Characteristics of (Sr,Sm)₂FeO~₄

Bull. Korean Chem. Soc. **1996**, Vol. 17, No. 4 321

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Characteristics of K_2NiF_4-Type Oxides $(Sr,Sm)_2FeO_{\sim4}$

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$Sr_{1+x}Sm_{1-x}FeO_{4-y}$, solid solutions with a composition range $0.00 \leq x \leq 1.00$ have been prepared at 1200 ℃ in air under normal atmospheric pressure. All the solutions exhibit the K_2NiF_4-type structure of tetragonal system. Mohr salt analysis shows that the mole ratio of Fe^{4+} ion to Fe^{3+} ion or the τ value increases with the x value. Nonstoichiometric chemical formulas have been formulated from the x, τ, and y values. Electrical conductivity was measured in the temperature range of 173-373 K under atmospheric air pressure. The conductivities of each sample are varied within the semiconductivity range. The conductivity at constant temperature increases steadily with x value and activation energies are varied from 0.14 to 0.32 eV. The conduction mechanism of the ferrite system may be proposed as a hopping model of conduction electrons between the mixed valence states. The Mössbauer spectrum for the composition of $x = 0.00$ shows a six line pattern by which the existence of Fe^{3+} (I.S. = 0.32 mm/sec) can only be identified. The spectra for the compositions of $x = 0.50$ and 1.00 presents broad single line patterns showing a mixed valence state.

Introduction

Up to date various oxides and halogenides showing the K_2NiF_4-type structure[1~7] have been investigated by many researchers. Those compounds are distinctive in chemical and physical properties because they show mixed valency of the transition metal ion, and consequently a considerable amount of oxygen deficiency. The K_2NiF_4-type structure can be described as a sequence of layers of tetragonally distorted octahedra with the K^+ ions alternating in 9-coordinated sites between the layers. As a result of relatively weak interplanar interactions between magnetic ions, K_2NiF_4-type compounds generally show the so-called 2-dimensional (2D) behaviour.[8~10] According to the results of many researches, 3d cations in octahedral sites can have two or more oxidation states. The perovskite type oxides[11~13] show considerable changes in their physical properties by partial replacement of the Fe(III) by the Fe(IV) ions. Especially, the electrical and magnetic properties are sensitive to the mixed valency state of the transition metal in the oxide system. In the present study solid solutions of the $(Sr,Sm)_2FeO_{\sim4}$ system have been prepared and the cell parameters and crystal system were determined by X-ray powder diffraction method. The mixed valency state between Fe^{3+} and Fe^{4+} ions in the system was analysed by Mohr salt titration method and then identified by Mössbauer spectroscopy. The electrical conductivities and the activation energies measured in the temperature range

of 173-373 K are discussed with taking the changes in the x and τ values into account.

Experimental

The starting materials such as Sm_2O_3 (99.99%), $SrCO_3$ (99.99%), and Fe_2O_3 (99.9%) were weighed in appropriate mole ratio to obtain five different samples with various x values. After mixing and grinding, the mixtures were heated at 1200 ℃ in air for 24hr and then quenched. The weighing, grinding, and heating process were repeated several times under the same conditions to obtain homogeneous solid solutions. After the heat treatment, the samples were analysed by the X-ray diffraction method to make sure the homogeneous phase of the solid solution. Each powder sample was pressed into a pellet under a pressure of 2 ton/cm² for 2 minutes and then all the pellets were sintered also under the same conditions as described above. The pellets were used for the study of the electrical conductivity. X-ray diffraction patterns of all compositions were obtained using X-ray diffraction powder method with monochromatized CuKα radiation. Comparing the observed d value with the theoretical d value calculated from the least-square method, we confirmed reasonable Miller indices of each line and then determined the crystal system, the lattice parameters, and the lattice volume of the unit cell.

