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Dependences on Heating Conditions and Applicabilities as an Additive for ECIA of $Sr_{1-x}Ba_xFe^{3+}{}_{1-\tau}Fe^{4+}{}_{\tau}O_{3-y}$ Ferrite System

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The solid solutions of the $Sr_{1-x}Ba_xFeO_{3-y}$ system (x = 0.0, 0.1, 0.2 and 0.3) having a perovskite structure were prepared in air at 1423 K and then heat-treated in air (A), O_2(O) and N_2(N) to examine possibility of controlling the nonstoichiometry and applicability as an additive for electrical conducting inorganic adhesives (ECIA). In the samples heated in N_2 stream, there existed almost no Fe^{4+} ions, and at constant temperature their electrical conductivities were considerably lower than those of the samples heat-treated in air or O_2. $Sr_{0.8}Ba_{0.2}Fe^{3+}{}_{0.49}Fe^{4+}{}_{0.51}O_{2.76}$ (SB2-A) whose Fe^{3+}/Fe^{4+} ratio was nearly 1 (0.96) and whose conductivity values (1.04 $ohm^{-1}cm^{-1}$ at 283 K and 1.88 $ohm^{-1}cm^{-1}$ at 673 K) were higher than any other samples, was found to be the best additive for ECIA.

Key Words : Solid solution, Heat-treated, Electrical conducting inorganic adhesives, Electrical conductivity, Nonstoichiometry

Introduction

Perovskite-related oxides have been well known to have peculiar characteristics, so it has been proposed that they can be used as sensors or electrodes for electrocatalysts[1-6] and photochemistry.[7] It has been observed that their properties (especially amounts of oxygen content) depend on the preparation conditions such as heating in air, oxygen or vacuum, maximum heating temperature, and cooling rate. This means that their properties such as electrical conductivities, oxygen amounts and valencies of transition metals could be controlled[8-11] by the thermal process. In general, perovskite-related materials show peculiar characteristics of mixed valency of transition metals and eventually relatively high conductivity.

In recent studies on various perovskite-related materials including K_2NiF_4-type compounds,[12] electrical conducting inorganic adhesives (ECIA) for high temperature containing either K_2NiF_4-type oxides like $Sr_{1.0}La_{1.0}Fe_{1.0}O_{4-y}$ system or perovskites like $(SrCa)_{1.0}Fe_{1.0}O_{3-y}$[13] have shown fine characteristics, as additives giving water-resistance and durability in alkaline bath. Among the samples of $Sr_{1.0-x}Ba_x La_{1.0}Fe^{3+}{}_{1-\tau}Fe^{4+}{}_{\tau}O_{4-y}$ system (x = 0.0, 0.1, 0.2 and 0.3) prepared in O_2 stream, $Sr_{0.9}Ba_{0.1}La_{1.00}$ $Fe^{3+}{}_{0.55}Fe^{4+}{}_{0.45}O_{4.225}$ and $Sr_{0.8}Ba_{0.2}La_{1.00}Fe^{3+}{}_{0.54}Fe^{4+}{}_{0.46}O_{4.230}$ had considerably high conductivity values ($ohm^{-1}cm^{-1}$) of -2.4 (at 283 K) ~ -0.7(at 573 K) and -2.8 (at 283 K) ~ -1.1 (at 573 K). Adding them into inorganic adhesive (AB-11, made from the reaction of the mixtures of SiC, ZnO_2 and NaOH) with several composition, various ECIAs for high temperature were prepared and, among them, ECIA-3[12] containing $Sr_{0.8}Ba_{0.2}La_{1.00}Fe^{3+}{}_{0.54}$ $Fe^{4+}{}_{0.46}O_{4.230}$ (70 wt%) exhibited the highest conductivity values of -3.24 $ohm^{-1}cm^{-1}$ at 290K and -1.99 $ohm^{-1}cm^{-1}$ at 773 K. In that study, however, the adhesive properties of ECIA-2 (containing $Sr_{0.9}Ba_{0.1}La_{1.00}Fe^{3+}{}_{0.55}Fe^{4+}{}_{0.45}O_{4.225}$(70 wt%)) and ECIA-3 (containing $Sr_{0.8}Ba_{0.2}La_{1.00}Fe^{3+}{}_{0.54}$ $Fe^{4+}{}_{0.46}O_{4.230}$ (70 wt%)) were not satisfactory because of their lower conductivity values than those of metals like Cu and Fe, and of their sensitiveness to curing conditions.

