Studies on the Chemical and Physical Properties of Perovskite-Type Ferrites Containing Strontium

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스트론티움을 포함하는 페롭스카이트형 페라이트의 화학적 · 물리적 성질에 관한 연구

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Abstract: At 1473 K under atmospheric pressure, the homogeneous samples of the $Sm_{1-x}Sr_xFe^{3+}_{1-t}Fe^{4+}_tO_{3-y}$ $(0.00 \leq x \leq 1.00)$ ferrite system were prepared. With the increase in x value, the amount of Fe^{4+} ion increased and the crystallographic structure was changed from orthorhombic symmetry to cubic symmetry. The electrical conductivity at constant temperature sharply increases and the activation energy decreases with the increase of Fe^{4+} ion. Mössbauer spectrum of the sample x=0.00 shows six-line pattern indicating the presence of Fe^{3+} ion in the octahedral sites.

요 약: 1473K, 대기압하에서 $Sm_{1-x}Sr_xFe^{3+}_{1-t}Fe^{4+}_tO_{3-y}$ $(0.00 \leq x \leq 1.00)$ 페라이트계에 대하여 균일상의 시료를 제조하였다. x값의 증가에 따라 Fe^{4+} 이온의 양이 증가하였으며 결정학적 구조는 orthorhombic에서 cubic으로 변화함을 알 수 있었다. Fe^{4+} 이온의 증가에따라 일정온도에서의 전기전도도는 급격히 증가하며, 활성화에너지는 감소한다. x=0.00 시료의 Mössbauer spectrum은 six-line 형태를 보이며 팔면체 자리에 Fe^{3+} 이온이 존재함을 확인시켜 주었다.

1. Introduction

Perovskite-type compounds[1-3] are very impo- rtant because of their unique properties and appli- cations to such as electroceramic devices and electrochemical fields[4, 5]. The presence of oxygen vacancy and mixed valency of transition metal has great influence on their electric and magnetic properties[6-12].

The perovskite-related compounds $RFeO_{3-y}$ (R= rare earth) are often called orthoferrites[13, 14]. Their space group is P_{bnm}, showing distorted per- ovskite. The unit cell of orthoferrite has four equi- valent iron ions. The iron environment remains basically octahedral but the axes of the four octahedral sites are in different directions. At the common apex of two adjacent octahdedra is the intervening anion that provides the superexchange

bond between two iron ions. So each iron ion is coupled by superexchange to six nearest neighbors, resulting in high Néel temperatures(T_N). In general, orthoferrites have T_N larger than 600K, and by the Mössbauer and magnetic studies, $SmFeO_3$ has been known to have T_N of around 674K.

In perovskite–type compounds containing iron such as $R_{1-x}Sr_xFeO_{3-y}$(R = rare earth like La, Dy etc) and $SrFeO_{3-y}$, iron ions are often in the state of mixed valencies of Fe^{3+} and Fe^{4+}, accompanied by oxygen nonstoichiometry. Among the oxides containing iron in the unusal valence state Fe^{4+}, the (La, Sr) FeO_{3-y} system is perhaps the most interesting for a study of the effects of oxygen vacancy and mixed valency.

Especially in the last few years, many works on electrochemical measurements of perovskite materials have been performed to develop new materials [4, 5]. Wattiaux et al. maintained that oxygen defects seem to play an important role with regard to electrocatalytic activity. Before the electrochemical study of the $Sm_{1-x}Sr_xFeO_{3-y}$ system which seems to have good electrochemical property is performed, the investigations of the physical and chemical properties of this system are essential. So, the solid solutions of the $Sm_{1-x}Sr_xFe^{3+}_{1-t}Fe^{4+}_tO_{3-y}$ system(x = 0.00, 0.25, 0.50, 0.75, and 1.00) were synthesized and the cell parameters and crystal symmetry were determined by powder X–ray diffraction. The mixed valency of iron were characterized by chemical analysis and Mössbauer spectroscopy. Nonstoichiometry of each sample was ensured from the chemical formula $Sm_{1-x}Sr_xFe^{3+}_{1-t}Fe^{4+}_tO_{3-y}$ (where, $y = (x-t)/2$). The electrical conductivity measurement of this system was carried out in the temperature range of 173–373 K to study correlation between electrical properties and mixed valency.

