

Mössbauer Spectroscopic Study of $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ ($0 \leq x \leq 0.5$) Solid-solution

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Received August 7, 2003

Tetragonal K_2NiF_4 -type $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ solid-solution have been synthesized by citrate based sol-gel method. The valence state of iron was determined by Mössbauer spectroscopy and subsequent iodometric titration clearly showed that the copper ions in this solid-solution are in the mixed valence state Cu(II/III) . When $x \leq 0.3$, Fe(III) is competing with the mixture of Cu(II) and Cu(III) and $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ exhibits a metallic character. No evidence for $\text{Cu(II)-O-Fe(IV)} \leftrightarrow \text{Cu(III)-O-Fe(III)}$ valence degeneracy was observed. In contrast, a small amount of Fe(IV) is observed with increasing x ($x = 0.4$ and 0.5), revealing a semiconducting behavior. These results suggest that the electronic interaction of Cu(III)-O-Fe(III) contributes greatly to the metallic character, while the electronic interaction of Cu(II)-O-Fe(IV) deteriorates the metallic character of $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$.

Key Words : $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$, Mössbauer spectroscopy, Electronic interaction

Introduction

K_2NiF_4 -type oxide La_2CuO_4 provides a wide variety of possibilities for diverse metal atom substitutions at the lanthanum and copper sites. The alkaline-earth metal substitution at the lanthanum site is particularly important for the superconducting behavior of this oxide.¹⁻⁴ More generally, the physical properties of $A_2\text{BO}_4$ oxides are largely dependent on the formal valence of transition metal ions (B) and/or the lattice volumes.^{5,6} Partial substitution at the A - and B -sites or variation of oxygen vacancy can vary the valence of B ions in $A_2\text{BO}_4$, which often gives rise to the change in the lattice constants because of the interaction between the transition metal ions and oxygen ions. Lattice expansion and contraction without any change in the formal valence also affects the properties of $A_2\text{BO}_4$. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ superconductor is one of good examples which exhibit all of these phenomena. It is reported that the crystallographic, magnetic, and electronic transport properties of $\text{La}_2\text{CuO}_{4+\delta}$ are extremely sensitive to the concentration δ of oxygen defects,⁷ and the superconducting properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ are also sensitive to the presence of oxygen defects.⁸

A series of $(\text{La,Sr})_2\text{FeO}_4$ with K_2NiF_4 -type structure shows different electrical properties depending on the valence of iron and/or the Sr/La ratio. La_2FeO_4 with Fe(II) is insulating with a resistivity of $>10^7 \Omega\text{cm}$ at room temperature but LaSrFeO_4 with Fe(III) is semiconducting with a resistivity of $2.4 \times 10^3 \Omega\text{cm}$.⁹ It seems that the resistivity of $(\text{La,Sr})_2\text{FeO}_4$ decreases as the concentration of the higher oxidation state of iron increases. Recent study on the electronic interaction of $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{M}_x\text{O}_4$ indicated that $M = \text{Ti, Mn, and Ru}$ members show a semiconducting/

insulating behaviors but a broad metal-semiconductor transition is observed for $M = \text{Fe}$ ($0 < x < 0.15$).¹⁰ Such an interesting transport behavior was correlated to the $\text{Cu(II)-O-Fe(IV)} \leftrightarrow \text{Cu(III)-O-Fe(III)}$ valence degeneracy. Because of an ambiguity of the oxidation states of transition metal ions, however, it should be pointed out that the exact valence of each transition metal (Cu, Fe) be determined in order to interpret more precisely electronic interactions. In this paper, the variation of oxidation state of iron ion was studied by Mössbauer spectroscopy. Subsequent iodometric titration gave a reasonable conclusion for the mixed valence state of copper ion. A correlation between variation of structure and electronic interaction in $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ could be induced from the comparison of valence state of iron and copper ions, XRD data, and temperature dependent behavior of the electrical resistivity.

Experimental Details

In order to prepare the highly homogeneous $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ samples, a citrate based sol-gel technique was used. Stoichiometric amounts of La_2O_3 , $\text{Sr}(\text{NO}_3)_2$, CuO , and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in nitric acid (about 3 M) solution. The excess citric acid was added to this solution, and the solution was gently dried on a hot plate. In the course of this manipulation, the pH was adjusted to about 4-6 with NH_4OH solution. The resulting gel was heated at 350°C to decompose the organic precursors. The dark-gray powder was ground and heated at 900°C for 24 h in air. Resulting powder was then pressed into pellets and heated at 1150°C for 45 h in air with intermittent grinding and pelletization.