Considering such previous works, this study was aimed at performing synthesis and heat-treatments of the $Sr_{1-x}Ba_xFeO_{3-y}$ system (x = 0.0, 0.1, 0.2 and 0.3) under various conditions (in air, in O_2 (1 atm) and in N_2 (1 atm)), at checking whether it is possible to control the nonstoichiometry of the $Sr_{1-x}Ba_xFeO_{3-y}$ system and eventually at investigating their applicability as additives for ECIAs for electrolytic oxygen evolution electrode[3,4] and solid oxide fuel cell.[5] The changes of oxygen contents with temperature, of mixed valency ratios of Fe^{3+} and Fe^{4+} and of conductivities were measured. Finally mixing each sample (20 wt%) with BG-11 inorganic adhesive,[14] ECIAs were prepared and their properties were examined.

Experimental Section

Four different samples of the $Sr_{1-x}Ba_xFeO_{3-y}$ perovskite system with the compositions x = 0.0(SB0-A), x = 0.1(SB1-A), x = 0.2(SB2-A) and x = 0.3(SB3-A) were synthesized from analytical reagents, $BaCO_3$ (99.999%), $SrCO_3$ (99.99 %), and Fe_2O_3 (99.99%) using standard ceramic techniques in air. Before weighing, the starting materials were dried at 673 K for 2 hours to exclude water content. To synthesize homogeneous solid solutions, all the materials were mixed and ground into fine powders for 3 hours using automatic mortar equipment (03-083-03, Samhwa). After mixing and grinding, to examine dependences on heating conditions, all the powder samples and their pellets of A series were heated at 1473 K in air(A), O_2(O) and N_2(N) for 12 hours and then cooled with reactor. Weighing, grinding, and heating process were repeated several times under the same conditions to

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Table 1. Nonstoichiometric Chemical Formulas, y values from Chemical Analysis after Heat Treatments and Activation Energies from Electrical Conductivity Measurements

Heat treatment	Sample	[a]Nonstoichiometric chemical formula	y value (standard deviation)	[b]E_a
air	SB0-A	$Sr_{1.0}Fe^{3+}_{0.40}Fe^{4+}_{0.60}O_{2.80}$	$0.20\ (1.11 \times 10^{-3})$	0.165
	SB1-A	$Sr_{0.9}Ba_{0.1}Fe^{3+}_{0.45}Fe^{4+}_{0.55}O_{2.78}$	$0.22\ (1.04 \times 10^{-3})$	0.107
	SB2-A	$Sr_{0.8}Ba_{0.2}Fe^{3+}_{0.49}Fe^{4+}_{0.51}O_{2.76}$	$0.24\ (1.08 \times 10^{-3})$	0.085
	SB3-A	$Sr_{0.7}Ba_{0.3}Fe^{3+}_{0.55}Fe^{4+}_{0.45}O_{2.73}$	$0.27\ (1.05 \times 10^{-3})$	0.132
O_2	SB0-O	$Sr_{1.0}Fe^{3+}_{0.18}Fe^{4+}_{0.82}O_{2.91}$	$0.09\ (1.18 \times 10^{-3})$	0.237
	SB1-O	$Sr_{0.9}Ba_{0.1}Fe^{3+}_{0.19}Fe^{4+}_{0.81}O_{2.91}$	$0.09\ (1.19 \times 10^{-3})$	0.191
	SB2-O	$Sr_{0.8}Ba_{0.2}Fe^{3+}_{0.43}Fe^{4+}_{0.57}O_{2.79}$	$0.21\ (1.26 \times 10^{-3})$	0.209
	SB3-O	$Sr_{0.7}Ba_{0.3}Fe^{3+}_{0.53}Fe^{4+}_{0.47}O_{2.74}$	$0.26\ (1.10 \times 10^{-3})$	0.170
N_2	SB0-N	$Sr_{1.0}Fe^{3+}_{0.92}Fe^{4+}_{0.08}O_{2.54}$	$0.46\ (1.19 \times 10^{-3})$	0.383
	SB1-N	$Sr_{0.9}Ba_{0.1}Fe^{3+}_{0.93}Fe^{4+}_{0.07}O_{2.54}$	$0.46\ (1.19 \times 10^{-3})$	0.388
	SB2-N	$Sr_{0.8}Ba_{0.2}Fe^{3+}_{0.94}Fe^{4+}_{0.06}O_{2.53}$	$0.47\ (1.29 \times 10^{-3})$	0.393
	SB3-N	$Sr_{0.7}Ba_{0.3}Fe^{3+}_{0.99}Fe^{4+}_{0.01}O_{2.51}$	$0.49\ (1.17 \times 10^{-3})$	0.514