The residual amount of Fe^{2+} ion of the Mohr salt which
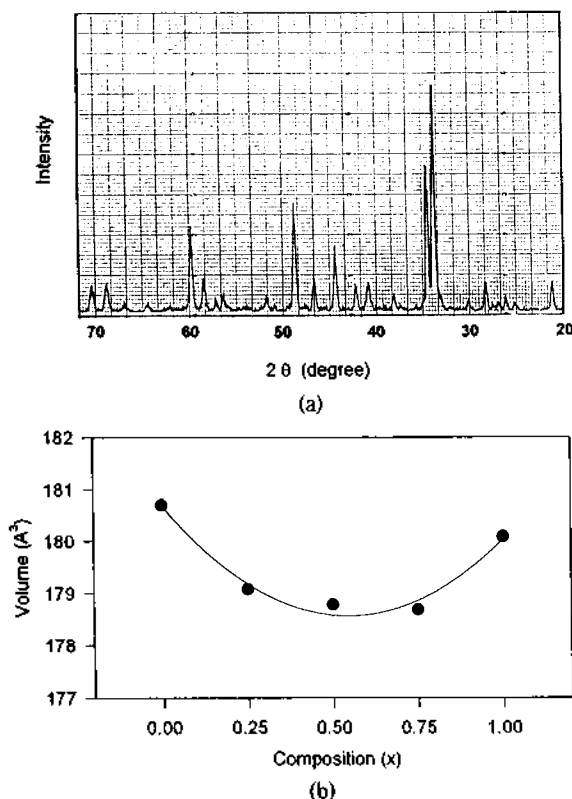
Figure 1. (a) The X-ray diffractogram of the $Sr_{2.00}FeO_{3.76}$ System. (b) Volume change with the increase in x value of the Sr_{1+x}-$Sm_{1-x}FeO_{4-y}$ System.

Table 1. Lattice Parameters, Volume, and Crystal System of the $Sr_{1+x}Sm_{1-x}FeO_{4-y}$ System

Composition (x)	Lattice parameter (Å)	Volume (Å³)	Crystal system
0.00	a 3.864	180.7	tetragonal
	c 12.10		
0.25	a 3.854	179.1	tetragonal
	c 12.06		
0.50	a 3.855	178.8	tetragonal
	c 12.03		
0.75	a 3.849	178.7	tetragonal
	c 12.06		
1.00	a 3.856	180.1	tetragonal
	c 12.11		

Table 2. Nonstoichiometric Chemical Fomulas of the Sr_{1+x}-$Sm_{1-x}Fe^{3+}_{1-\tau}Fe^{4+}_{\tau}$ O_{4-y} System $[y=(x-\tau)/2]$

Composition	τ value	y value	Chemical formulas
0.00	0.21	−0.11	$Sr_{1.00}Sm_{1.00}Fe^{3+}_{0.79} \cdot Fe^{4+}_{0.21}\ O_{4.11}$
0.25	0.30	−0.02	$Sr_{1.25}Sm_{0.75}Fe^{3+}_{0.70}Fe^{4+}_{0.30}\ O_{4.02}$
0.50	0.45	0.02	$Sr_{1.50}Sm_{0.50}Fe^{3+}_{0.55}Fe^{4+}_{0.45}\ O_{3.98}$
0.75	0.55	0.10	$Sr_{1.75}Sm_{0.25}Fe^{3+}_{0.45}Fe^{4+}_{0.55}\ O_{3.90}$
1.00	0.51	0.24	$Sr_{2.00}Fe^{3+}_{0.49}Fe^{4+}_{0.51}\ O_{3.76}$

was reacted with Fe^{4+} ion to produce Fe^{3+} ion has been titrated by 0.1 N-$K_2Cr_2O_7$ solution. The mole ratio of Fe^{4+} ion to Fe^{3+} ion or the τ value could be calculated by the back titration and also the oxygen nonstoichiometry or the y value was obtained. The Mössbauer spectra of the solutions were recorded at room temperature using the spectrometer equipped with a 308-channel pulsed-height analyzer. The electrical conductivities of the sample have been measured by four probe method in the temperature range 173-373 K under atmospheric air pressure. Independent measurements of voltage and current for the conductivities were performed with the inner two probes connected to potentiometer (Keithley, 642 digital multimeter) and the outer two probes to electrometer (Keithley 616 digital electrometer), respectively.