2. Experimental

Samples of the composition x = 0.00, 0.25, 0.50, 0.75, and 1.00 were prepared from stoichiometric mixtures of Sm_2O_3, $SrCO_3$, and Fe_2O_3. Each mixture was ground and fired at 1473 K in an alumina crucible for 24 hours and then air quenched. The prepared sample was weighed and studied by X–ray diffraction. This process was repeated several times in the same condition to facilitate homogeneous solid solution. Each powder sample was pressed into a pellet under the pressure of 2 ton/cm² and then sintered under the same conditions as depicted above The pellet was used for the study of electrical conductivity. X–ray diffraction studies were carried out using monochromatized CuKα radiation (diffractometer: PHILIPS(PW1710), recorder: PHILIPS(PW8203A), wavelength: 1.5418 * 10⁻¹ nm). The X–ray patterns were indexed on the basis of the orthoferrites or typical cubic perovskites. Applying the Cohen's method[15], we could reasonably confirm Miller indice of each line and finally determine the crystal system, lattice parameter, and reduced lattice volume of unit cell. In the solution of third order simultaneous equation, we used the program based on the Gauss–Seidel method[16, 17]. The oxygen content was determined by chemical analysis using Mohr salt and 0.1 N $K_2Cr_2O_7$ solution. Monitoring the oxidation of Fe^{2+} to Fe^{3+} in a standard solution by iron of a higher oxidation from the sample, we were able to evaluate the Fe^{4+} content and ultimately chemical formula. Electrical conductivities of sintered bodies were measured by four probe method in the temperature range of 173–373K in air. Voltage and current were measured independently with the inner two probes connected to the potentiometer(Keithley Ins., 642 digital multimeter) and the outer two probes to the electrometer(Keithley Ins., 616 digital electrometer). To maintain thermal equilibrium, the temperature was raised at the rate of 1 K/min. The electrical conductivities were calculated by Laplume's equation [18]. The Mössbauer spectrum of the sample x = 0.00 at room temperature was taken using the spectrometer equiped with a 308 channel pulse–height analyzer. The source was cobalt–57 dispersed in Rh with 14.4 KeV γ–radiation. An absorber was

Table 1. Indexations of X–ray Diffraction Spectrum of the Sample x=0.00 (d:nm)

d_{obs}	h	k	l	d_{cal}	I/I_0
0.1566	2	0	4	0.1568	24
0.1588	0	2	4	0.1586	9
0.1604	1	3	2	0.1601	7
0.1718	1	3	1	0.1717	13
0.1885	0	2	3	0.1891	13
0.1926	0	0	4	0.1926	14
0.1941	2	2	0	0.1941	19
0.2264	0	2	2	0.2262	8
0.2630	0	2	1	0.2627	9
0.2698	2	0	0	0.2697	29
0.2736	1	1	2	0.2734	100
0.2798	0	2	0	0.2794	21
0.3463	1	1	1	0.3466	15
0.3880	1	1	0	0.3881	23

made from the highly ground sample (x=0.00) to have a diameter of 25.4mm and a thickness of about 0.5mm.

3. Results and Discussion

The X–ray data refined by Cohen's least square method are shown in Table 1 for x=0.00 system, where d_{obs} means observed d value and d_{cal} calculated d value. Each line in the X–ray diffractogram was indexed on the basis of the orthoferrite for the samples x=0.00−0.25 and the typical cubic perovskite materials for x=0.50−1. 00. Confirming tha the d_{obs} values and the d_{cal} values were in good agreement, we determined crystal system and lattice parameter.