[a]complete chemical formula : $Sr_{1-}BaFe^{3+}_{1-\tau}Fe^{4+}_{\tau}O_{3-y}$ (where, $y = (1-\tau)/2$). [b]E_a : activation energies from conductivity data in the temperature range of 283~673 K (Least Square Method).

obtain homogeneous solid solutions. After pressing each powder sample into pellets under a pressure of 400 kg/cm^2 for 5 minutes, the powder samples and pellets (about 0.9 g) with respective compositions were heated at 1423 K in air(A), O_2(O) and N_2(N) for 12 hours and the sintered pellets were slowly cooled with the reactor to room temperature.

As discussed before, the purpose of this study is to check whether it is possible to control the nonstoichiometries of the $Sr_{1-x}Ba_xFeO_{3-y}$ system under various heat-treatment conditions such as in air, in O_2 (1 atm) and in N_2 (1 atm). After the heat treatments, the nonstoichiometric chemical formulas of the powder samples (Table 1) were examined using Mohr salt redox titration method.[15,16]

Using 0.1 N-$K_2Cr_2O_7$ solution, the residual amount of Fe^{2+} ion from the Mohr salt ($(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$) which was left after the reaction with Fe^{4+} ion to produce Fe^{3+} ion was back-titrated. The indicator was $C_{24}H_{20}O_6N_2S_2Ba$ and at the end point the color of the solution changed from weak yellow to dark violet. The mole ratio of Fe^{4+} ion to Fe^{3+} ion (τ value) could be calculated using the following formula

$$\tau = \frac{N\Delta VM}{m - 8N\Delta V}$$

(where, N: normality of $K_2Cr_2O_7$ solution, V: volume difference between the blank test and sample test, M: formula weight of each sample, m: sample weight). Because the heat-treated samples could lose their characteristics when exposed to atmospheric pressure, the titrations for each composition were performed with great care and rapidity. After put out from the reactors, each powder sample was weighed and dropped into solutions for the chemical analysis containing such reagents as Mohr salt ($(NH_4)_2$-$Fe(SO_4)_2\cdot 6H_2O$) and acids (H_2SO_4, HCl).

Considering the ideas of some studies[7,13] on perovskite materials, thermal analysis (TG/DTA experiments) was executed for each sample in air to examine the behavior in heating and cooling process. TG/DTA instrument was model TG/DTA 220(Seiko Instruments Inc.) and reference material was platinum wire (15.520 mg). In this TG/DTA study temperature was raised at 40 K/min in the range of 293~1073 K. After two containers of reference material and sample were put onto their sites, small furnace encompassed them and the measured weights with temperature were saved in main terminal.

Applying four-probe method,[17] conductivity measurements of each pellet sample were carried out using 236 SMU instrument (Keithley Co.). Maintaining the current constant, changes of voltage were measured at the interval of 50 K in the temperature range 283~1173 K under atmospheric air pressure. For the conductivity measurement at high temperature, a special apparatus manufactured with quartz

Table 2. Amounts of Additives, Verifications of Adhesive Powers and Electrical Conductivities of the Specimens