Powder X-ray diffraction data were obtained with

Shimadzu XRD-6000 using Ni-filtered Cu-K α radiation. The valence states of transition metals (Cu and Fe) were estimated by iodometric titration. The Mössbauer spectroscopy studies were carried out at 300 K and 80 K with Co⁵⁷ source doped in metallic rhodium which was oscillated in a sinusoidal mode. The doppler velocity of spectra was calibrated with α -Fe foil (25 μ m in thickness). The electrical resistance of polycrystalline pellets was measured using a standard four probe method.

Results and Discussion

La_{2-2x}Sr_{2x}Cu_{1-x}Fe_xO_{4-y} ($x = 0.1, 0.2, 0.3, 0.4,$ and 0.5) compounds could be readily prepared by sol-gel technique. All the members are the single phases with K₂NiF₄-type structure as shown in Figure 1. The unit cell parameters and oxygen contents determined by iodometric titration are compared in Table 1. With increasing x value, unit cell a parameter is reduced but the c axis is enlarged until $x \leq 0.3$. In contrast, the shorter a and longer c parameters are observed for $x = 0.4$ in comparison with those for $x = 0.5$. The c/a ratio increases showing a maximum at $x = 0.2$ and decreases for $x \geq 0.4$. If we consider the lattice parameters of La₂CuO₄ ($a = 3.810$ Å and $c = 13.150$ Å) and Sr₂FeO₄ ($a = 3.863$ Å and $c = 12.406$ Å),¹⁰ it could be expected that the variation of lattice parameters is dependent on the electronic configuration of Cu(III) and Fe(IV) in La_{2-2x}Sr_{2x}Cu_{1-x}Fe_xO_{4-y} series. The oxygen contents of La_{2-2x}Sr_{2x}Cu_{1-x}Fe_xO_{4-y} reveal that the samples are oxygen deficient, indicating that all samples have the mixed valence of copper and iron. The degree of deviation from oxygen stoichiometry increases with higher substitution ratio of iron, which means that Fe(III)^{11,12} is the more stable valence of iron stabilized in perovskite related metal oxides. On the contrary, Fe(IV) can be stabilized under unusual preparation conditions. For instance, SrFe(IV)O₃ and CaFe(IV)O₃ can be prepared under high oxygen pressures^{13,14} and by electrochemical oxidation.¹⁵

Iodometric titration can give us a valuable information on the valence state of iron stabilized in the perovskite-related

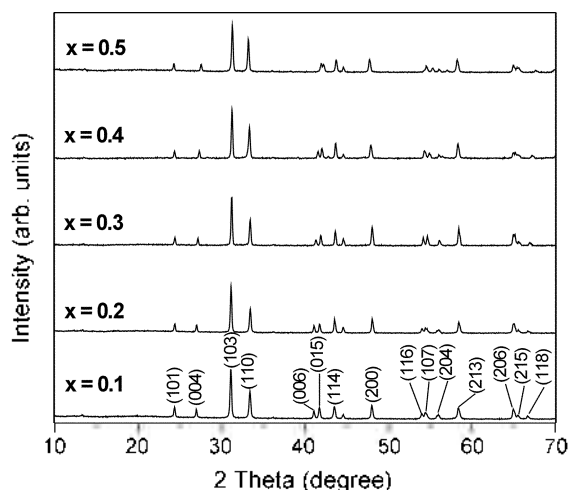


Figure 1. XRD patterns of La_{2-2x}Sr_{2x}Cu_{1-x}Fe_xO_{4-y} as a function of x .

Table 1. Unit Cell Parameters and Oxygen contents of La_{2-2x}Sr_{2x}Cu_{1-x}O_{4-y}

Compound	Unit cell parameters			Oxygen defect (y)
	a (Å)	c (Å)	c/a	
La _{1.8} Sr _{0.2} Cu _{0.9} Fe _{0.1} O _{4-y}	3.792(3)	13.187(6)	3.478	0.02(4)
La _{1.6} Sr _{0.4} Cu _{0.8} Fe _{0.2} O _{4-y}	3.794(8)	13.281(4)	3.501	0.04(2)
La _{1.4} Sr _{0.6} Cu _{0.7} Fe _{0.3} O _{4-y}	3.789(5)	13.225(7)	3.490	0.07(3)
La _{1.2} Sr _{0.8} Cu _{0.6} Fe _{0.4} O _{4-y}	3.815(9)	13.207(2)	3.462	0.11(6)
LaSrCu _{0.5} Fe _{0.5} O _{4-y}	3.824(4)	13.129(3)	3.433	0.14(8)

