, corresponding to the average bond distance of Fe–O ($R_{\text{Fe-O}}$). Due to the phase shift of photoelectron backscattering, this peak was shifted by ~ 0.5 Å on the R axis from the standard value.²⁵ Table I also presents the average values of $R_{\text{Fe-O}}$ estimated for the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds. In previous work, Ryu et al.²⁴ showed that the Fe–O distances in the parent $\text{Ca}_2\text{Fe}_2\text{O}_5$ lie in the range of 1.963 Å to 1.977 Å for Fe– O_6 and 1.884 Å to 1.858 Å for Fe– O_4 . Their average distance of ~ 1.911 Å is very close to the value $R_{\text{Fe-O}} = 1.910$ Å obtained for our $\text{Ca}_2\text{Fe}_2\text{O}_5$ compound. In particular, with increasing x , there was a gradual increase of $R_{\text{Fe-O}}$ from 1.924 Å for $x = 0.1$ to 2.001 Å for $x = 1$, as shown in Table I. This enhancement of $R_{\text{Fe-O}}$ is related to the structural transformation tendency from $\text{Ca}_2\text{Fe}_2\text{O}_5$ through $\text{LaCa}_2\text{Fe}_3\text{O}_8$ to LaFeO_3 , because the perovskite

Fig. 5. k^2 -weighted FT EXAFS spectra collected at the Fe K-edge for typical $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds.

LaFeO_3 contains only FeO_6 octahedron with $R_{\text{Fe-O}} = 1.974 \text{ \AA}$ to $2.006 \text{ \AA}$,^{24,26} fairly close to the $R_{\text{Fe-O}}$ values of our compounds with $x = 0.7$ and 1 .

Together with the peak shift of $R_{\text{Fe-O}}$, its intensity also increased with increasing x in the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds. This is thought to be due to an increase in the coordination number of oxygen atoms surrounding the Fe atom, because the EXAFS spectrum is the sum of outgoing and incoming waves, which depend on the immediate environment of the absorbing atom.²⁵ In other words, δ in $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ tends to increase with increasing x , in good agreement with the XRD analysis above. In summary, the studies of the geometric and electronic structures demonstrate that: (1) only Fe^{3+} ions are present in $\text{Ca}_2\text{Fe}_2\text{O}_5$ ($x = 0$), (2) both Fe^{3+} and Fe^{4+} ions coexist in $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ with $x > 0$, (3) the concentration of Fe^{4+} ions tends to increase with increasing x , and these ions are thought to be favored in the Grenier and perovskite structures, and (4) increase of x above 0.05 leads to the structural phase transformation $\text{Ca}_2\text{Fe}_2\text{O}_5 \rightarrow \text{LaCa}_2\text{Fe}_3\text{O}_8 \rightarrow \text{LaFeO}_3$, due to the increase of the oxygen content. These changes directly influence the magnetic and electrical properties of the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds.

Magnetic Properties

The magnetic properties of the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds at room temperature were studied by means of ESR and magnetization measurements. Their ESR spectra indicated that the signal intensity (Int) was very weak for $x = 0$, but became strong on increasing x from 0.05 to 1 (Figs. 6 and 7a). Concurrently, the spectral line width (ΔH) and resonant field (H_r) also changed (Fig. 7b and c). In our work, the H_r values (3040 Oe to 3200 Oe) are

Fig. 6. Room-temperature ESR spectra of the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds.

Fig. 7. Variation of ESR spectral parameters for $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds as function of x : (a) Int, (b) ΔH , and (c) H_r .

smaller than the H_r value of free/unpaired electrons ($\sim 3300 \text{ Oe}$),²⁷ and depend on x . This proves that the resonant signals mainly arise from FM and/or AFM coupling between the magnetic moments of Fe^{3+} and Fe^{4+} ions. For the parent compound $\text{Ca}_2\text{Fe}_2\text{O}_5$ ($x = 0$), its weak intensity indicates $\text{Fe}^{3+}\text{--Fe}^{3+}$ AFM pairs persisting up to

Fig. 8. Room-temperature $M(H)$ loops of typical $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds. Inset shows enlarged view of $M(H)$ curves for the compounds with $x = 0$ to 0.3 .