Sample	Additives and its amount (weight %)	*Adhesive Power Test	Electrical Conductivity	
			Temperature (K)	log σ ($ohm^{-1}\cdot cm^{-1}$)
ECIA-SB0-A	SB0-A (20)	D	297	-1.341
			673	0.450
ECIA-SB0-O	SB0-O (20)	A	297	-3.133
			673	-0.815
ECIA-SB1-A	SB1-A (20)	A	297	-0.911
			673	0.153
ECIA-SB1-O	SB1-O (20)	A	297	-0.954
			673	0.121
ECIA-SB2-A	SB2-A (20)	A	297	0.543
			673	1.432
ECIA-SB2-O	SB2-O (20)	A	297	-1.720
			673	0.311
ECIA-SB3-A	SB3-A (20)	A	297	-0.905
			673	0.389
ECIA-SB3-A	SB3-O (20)	A	297	-0.711
			673	0.992

*Adhesive Power Test: KS standard method of M3734 using weights (2 Kg) (D: detached/A: attached) and platinum wire was used. Four sharp platinum wires were contacted on the shallow holes on pellet surface, and to prevent the contacts from getting loose, spring made of platinum wire was also used. Conductivity data were processed applying the Valde's method.[18]

Considering the overall properties of each sample, ECIAs were manufactured by mixing the previous samples with the inorganic adhesive solution of BG-11.[14] Appropriate amount of additives were determined to be 20 weight percent by trial and error method. Excluding all the N samples and mixing each sample with the inorganic adhesive of BG-11 (Table 2), eight ECIAs were prepared. Two kinds of specimens of each ECIA were prepared. First, two glasses (35 mm × 16 mm × 3 mm) were attached using the ECIAs to examine the adhesive powers of each sample applying KS standard method of M3734 for tensile strength test with increasing weights (0.5 kg) up to 2 kg. Second, each ECIA was painted on glasses with the area of about 150 mm^2 (~10 mm × 15 mm) to measure conductivity applying the standard 4-probe DC method after heat-treatments. After curing at 473 K for 2 hours and dipping into water and alkaline solution (1.0 N-NaOH) for 24 hours, respectively, all the specimens were verified to be stable.

Results and Discussion

In air the powder samples, SB0-A : $Sr_{1.0}Fe^{3+}{}_{0.40}Fe^{4+}{}_{0.60}O_{2.80}$, SB1-A : $Sr_{0.9}Ba_{0.1}Fe^{3+}{}_{0.45}Fe^{4+}{}_{0.55}O_{2.78}$, SB2-A : $Sr_{0.8}Ba_{0.2}Fe^{3+}{}_{0.49}Fe^{4+}{}_{0.51}O_{2.76}$ and SB3-A : $Sr_{0.7}Ba_{0.3}Fe^{3+}{}_{0.55}Fe^{4+}{}_{0.45}O_{2.73}$ were synthesized by direct solid state reaction of the starting materials in air at 1473 K for 12 hours and then by cooling slowly with reactor. As has been done in some studies[19,20] for perovskite-type compounds, the X-ray powder patterns (Figure 1) of the solid solutions of A series were indexed[21] reasonably by referring to the JCPDS data (#28-1227) and the samples of A series were found to have cubic symmetries (SB0-A : a = 3.869 Å (standard deviation; s = 9.12×10^{-2}), SB1-A : a = 3.874 Å (s = 8.90×10^{-2}), SB2-A : a = 3.878 Å (s = 9.73×10^{-2}) and SB3-A : a = 3.897 Å (s = 9.16×10^{-2})). There have been several data for the perovskite $SrFeO_{3-y}$ systems such as $SrFeO_{2.86}$ (#39-954, tetragonal, a = 10.934 Å, c = 7.705 Å), $Sr_2Fe_2O_5$ (#28-1227, cubic, a = 3.86 Å) and $SrFeO_{2.5}$ (#17-932, orthorhombic, a = 5.671 Å, b = 15.59 Å, c = 5.528 Å). In this study, however, the X-ray diffractograms of A series samples were analyzed to have cubic patterns. Comparing the lattice parameters, it was confirmed that the partial replacement of Sr by Ba results in a volume expansion from 57.916 $Å^3$ (SB0-A) to 59.182 $Å^3$ (SB3-A).