The X–ray data analysis showed that the samples with compositional range x=0.00−0.25 were monophasic perovskite–like compounds with orthorhombic symmetry(Table 2). The orthoferrites discussed above contains four equivalent iron ions(four distorted pseudo–cell[11]). Accordingly, the volumes of the unit cell of the two samples can be reduced to 5. 805×10^{-2} nm^3(x=0.00) and 5.815×10^{-2} nm^3 (x= 0.25). When Sr content is over x=0.50, appears the cubic perovskite structure(Table 2). The lattice parameter a of the sample x=1.00 is in agreement with that of the (Dy, Sr) FeO_{3-y} system(a=3.865× 10^{-1}nm) [2]. As previously shown, the brownmillerite system $SrFeO_{2.5}$ [19] can be prepared with changing the heat treatment conditions (for example, in vacuum). The crystallographic structure of $SrFeO_{2.5}$ is related to that of $CaFeO_{2.5}$ (orthorhombic, space group p_{nma}) and considered to be the RMO_3 perovskite–type where oxygen vacancies are ordered along alternate rows $[101]_c=[100]_B$ [1, 3]. In this study, however, the heat treatment was carried out in air and the chemical analysis shows that the oxygen deficiency (y value) of the sample x=1.00 is not so large as that of $SrFeO_{2.5}$ system (Table 3). In the X–ray study performed by MacChesney et al. for $SrFeO_{3-y}$ system[20], they concluded that the system $SrFeO_{2.72}$ was tetragonal with the values a=0.3853nm, c=0.3882nm, but the sample x=1.00 in this study showed simple cubic pattern. So, the sample x=1.00 can be considered to be quasi–cubic system.

Table 2. Lattice parameters, Reduced Lattice Volume, and Crystal System Obtained from the Least Square Method

x value	0.00	0.25	0.50	0.75	1.00
lattice parameter (nm)	a=0.5394 b=0.5588 c=0.7705	a=0.5405 b=0.5582 c=0.7710	a=0.3871	a=0.3865	a=0.3861
volume (nm^3)	$(5.805\times10^{-2})^*$ 2.322×10^{-1}	$(5.815\times10^{-2})^*$ 2.326×10^{-1}	5.801×10^{-2}	5.774×10^{-2}	5.756×10^{-2}
crystal symmetry	orthorhombic	orthorhombic	cubic	cubic	cubic

* reduced volume

Table 3. Results of the Chemical Analysis Using Mohr Salt

| composition(x)	0.00	0.25	0.50	0.75	1.00
amount of Fe^{3+}	1.0	8.4×10^{-1}	7.5×10^{-1}	6.8×10^{-1}	5.5×10^{-1}
amount of Fe^{4+}	0.0	1.6×10^{-1}	2.5×10^{-1}	3.2×10^{-1}	4.5×10^{-1}
oxygen content (3-y value)	3.00	2.96	2.88	2.78	2.73

Fig. 1 shows the volume change with the increase in x value. On the contrary to the tendency that was seen in (Dy, Sr) FeO_{3-y}, the volume decreases steadily except x=0.25, So, among the three main factors that affect the unit cell volume discussed by Yo et al.[2], the factors(a) the formation of oxygen vacancy and (b) the increase of the relative amount of Fe^{4+} ions (the mixed–valence state of iron) can be regarded as dominating in this system. When x=0.25, Mohr salt analysis [2, 4] shows relatively small oxygen deficiency and maybe the factor (c) the substitution of larger Sr^{2+} at Sm^{3+} sites exerts a considerable influence.

Those phases prepared can be considered as oxidized ferrites and formulated $Sm_{1-x}Sr_xFe^{3+}_{1-t}Fe^{4+}_tO_{3-y}$. The value of the nonstoichiometry ratio y has been calculated from the chemical determination of the amount of tetravalent iron t (y=x−t/2) using the redox reaction: $Fe^{4+}+Fe^{2+} \rightarrow 2Fe^{3+}$. While $SmFeO_3$ (x=0.00) is stochiometric compound, the rest of the samples show nonsoichiometry of oxygen. As has been seen in many researches, the substitution effect of aliovalent cation in stochiometric compounds can be compensated for by two different factors; (1) change in the oxidation state of Fe and (2) formation of oxygen vacancies. The amount of oxygen vacancy is sensitive to the condition of heat treatment and can be controlled by such conditions as oxygen pressure, heating temperature, and cooling condition [7–9]. In case of x=1.00, brownmllerite type[10] $SrFeO_{2.5}$ can be synthesized by reduction in a stream of $Ar+H_2$ or under vacuum. On the other hand, ideal perovskite $SrFeO_3$ also may be produced in high oxygen pressure. Our samples were heat–treated in air at 1473 K, and the two factors disscussed above were observed simultaneously. The t value (the amount of oxygen deficiency) increases linearly with x value(Fig. 2). Putting all the studies on the effects of the substitution of aliovalent cations together, we can conclude that, whatever the heat treatment may be, the oxygen vacancy concentration will continuously increase with x value.