$T_N \approx 700$ K,^{8–10} because only Fe^{3+} ions are present in this compound. With increasing x from 0.05 to 0.2 , in which range the brownmillerite and Grenier phases coexist, the appearance of Fe^{4+} ions results in $\text{Fe}^{3+}\text{--Fe}^{4+}$ FM and $\text{Fe}^{4+}\text{--Fe}^{4+}$ AFM exchange pairs, enhancing Int. For the compounds with $x > 0.2$, the complex variations in the spectral parameters are related to the coexistence of the Grenier and perovskite phases, and creation of more $\text{Fe}^{4+}\text{--Fe}^{4+}$ AFM pairs in addition to $\text{Fe}^{3+}\text{--Fe}^{4+}$ FM pairs. Here, the different variation tendencies of Int, ΔH , and H_r are due to their different nature and depend on the volume fractions of the crystal phases in the compounds. While Int is mainly associated with the magnetic susceptibility, ΔH is associated with the total magnetic moments that contribute to resonance. Meanwhile, H_r is dependent on the Landé g -factor characteristic of spin–spin and spin–orbit couplings²⁷ of Fe^{3+} and Fe^{4+} ions. Obviously, together with EXAFS studies, use of ESR spectroscopy as an auxiliary tool is very helpful to detect small changes in the concentration of Fe^{4+} in $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$, particularly for the compounds with $x = 0.05$ to 0.2 .

Considering the $M(H)$ results (Fig. 8), it emerges that all the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds exhibit magnetic hysteresis loops with weak FM/AFM order at room temperature. These $M(H)$ data can be divided into two characteristic groups. The first group includes the compounds with $x \leq 0.3$, whose loop areas at magnetic fields $H < 2$ kOe are narrow; at higher fields, no loop is observed and M increases linearly with increasing H . The other group includes the compounds with $x > 0.3$, whose loop areas are much larger than those of the first group; at magnetic fields $H > 7$ kOe, there is no hysteresis loop and the $M(H)$ dependences are linear. Such linear $M(H)$ dependence at high field could be

Fig. 9. M_s and H_c versus x in $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$. Dotted lines are guides to the eye only; 5% error bars are shown.

related to various effects such as (1) the magnetic moments in FM/AFM regions have not yet reached saturation state, (2) short-range FM order, and/or (3) paramagnetism of isolated $\text{Fe}^{3+}, \text{Fe}^{4+}$ ions. For the hysteresis loop regions associated with FM/AFM interactions, one can analyze the x dependence of the saturation magnetization (M_r) and coercivity (H_r), as shown in Fig. 9. For the first group, M_r gradually decreased from 0.047 emu/g for $x = 0$ to ~ 0.038 emu/g for $x = 0.3$, while H_c changed less (86 Oe to 129 Oe). However, for the second group, both M_s and H_c increased rapidly with increasing x from 0.4 to 1 . These variations of M_s and H_c are associated with the changes in the $\text{Fe}^{3+}/\text{Fe}^{4+}$ ratio and structural phases. As mentioned above, brownmillerite phase is dominant for $x < 0.3$, where the $\text{Fe}^{3+}\text{--Fe}^{3+}$ AFM interaction plays a pivotal role. The appearance of Fe^{4+} leads to addition of the $\text{Fe}^{3+}\text{--Fe}^{4+}$ FM interaction, which competes with the AFM one, slightly reducing M_s . For the Grenier phase with dominantly AFM-ordered Fe^{3+} ions,¹⁸ we believe that the presence of Fe^{4+} in this structure also does not enhance M_s and H_c , because its volume fraction is relatively large, in the range of $x = 0.1$ to 0.3 . However, for the compounds with $x > 0.3$, higher x results in development of perovskite phase, creating more $\text{Fe}^{3+}\text{--Fe}^{4+}$ FM pairs. These factors enhance M_s and H_c , similar to the case of $\text{La}_{1-x}\text{Ca}_x\text{FeO}_3$ compounds.^{28,29} In other words, the enhanced FM behavior for $x > 0.3$ is related to Fe^{4+} ions in the perovskite rather than brownmillerite or Grenier structure. Although $\text{Fe}^{3+}\text{--Fe}^{4+}$ FM pairs are present in the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds with $x > 0.3$, the AFM interaction due to $\text{Fe}^{3+}\text{--Fe}^{3+}$ and $\text{Fe}^{4+}\text{--Fe}^{4+}$ pairs remains dominant. The narrowing of the $M(H)$ loop for fields $H < 2.5$ kOe for $x = 1$ is thus ascribed to competition between the two FM and AFM phases in different crystal phases. The variation tendency of M_s (Fig. 9) and H_r (Fig. 7c) versus x is more or less the same. This is due to their

correlation to FM resonance, as described by the Kittel formulae.³⁰

Electrical Properties

We measured the resistivity, ρ , of the $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds in the temperature range of $T = 20$ K to 400 K. However, the ρ for the compounds with $x = 0$ and 0.05 was above $5 \times 10^6 \Omega \text{ cm}$, lying beyond the measurement range of our device. For the other compounds ($x \geq 0.1$), we recorded their resistivity at temperatures of $T > 120$ K, as shown in Fig. 10. Depending on x and T (from 120 K to 400 K), ρ varied over a wide range from $1 \Omega \text{ cm}$ to $10^6 \Omega \text{ cm}$. For given x value, ρ decreased exponentially with increasing T , being a typical characteristic of semiconductors. In particular, the ρ - T dependences can be described based on the adiabatic small polaron hopping (SPH) model formulated as