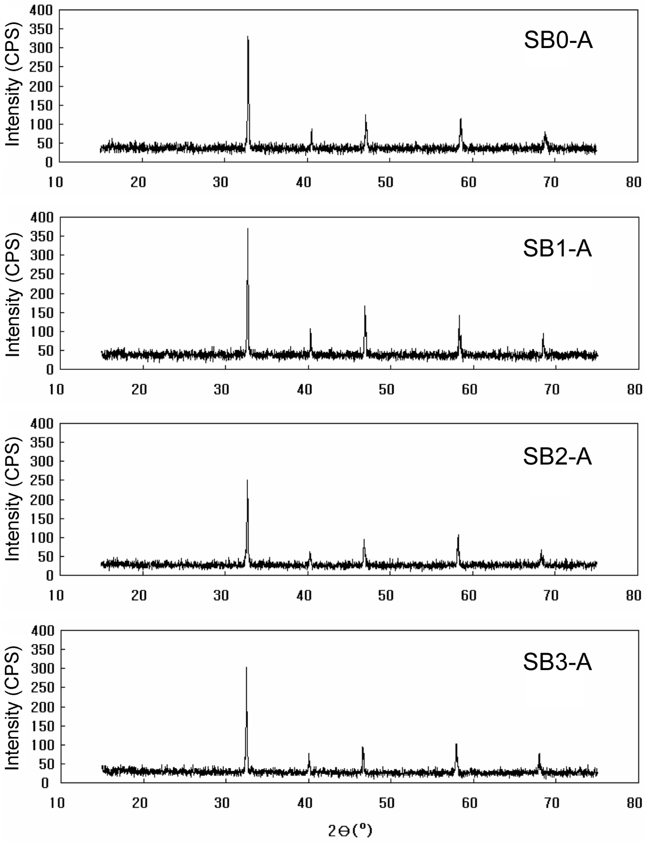

Figure 1. X-ray powder diffractograms of SB0-A, SB1-A, SB2-A and SB3-A samples of $Sr_{1-x}Ba_xFe^{3+}{}_{1-\tau}Fe^{4+}{}_{\tau}O_{3-y}$ system.

The chemical analysis procedures were performed very carefully to avoid probable changes of their characteristics when exposed to atmospheric pressure. The nonstoichiometric formulas of each sample, *i.e.* mole ratios of Fe^{3+} and Fe^{4+} ion and the amount of oxygen nonstoichiometry(y values) are presented in Table 1. As can be seen from Figure 2, partial substitution of Ba^{2+} for Sr^{2+} ions resulted in steady decrease of Fe^{4+} ions. Depending on heating conditions, there were distinctive differences in Fe^{4+} amounts and oxygen contents. While all the samples of the $Sr_{1.0-x}Ba_xLa_{1.0}Fe^{3+}{}_{1-\tau}Fe^{4+}{}_{\tau}O_{4-y}$ system[12] (x = 0.0, 0.1, 0.2 and 0.3) were sintered at 1473 K in O_2 stream (20 mL/sec) for 24 hours and cooled with reactor slowly at the rate of 50 K/hr in order to introduce as much Fe^{4+} ions as possible, heat treatments only in air made this $Sr_{1-x}Ba_xFe^{3+}{}_{1-\tau}Fe^{4+}{}_{\tau}O_{3-y}$ system have considerable amount of Fe^{4+} ions. The chemical formula of SB0-A sample was determined to be $SrFeO_{2.80}$; the oxygen content (3-y = 2.80) is nearly the same as the results of J. B. MacChesney[10] ($SrFeO_{2.84}$ which was synthesized in O_2

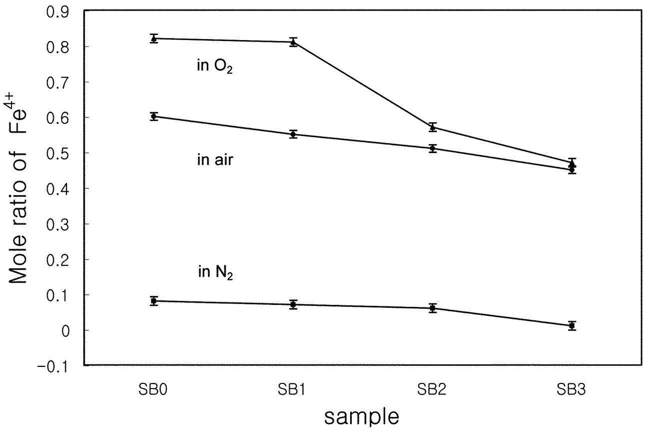

Figure 2. Changes of τ values (Fe^{4+} mole ratios) of the $Sr_{1-x}Ba_xFe^{3+}{}_{1-\tau}Fe^{4+}{}_{\tau}O_{3-y}$ samples.