metal oxides. In case that the metal oxides are composed of binary transition metals (Cu and Fe), the valence states of iron can be determined assuming that the valence state of Cu is invariable. However, the valence states of iron and copper are evidently variable. Moreover, the total amount of oxygen is calculated in the iodometric titration on the basis of an ideal chemical formula with no oxygen deficiency. Therefore, another method should be used in order to compensate for an ambiguity for the valence state of iron determined by iodometric titration. In this respect, Mössbauer spectroscopy is quite useful for the characterization of valence state and coordination structure of iron. The valence states of iron stabilized in certain crystal lattice are estimated from the isomer shift (δ in mm/s) and quadrupole splitting (Δ in mm/s). When we have an exact information for the electronic configuration of iron ion, the valence state of copper can be reasonably determined by iodometric titration.

Figure 2 shows Mössbauer spectra of La_{2-2x}Sr_{2x}Cu_{1-x}Fe_xO_{4-y}. The determined Mössbauer parameters at room temperature and 82 K are summarized in Table 2. For $x = 0.1, 0.2,$ and 0.3 , all of iron ions are stabilized in the valence state of Fe(III) within experimental error, which corresponds to the isomer shift, $\delta = 0.30, 0.30,$ and 0.28 mm/s, respectively. For $x = 0.4$ and 0.5 sample, it is evident that a small amount of Fe(IV) is formed with isomer shifts $\delta = 0.09, -0.05,$ respectively. Moreover, for the sample with $x = 0.5$, no

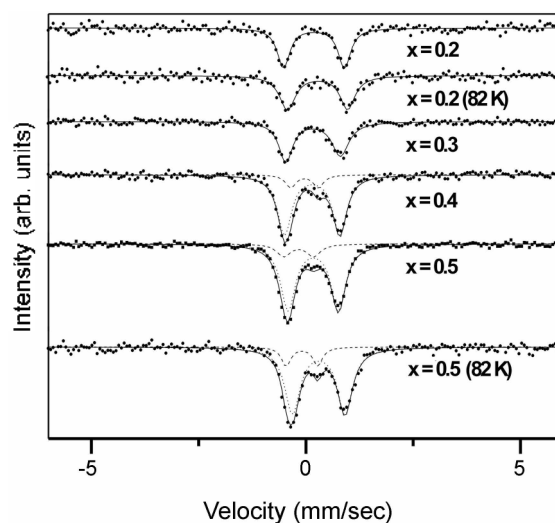


Figure 2. Mössbauer spectra of La_{2-2x}Sr_{2x}Cu_{1-x}Fe_xO_{4-y} collected at room temperature and 82 K.

Table 2. Mössbauer Parameters for $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ at room Temperature and 82 K

Compound	δ (mm s^{-1})	ΔE_Q	I (%)	Valence state ratio (%)			
				Fe $^{3+}$	Fe $^{4+}$	Cu $^{2+}$	Cu $^{3+}$
$\text{La}_{1.8}\text{Sr}_{0.2}\text{Cu}_{0.9}\text{Fe}_{0.1}\text{O}_{3.98}$	0.30(1)	1.54(3)	100	100	0	93	7
$\text{La}_{1.6}\text{Sr}_{0.4}\text{Cu}_{0.8}\text{Fe}_{0.2}\text{O}_{3.96}$	0.30(5)	1.41(2)	100	100	0	86	14
$\text{La}_{1.6}\text{Sr}_{0.4}\text{Cu}_{0.8}\text{Fe}_{0.2}\text{O}_{3.96}$ (82 K)	0.39(6)	1.40(3)	100	100	0	86	14
$\text{La}_{1.4}\text{Sr}_{0.6}\text{Cu}_{0.7}\text{Fe}_{0.3}\text{O}_{3.93}$	0.28(2)	1.27(7)	100	100	0	76	24
$\text{La}_{1.2}\text{Sr}_{0.8}\text{Cu}_{0.6}\text{Fe}_{0.4}\text{O}_{3.89}$	0.26(4)	1.29(5)	86	86	14	78	22
$\text{LaSrCu}_{10.5}\text{Fe}_{0.5}\text{O}_{3.86}$	0.09(2)	0.65(6)	14				
	0.29(4)	1.17(8)	85	85	15	72	28
$\text{LaSrCu}_{10.5}\text{Fe}_{0.5}\text{O}_{3.86}$ (82 K)	-0.05(2)	0.70(6)	15				
	0.41(4)	1.23(7)	85	85	15	72	28
	0.02(5)	0.73(2)	15				

difference is observed in Mössbauer parameters between at room temperature and 82 K. Based on the valence of iron determined by Mössbauer spectroscopy, the valence states of copper are determined using iodometric titration as shown in Table 2. It is pointed out that the result of combined Mössbauer spectroscopy and iodometric titration gives no evidence for $\text{Cu(II)-O-Fe(IV)} \leftrightarrow \text{Cu(III)-O-Fe(III)}$ valence degeneracy. Thus, the ratio of mixed valence state of Fe(III) and Fe(IV) and consequently Cu(II) and Cu(III) is independent on the temperature.