Conductivity measurements have been studied on pellets at the temperature range of 173K–373K by the four probe method using platinum probe and dc current. The dependence of the logarithm of the conductivity with the inverse of temperature is plotted in Fig. 3. The observed behabior of the sample x=0.00 characterizes semiconductivity with a rather high activation energy of 5.1×10^{-1} eV

Fig. 1. Plot of reduced lattice volume vs. x value.
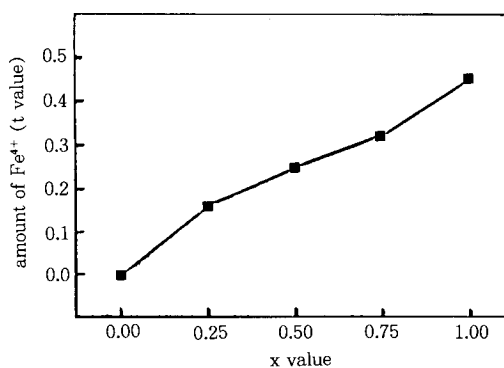
Fig. 2. Plot of t value vs. composition(x).
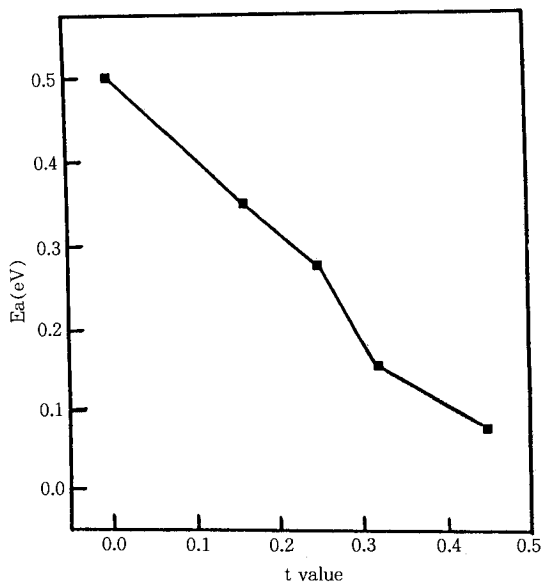
Fig. 3. Plots of log conductivity vs. 1000/T.
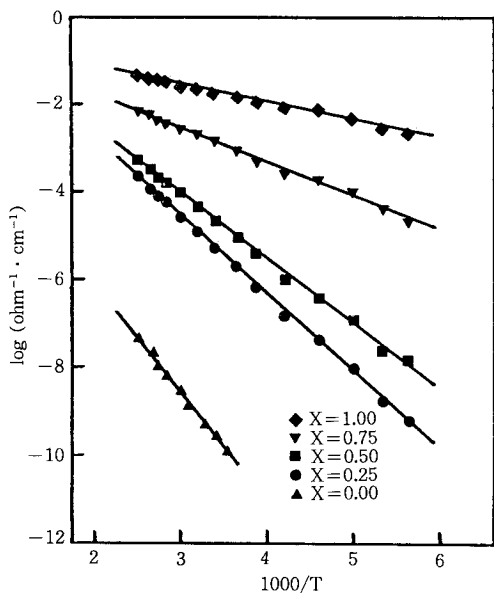
Fig. 4. Plot of activation energy(Ea) vs. t value.

(1.18×10Kcal/mole) for x = 0.00. With the increase in x value, however, the activation energy decreases (Fig. 4) [5]. Emphasis has to be placed upon the tendency that the conductivities of the samples increase with increase in t value. As has been discussed by several researchers, such a phenome-
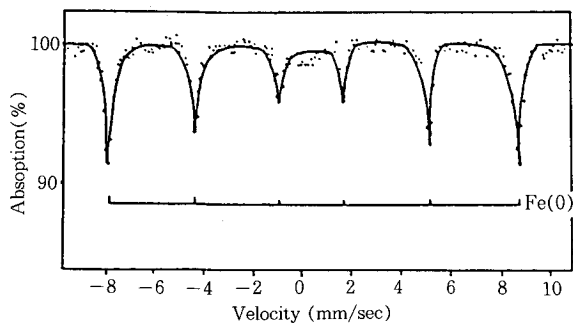
Fig. 5. Mössbauer spectrum of the sample x=0.00 at 293 K.