$$\rho(T) = \rho_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (2)$$

where E_a is the polaron formation energy and k_B is the Boltzmann constant. The resistivity coefficient ρ_0 can be determined from the following equation:

$$\rho_0 = \frac{k_B}{n(1-x)e^2 d}, \quad (3)$$

where n is the charge carrier density, x is the hole (Fe^{4+}) concentration, and d is the polaron diffusion constant, which depends on the lattice constants and the characteristic frequency of the longitudinal optical (LO) phonon carrying polarons through the lattice.³¹ The motion of charge carriers in the adiabatic region is considered to be faster than lattice vibrations. Using Eq. 2 to fit the $\rho(T)$ data in the range of $T = 130$ K to 400 K (Fig. 11), we determined the values of E_a , as shown in Table I and the inset of Fig. 11. The results reveal that E_a varied as a function of x , being 123.8 meV for $x = 0.1$ but decreasing rapidly to 94.8 meV for $x = 0.2$. In the range of $x = 0.3$ to 0.7, E_a (95 meV to 97 meV) remained relatively unchanged, but slightly increased at $x = 1$. These values indicate a close relation between ρ , E_a , and Fe^{4+} ions. In other words, the decrease in ρ is due to an increase in the Fe^{4+} concentration (with increased density of charge carriers) that reduces E_a . Small polarons involved in nearest-neighbor hopping become more mobile versus thermal activation processes. Recently, Malveiro et al.¹⁴ studied brownmillerite $\text{Ca}_2\text{FeAl}_{1-x}\text{Mg}_x\text{O}_5$ ($x = 0$ and 0.05), finding large values of E_a (260 meV to 620 meV), which tended to decrease if more Fe^{4+} ions were added to the brownmillerite lattice. Apart from the important role of Fe^{4+} ions, we believe that structural changes and grain-boundary-related effects also influence ρ and E_a ,

Fig. 10. Temperature-dependent resistivity, $\rho(T)$, of $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds ($x \geq 0.1$) as function of x .

Fig. 11. $\text{Log}(\rho/T)$ versus $1000/T$ data (symbols) of $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds with $x > 0.1$ fit to the SPH model (solid lines, Eq. 2). Inset shows x dependence of E_a varying on the meV scale; the solid line is a guide to the eye only.

because the LO phonon frequency and the hopping of polarons would be modified by these factors.^{14,32}

CONCLUSIONS

Detailed analysis of the XRD patterns, Fe K-edge XANES spectra, and ESR spectra of $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ compounds ($x = 0$ to 1) at room temperature revealed the following: (1) only Fe^{3+} ions exist in the parent $\text{Ca}_2\text{Fe}_2\text{O}_5$ ($x = 0$), (2) there is a mixture of Fe^{3+} and Fe^{4+} ions in $\text{Ca}_{2-x}\text{La}_x\text{Fe}_2\text{O}_{5+\delta}$ with $x > 0$, (3) the Fe^{4+} content tends to increase with increasing x , and these Fe^{4+} ions preferably locate in the Grenier $\text{LaCa}_2\text{Fe}_3\text{O}_8$ and perovskite LaFeO_3 structures, and (4) increase of x from 0.1 to 1 causes a

structural phase transformation due to the increasing oxygen and Fe^{4+} contents. $M(H)$ measurements at room temperature also revealed magnetic phase separation with two characteristic groups. For the first group, M_r gradually decreased from 0.047 emu/g for $x = 0$ to ~ 0.038 emu/g for $x = 0.3$, while H_c changed less (86 Oe to 129 Oe). However, for the second group, both M_s and H_c increased rapidly with increasing x from 0.4 to 1. These variations of M_s and H_c are tightly related to the changes in the $\text{Fe}^{3+}/\text{Fe}^{4+}$ ratio and structural phases. Study of the temperature-dependent resistivity in the range of $T = 20$ K to 400 K revealed that all the compounds are insulators. Although the $\rho(T)$ values for the compounds with $x = 0$ and 0.05 lay beyond our measurement capability of $5 \times 10^6 \Omega \text{ cm}$, the compounds with $x \geq 0.1$ showed lower $\rho(T)$ values that decreased with increasing x from 0.1 to 1 and T from 120 K to 400 K. We also found that the $\rho(T)$ data for $x \geq 0.1$ obeyed the adiabatic SPH model, with rapidly decreasing polaron formation energy E_a for $x > 0.1$. Apart from the important role of Fe^{4+} ions, structural changes and grain-boundary-related effects are also thought to influence ρ and E_a .