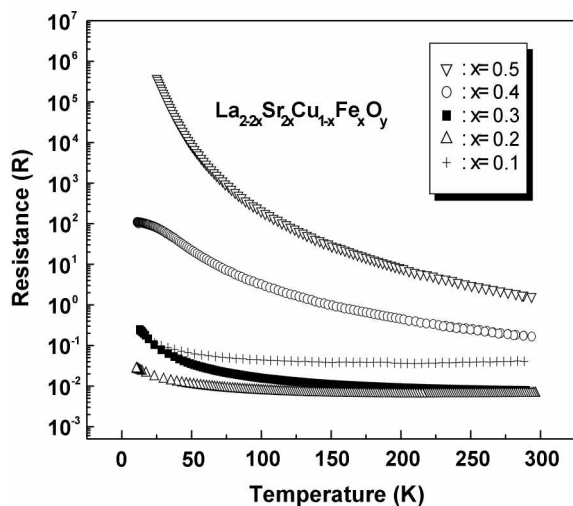
The electrical resistances of $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ series are shown in Figure 3. The temperature dependence of the resistance shows that the samples are metallic over a wide temperature range when $x \leq 0.3$. In contrast, the samples of $x = 0.4$ and 0.5 show the semiconducting behavior in the measured temperature range. Such a result would be correlated with the variation of the lattice parameters of $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ compounds. The sample of $x = 0.2$ showing the largest c/a ratio gives rise to the lowest resistance. The c/a ratio is gradually decreased with increasing substitution ratio of iron. The highest resistance is ultimately exhibited with the sample of $x = 0.5$ showing the smallest c/a ratio. This correlation is quite similar to the behaviors of

Sr_2FeO_4 as previously reported.¹⁶

The variation of electrical resistance is most likely originated from the electronic structure/configuration of Cu and Fe. Considering that the Fe ions in $x \leq 0.3$ members are in trivalent states as evidenced by corresponding Mössbauer spectra, Cu(II) is oxidized to Cu(III) in proportion to the substituted Sr ratio. In contrast, 14% and 15% of Fe(IV) is mixed with Fe(III) in $x = 0.4$ and 0.5 members, respectively. As a consequence, a competition between Cu(III) + Fe(III) and Cu(II) + Fe(IV) valence states can be induced in these compounds. The electronic interaction between Cu(III) and Fe(III) would contribute to the metallic character because of the itinerant electron conduction in the whole composition range. The interaction between Cu(II) and Fe(IV) is not likely itinerant. As previously reported, the Sr substitution for La in La_2CuO_4 lattice is a good example of the hole-carrier doping leading to the appearance of superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The Sr substitution for La in La_2CuO_4 is known to supply the CuO_2 plane with the hole carriers, which results in the formation of Cu(III).¹⁷ Therefore, it is suggested that Cu(III) plays a more important role in the transporting properties of $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ system. The lower electrical resistance for $x \leq 0.3$ is consistent with Cu(III) + Fe(III) valence states. A presence of Fe(IV) at Cu(II/III) sites of CuO_2 sheets in La_2CuO_4 structure deteriorates the metallic character of $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ system.

Conclusion

$\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$ series have been synthesized by citrate-based sol-gel technique. The samples exhibit well crystallized K_2NiF_4 -type structure. From the comparison of Mössbauer spectroscopic and iodometric titration results, the Fe ions are stabilized in trivalent state and the copper ions are in the mixed valent states Cu(II/III) when $x \leq 0.3$. The small amount of Fe(IV) coexists with Fe(III) and Cu(II/III) mixture when $x = 0.4$ and 0.5 . Strong increase in electrical resistivity stems from an existence of tetravalent iron ion. Thus, it is concluded that the metallic character is closely related to the electronic interaction of Cu(III)-O-Fe(III), while the semiconducting behavior is contributed from the electronic interaction of Cu(II)-O-Fe(IV).

**Figure 3.** Temperature dependence of electrical resistances of $\text{La}_{2-2x}\text{Sr}_{2x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{4-y}$.

Acknowledgment. This work was supported by grant No. R01-2002-00045 from the KOSEF.

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