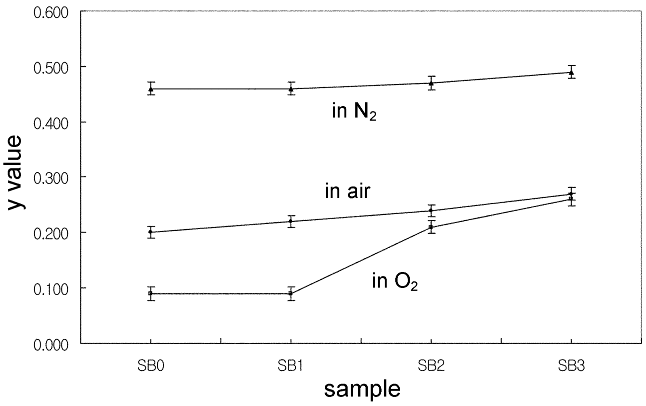

Figure 3. Variations of y values of the Sr$_{1-x}$Ba$_x$Fe$^{3+}_{1-\tau}$Fe$^{4+}_{\tau}$O$_{3-y}$ samples.

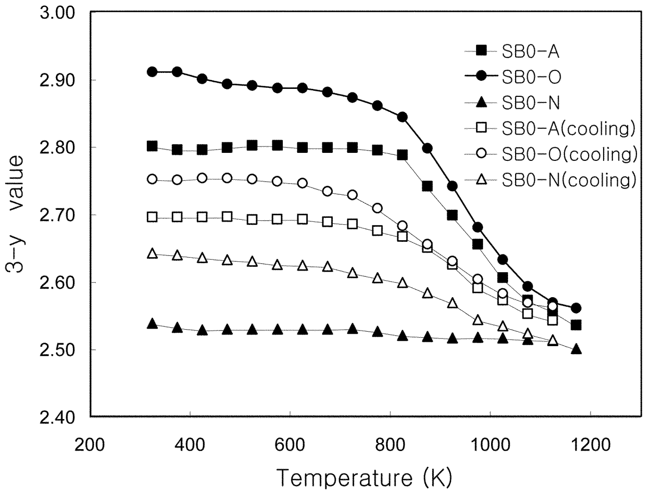

Figure 4. Thermogravimetric analysis of the SB0-A, SB0-O and SB0-N samples with heating (293 K~1073 K) and cooling (1073 K~293 K).

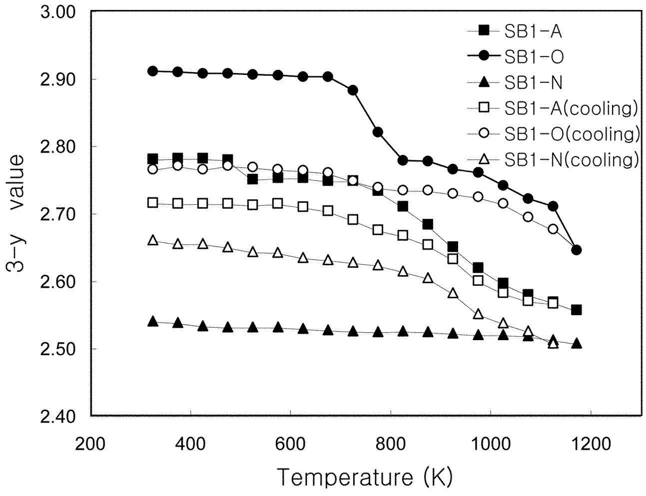

Figure 5. Thermogravimetric analysis of the SB1-A, SB1-O and SB1-N samples with heating (293 K~1073 K) and cooling (1073 K~293 K).

(pressure = 0.2 atm)).