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REFERENCES

- Q. Lu and B. Yildiz, *Nano Lett.* 16, 1186 (2016).
- C.P. Jijil, M. Lokanathan, S. Chithiravel, C. Nayak, D. Bhattacharyya, S.N. Jha, P.D. Babu, B. Kakade, and R.N. Devi, *ACS Appl. Mater. Interfaces* 8, 34387 (2016).
- M.D. Rossell, O.I. Lebedev, G. Van Tendeloo, N. Hayashi, T. Terashima, and M. Takano, *J. Appl. Phys.* 95, 5145 (2004).
- M. Ismail, W. Liu, M.S.C. Chan, M.T. Dunstan, and S.A. Scott, *Energy Fuels* 30, 6220 (2016).
- K. Gupta, S. Singh, and M.S.R. Rao, *Nano Energy* 11, 146 (2014).
- T.C. Gibb, A.J. Herod, D.C. Munro, and N. Peng, *J. Mater. Chem.* 4, 1451 (1994).
- J.M. Gonzalez-Calbet, M. Vallet-Regi, and M.A. Alario-Franco, *J. Solid State Chem.* 60, 320 (1985).
- T. Takeda, Y. Yamaguchi, S. Tomiyoshi, M. Fukase, M. Sugimoto, and H. Watanabe, *J. Phys. Soc. Jpn.* 24, 446 (1968).
- K. Gupta, S. Singh, M. Ceretti, M.S.R. Rao, and W. Paulus, *Phys. Status Solidi A* 210, 1771 (2013).
- T. Labii, M. Ceretti, A. Boubertakh, W. Paulus, and S. Hamamda, *J. Therm. Anal. Calorim.* 112, 865 (2013).
- D. Petrov and B. Angelov, *Acta Phys. Pol. A* 122, 737 (2012).
- D. Petrov, B. Angelov, and V. Lovchinov, *J. Alloys Compd.* 509, 5038 (2011).
- P.M. Woodward, D.E. Cox, E. Moshopoulou, A.W. Sleight, and S. Morimoto, *Phys. Rev. B* 62, 844 (2000).
- J. Malveiro, T. Ramos, L.P. Ferreira, J.C. Waerenborgh, M.R. Nunes, M. Godinho, and M.D. Carvalho, *J. Solid State Chem.* 180, 1863 (2007).
- S. Dhankhar, K. Gupta, G. Bhalerao, N. Shukla, M. Chandran, B. Francis, B. Tiwari, K. Baskar, and S. Singh, *RSC Adv.* 5, 92549 (2015).
- N. Abe, N.D. Khanh, T. Sasaki, and T. Arima, *Phys. Rev. B* 89, 054437 (2014).
- J.A. Bearden and A.F. Burr, *Rev. Mod. Phys.* 39, 125 (1967).
- J.M. Hudspeth, D.J. Goossens, A.J. Studer, R.L. Withers, and L. Norén, *J. Phys. Condens. Matter* 21, 124206 (2009).
- P.M. Price, N.D. Browning, and D.P. Butt, *J. Am. Ceram. Soc.* 98, 2248 (2015).
- C. Didier, J. Claridge, and M. Rosseinsky, *J. Solid State Chem.* 218, 38 (2014).
- I.V. Spesivtseva, N.A. Kochetova, E.M. Gorbunova, and I.E. Animitsa, *Russ. J. Phys. Chem. A* 85, 1816 (2011).
- G.J. Redhammer, G. Tippelt, G. Roth, and G. Amthauer, *Am. Miner.* 89, 405 (2004).
- A.E. True, R.C. Scarrow, C.R. Randall, R.C. Holz, and L. Que Jr, *J. Am. Chem. Soc.* 115, 4246 (1993).
- K.H. Ryu, K. Sakaue, H. Terauchi, and C.H. Yo, *Bull. Korean Chem. Soc.* 18, 1047 (1997).
- B.K. Teo, *Basic Principles and Data Analysis* (Berlin: Springer, 1986).
- M. Marezio and P.D. Dernier, *Mater. Res. Bull.* 6, 23 (1971).
- M. Ikeya, *New Applications of Electron Spin Resonance* (Singapore: World Scientific, 1993).
- Z.C. Xu, M.F. Liu, C.C. Chen, and X.N. Ying, *J. Appl. Phys.* 115, 123516 (2014).
- E.K. Abdel-Khalek and H.M. Mohame, *Hyperfine Interact.* 222, S57 (2013).
- C. Kittel, *Introduction to Solid State Physics*, 8th ed. (Hoboken: Wiley, 2004).
- D. Varshney and N. Dodiya, *J. Theor. Appl. Phys.* 9, 45 (2015).
- W. Luo, H.M. Yao, P.H. Yang, and C.S. Chen, *J. Am. Ceram. Soc.* 92, 2682 (2009).