Results and Discussion

A series of solid solution of $Sr_{1+x}Sm_{1-x}FeO_{4-y}$ system for the compositions of $x=0.00$, 0.25, 0.50, 0.75, and 1.00 have been synthesized by heating the mixtures of the reactants at 1200 °C under atmospheric air pressure. The solid solution in which Sm^{3+} ion is replaced by Sr^{2+} over the whole x range have been confirmed to be an uniphase or homogeneous. X-ray powder patterns (Figure 1-(a)) of the solid solutions are indexed reasonably by referring to the K_2NiF_4-type structure. All the phases of the samples are found to be tetragonal system. Lattice parameter, unit cell volume, and crystal system for each composition are listed in Table 1. The lattice parameters of the composition of $x=1.00$ are $a=$

3.856 Å and $c=12.11$ Å which are almost same as those reported in JCPDS card. The spectra of other compositions are similar to that of the compositions of $x=1.00$. The differences between a and c values show that the $Sr_{1+x}Sm_{1-x}$-FeO_{4-y} system belongs to a layered structure of the K_2NiF_4 type. Compared with the perovskite $Sr_xDy_{1-x}FeO_{3-y}$ system,[11] all the structures of the compositions have much elongated c-axis. The distance between the K_2NiF_4 layers has been reported to be double the distance between two neighboring Ni^{2+} ions. Accordingly, we can apply to this system the explanation that K_2NiF_4 type materials have 2-dimensional character[7~10] which can be characterized to have (Sr,Sm)-O layer between perovskite layers. This kind of tendency, the elongation of c axis, also appears to be much increased in the $A_2B_2O_7$ type system.[14] The a values are similar to those of $SrLaFeO_4$[1,4] and $SrDyFeO_4$[2] system. The c value of the $SrLa$-FeO_4 is about 12.7 Å and longer than the c value of this system.

When we consider the larger ionic radius of La (1.15 Å), such a difference can be explained. As shown in Figure 1-(b) and Table 1, the unit cell volume gradually decreases to $x=0.75$, but increases at $x=1.00$. Considering the explanation which was discussed by Yo *et al.*,[11] there may be three factors affecting the cell volume, say, (1) substitution of Sr^{2+} at Sm^{3+} sites, (2) formation of oxygen vacancies (or excessive oxygen sites as seen in this study) and (3) formation of mixed valence state of Fe^{3+} and Fe^{4+}. In the range of $x=0.00$-0.75, the unit cell volume decreases with x and the factors (2) and (3) may be dominating in this range. In the case of $x=1.00$, however, the unit cell volume increases probably due to the factor.[1]
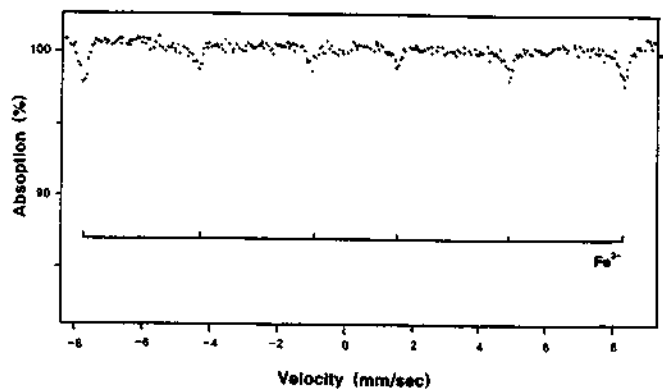
Figure 2. Mössbauer spectrum of the $Sr_{1.00}Sm_{1.00}Fe^{3+}_{0.79}Fe^{4+}_{0.21}$-$O_{4.11}$ System.
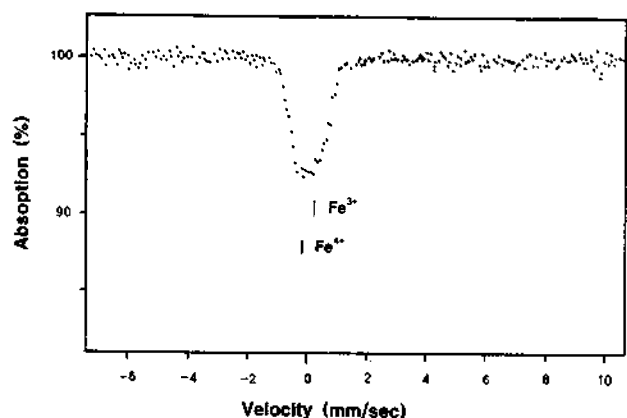
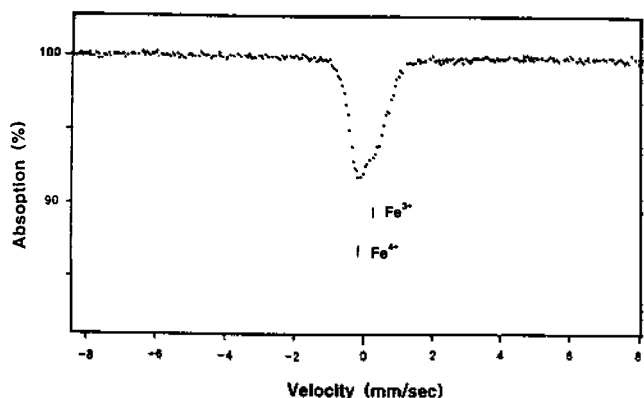**Figure 3.** Mössbauer spectrum of the $Sr_{1.50}Sm_{0.50}Fe^{3+}_{0.55}Fe^{4+}_{0.45}$-$O_{3.98}$ System.