After the heat treatment at 1073 K in N$_2$ stream for 48 hours, the amount of Fe^{4+} ions decreased almost to 0, and all the samples of A series lost their oxygen (Figure 3), *i.e.*, all the y values approached 0.5, which corresponds to Brownmillerite type.[20] In this system the increase of O$_2$ content which was observed in the study of L. Fournes *et al.*[22] at around 773 K was not happened maybe because the rate of raising temperature was so fast. On the contrary, heat treatment at 1073 K in O$_2$ stream for 48 hours didn't show a consistency. While considerable decreases (Table 1, Figure 3) in oxygen deficiency for SB0-O (y = 0.20 to 0.09) and SB1-O (y = 0.22 to 0.09) were observed, SB2-O and SB3-O didn't show such changes in mole ratios of Fe^{4+} (Figure 2) and changes in y values (Figure 3). Comparing the oxygen content values of the O samples and those of the samples of J. B. MacChesney,[10] the cooling conditions are noticeable. That is, however high the oxygen pressure is (PO$_2$ = 1.0 atm), quenching might result in lower oxygen content (3-y = 2.72 or 2.78).

Thermogravimetric (TG) analysis of each powder samples was carried out with increasing temperature from 323 K to 1173 K and with decreasing temperature to 323 K in air. The y axes in the Figure 4~7 stand for 3-y values, not weights. Because the starting weights of each sample were not the same, simple comparison of the raw data is meaningless. Assuming that the cause of the weight changes observed in this study might be the going-in and going-out of oxygen, weight changes were converted into 3-y values. In the weight change data conversion, the 3-y values were calculated using the next equation.

$$3\text{–}y = [FW \times \left(1 + \frac{\Delta m}{m \times 1000}\right) - W] \times \frac{1}{16}$$

where FW : formula weight of each sample determined by Mohr salt analysis, Δm: weight change (μg), m : initial weight (mg), and W : formula weight of each sample excluding O$_{3-y}$ part.

TG analysis was carried out in air for all the samples regardless of their preparation process (Figure 4~7). In heating process from 323 K to 1173 K, all the A and O samples showed steady decrease of weight. In cooling process, the rate of cooling was slower than 40 K/min and reversible weight change was not observed in each sample. That is, for SB0-A sample (Figure 4), 3-y value was 2.80 in 323 K and 2.54 at maximum temperature of 1173 K and after cooling process completed it went to 2.70. The other A samples showed similar tendencies to the SB0-A. It was known by J. Homo *et al.*[7] that to give rise to almost reversible weight changes the heated samples must be cooled slowly (3 K/min). As depicted in the Figure 4-7, all the N samples which were heat-treated in N$_2$ stream, showed almost no changes of weight in heating process. In cooling process, however 3-y values of N samples increased to 2.6~2.7 range. In the study of Sr$_{1.0-x}$Ba$_x$La$_{1.0}$Fe$^{3+}_{1-\tau}$Fe$^{4+}_{\tau}$O$_{4-y}$ system[12] which was performed in the same conditions as their preparation processes, such an increase of weight in cooling process was not observed.

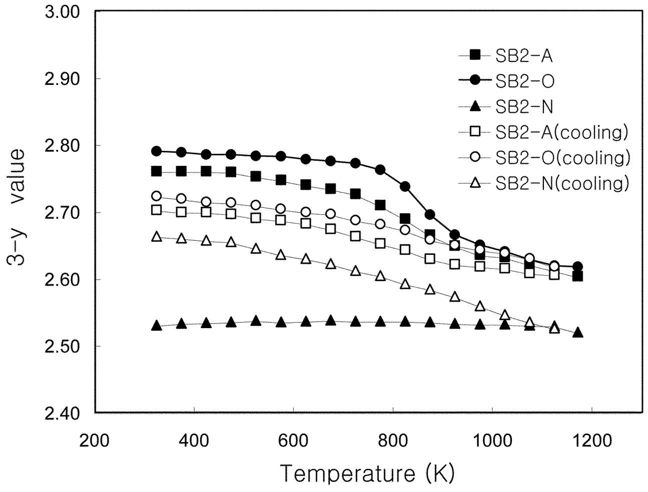

Figure 6. Thermogravimetric analysis of the SB2-A, SB2-O and SB2-N samples with heating (293 K~1073 K) and cooling (1073 K~293 K).