Table 4. Activation Energies(E_a) from the Electrical Conductivity Measurements

x value	0.00	0.25	0.50	0.75	1.00
t value	0.0	1.6×10^{-1}	2.5×10^{-1}	3.2×10^{-1}	4.5×10^{-1}
E_a, Kcal/mol (eV)	1.18×10 (5.1×10^{-1})	8.07 (3.5×10^{-1})	6.69 (2.9×10^{-1})	3.46 (1.5×10^{-1})	1.84 (8.0×10^{-2})

Table 5. Mössbauer Data of the Sample x=0.00 at 293K

x value	I. S. (mm/sec)	H_{int} (KOe)	E_Q (mm/sec)	C. N.
0.00	3.7×10^{-1}	5.21×10^2	-7.0×10^{-2}	6

non can be explained by electron hopping mechanism between the mixed valence iron ions. And, as has been proposed by Wattiaux et al. [5], the samples with good electrical conductivity may meet one of the required conditions for utilizing such materials as oxygen electrodes.

The Mössbauer spectrum of the sample x=0.00 at 293K is given in Fig. 5. The Mohr salt analysis mentioned previously(Table 3) showed that the sample x=0.00 is stoichiometric compound($SmFeO_3$), and there was no sign of the existance of Fe^{4+} ions. The result of Mohr salt analysis could be reaffirmed by Mössbauer spectroscopy, i.e. the spectrum shows characteristic 6–line pattern of antiferromagnatic orthoferrites which have only Fe^{3+} ions. And the isomer shift value is 3.7×10^{-1}mm/sec which is comparable to $LaFeO_3$(I.S.=3.9×10^{-1}mm/sec). The

internal magnetic field(H_{int}) is 5.21×10^2 KOe. And the Mössbauer parameters agree well with the previously reported values for octahedrally surrounded Fe^{3+} in orthoferrites[6]. The Mössbauer parameters are given in Table 5. In the $La_{1-x}Sr_xFeO_3$ system(0.00≤x≤1.00) studied by U. Shimony et al. [11], $LaFeO_3$ has been found to have G–type spin ordered antiferromagnetic structure and each Fe atom has its spin antiparallel to those of its six nearest Fe neighbors. And the most important point is that the T_N of $LaFeO_3$ (750K) decreases as more Sr is introduced. When x is over 0.4, all the samples showed paramagnetic property at room temperature. So we expect that, with increase in x value, six–line pattern would change into single line and paramagnetism rather than antiferromagnetism would be predominant magnetic property.

4. Conclusions

1. The homogeneous samples of the perovskite $Sm_{1-x}Sr_xFe^{3+}{}_{1-t}Fe^{4+}{}_tO_{3-y}$ ferrite system for the compositions of x=0.00, 0.25, 0.50, 0.75, and 1.00 were obtained.

2. The samples x = 0.00 (a = 0.5394 nm, b = 0.5588nm, c = 0.7705nm) and x=0.25 (A=0.5405 nm, b=0.5582nm, c=0.7710nm) have orthorhombic symmetry, and the rest of the samples, x=0.50 (a =0.3871nm), x=0.75 (a=0.3865nm), x=1.00 (a= 0.3861nm) show cubic symmetry. The crystallographic volume of this system decrease steadily except x=0.25.

3. With increase in x value, the amount of Fe^{4+} ion (t value) increases from 0 to 4.5×10^{-1} and oxygen deficiency (y value) increases from 0 to 2.7×10^{-1}.

4. The electrical conductivity of the samples at a constant temperature shaply increases and activation energy decreases with increase in x value.

5. The Mössbauer parameters of the sample x=0.00 at 293K is I. S.=3.7 x 10^{-1}mm/sec, E_Q= -7.0×10^{-2}mm/sec, and H_{int}=5.21×10^2 KOe which are comparable to the reported values of the ortho-

ferrites. And there was no sign of the existance of Fe^{4+} ions in the sample x=0.00.

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