Figure 4. Mössbauer spectrum of the $Sr_{2.00}Fe^{3+}_{0.49}Fe^{4+}_{0.51}O_{3.76}$ System.

The nonstoichiometric chemical formulas of the products, resulting from chemical analysis with Mohr salt, are listed in Table 2 where τ means Fe^{4+} ion ratio, y oxygen deficiency. In the case of $x=0.00$ and $x=0.25$ y values are negative, which means oxygen excess compared to the ideal formula, K_2NiF_4. $Sr_{1+x}Dy_{1-x}FeO_{4-y}$ system also showed oxygen excess ($y=-0.04$ for $x=0.00$). With increase in x, the amount of Fe^{4+} increases and the system shows oxygen deficiency. Similar tendency has been observed in the $Sr_{1+x}Dy_{1-x}FeO_{4-y}$

Table 3. Mössbauer Parameters for Compositions of the Sr_{1+x}-$Sm_{1-x}FeO_{4-y}$ System

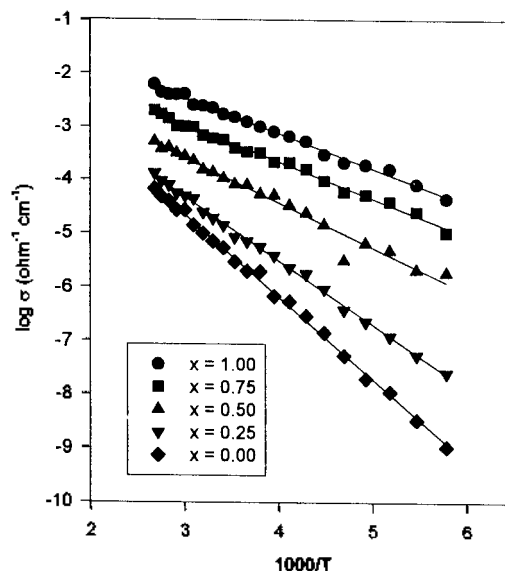| Composition (x)	valency	I.S. (mm/sec)	E_Q (mm/sec)	H_{int} (KOe)
0.00	3+	0.32	0.01	506
0.50	3+	0.34	—	—
	4+	−0.22	—	—
1.00	3+	0.31	—	—
	4+	−0.21	—	—

Figure 5. Plot of log conductivity vs 1000/T for the Sr_{1+x}-$Sm_{1-x}FeO_{4-y}$ System.

system.

The Mössbauer spectra obtained at 290 K of $x=0.00$, 0.50, and 1.00 are shown in Figure 2-4. The spectra of $x=0.00$ shows 6-line pattern, and the isomer shift value is 0.32 mm/sec which corresponds to the Fe^{3+} ions. The value of quadruple splitting (E_Q) and internal magnetic field (H_{int}) are 0.01 mm/sec and 506 KOe (Table 3). In contrast to the (Sr, Dy)FeO$_{4-y}$ system where the existence of Fe^{4+} was confirmed by the peaks at the center for the sample $x=0.00$, in this study Fe^{4+} peaks were not found maybe owing to the rapid electronic exchange between two kinds of iron ions, or experimental error caused by weak gamma ray source.

It is worth while to compare the isomer shift value (I.S. = 0.32 mm/sec) and six-line pattern with SrLaFeO$_4$ (I.S. = 0.33 mm/sec, $T_N=380$ K)[4] and $Sr_2FeO_{3+x}F_{1-x}$ (I.S. = 0.42 mm/sec, $T_N=358$).[3] The two systems showed a six-line pattern at room temperature, so the sample $x=0.00$ will have the Néel temperature over 350 K. In the case of $x=0.50$ and 1.00, a broad single peak appears ranging from -0.2 to 1.0 mm/sec. The isomer shift values of two kinds of iron are shown in Table 3. In contrast to the sample $x=0.00$, the sample $x=0.50$ and $x=1.00$ will have the Néel temperature lower than room temperature.[6]

Figure 5 shows the logarithm of electrical conductivity as a function of temperature. Each product shows semiconducting behaviour in the whole temperature range and electrical

324 *Bull. Korean Chem. Soc.* **1996**, Vol. 17, No. 4

Dae-Bok Kang

Table 4. Activation Energies of the $Sr_{1+x}Sm_{1-x}FeO_{4-y}$ System as a Function of x Values

Composition (x)	Activation energy (eV)
0.00	0.32
0.25	0.26
0.50	0.17
0.75	0.15
1.00	0.14

conductivity increases with temperature. As has been observed in perovskite and K_2NiF_4 system, the ratio of Fe^{4+} ion seems to play an important role in conduction mechanism. When very small amount of Fe^{4+} exists or only Fe^{3+} exists in a ferrite, the conductivity is very low. However, the conductivity of ferrite containing considerable amount of Fe^{4+} shows much increased conductivity at constant temperature. In the system, unlike $Sr_{1+x}Dy_{1-x}FeO_{4-y}$ system where the sample of $x=0.00$ had low conductivity, all the samples shows slight change in conductivity with x value. Such a difference can be explained using Table 2. The sample of $x=0.00$ has about 20% of Fe^{4+} ion, and accordingly shows relatively higher conductivity than $Sr_{1.00}Dy_{1.00}FeO_{4.04}$ system.

In $Sr_2FeO_{3+x}F_{1-x}$ system, $Sr_2FeO_{3.20}F_{0.80}$ where Fe^{4+} content was 20% was prepared under 1300 K in air. The study of thermal variation of the conductivity for $Sr_2FeO_{3.20}F_{0.80}$ shows typical semiconductivity, and the activation energy is 0.26 eV. The activation energy value is similar to that of the sample with $x=0.25$ (Fe^{4+} content is 30%) in our system. The activation energy decreases with increase in x value

(Table 4).

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Electronic Structure Study of the Formal Oxidation States of Lead and Copper in Pb₂Sr₂ACu₃O₈ (A=Ln, Ln+Sr, or Ln+Ca) and Their Possible Changes upon Oxidation

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We examined the formal oxidation states of Pb and Cu in the Pb_2CuO_4 slab of $Pb_2Sr_2ACu_3O_8$ ($A=Y_{1-x}Ca_x$ or $Nd_{1-x}Sr_x$) and their possible changes by oxygen incorporation in the Cu layer of the slab by performing tight-binding band electronic structure calculations on the $Pb_2CuO_{4+\delta}$ slab. Our results show that the most likely oxidation state of Pb is $+2$ and that of Cu is $+1$ for the Pb_2CuO_4 slab prior to oxidation. With small δ values, the oxygen incorporation occurs by the formation of such chain fragments as in $YBa_2Cu_3O_{7-y}$ along the $a+b$ axis. The four-coordinate Cu atoms in the chain fragments are in the $+3$ oxidation states. For values of δ larger than 0.5, however, an additional oxygen (O_{ad}) goes to the site along the b axis to form short $Pb-O_{ad}$ distances oxidizing Pb^{2+} to Pb^{4+}. This change in the Pb oxidation state leads to the suppression of superconductivity due to the decrease of holes in the CuO_2 layer.

Introduction

High-temperature superconductivity ($T_c \sim 70$ K) has been identified in a family of Pb-containing copper oxide materials with formula $Pb_2Sr_2ACu_3O_{8+\delta}$, where A is a mixture of lanthanide (Y, Nd etc) and alkaline earth (Ca or Sr) elements