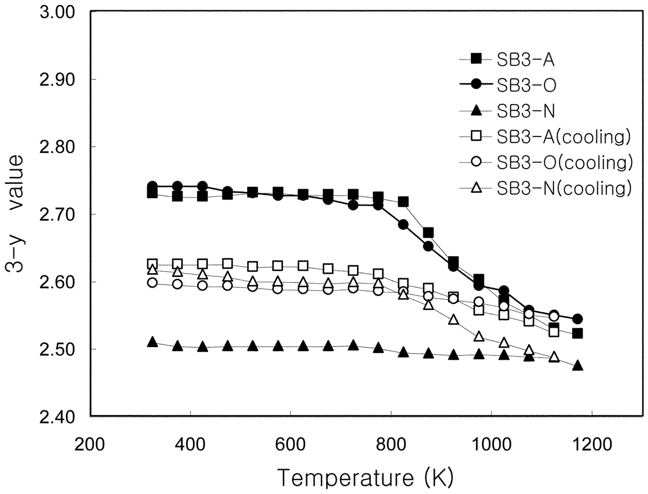

Figure 7. Thermogravimetric analysis of the SB3-A, SB3-O and SB3-N samples with heating (293 K~1073 K) and cooling (1073 K~293 K).

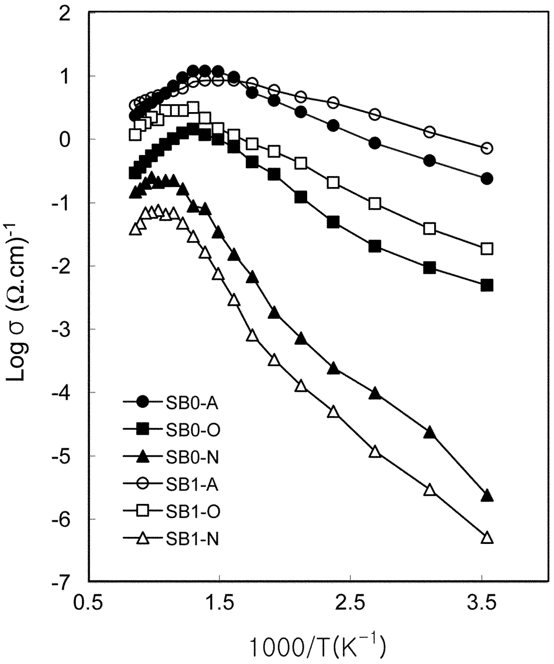

Figure 8. Temperature dependence of Log conductivity for SB0 and SB1 samples measured in 283~1173 K.

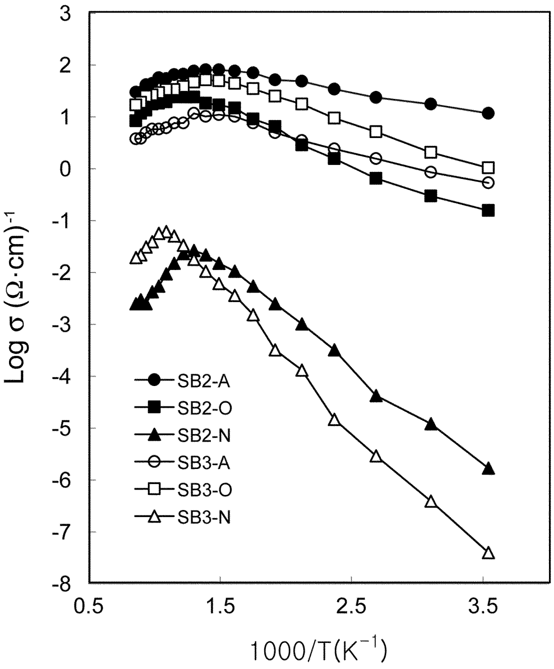

Figure 9. Temperature dependence of Log conductivity for SB2 and SB3 samples measured in 283~1173 K.

There are the electrical conductivity data (σ) as a function of temperature in the temperature range 283~1173 K under atmospheric air pressure in Figure 8 and Figure 9. Plots of log versus 1000/T of all the samples exhibited typical semiconducting behaviors; below their peaks conductivities of each sample increased with temperature and above those peaks their electrical properties changed into metallic. These kinds of phenomena have been believed to be resulted from the formation[7] of oxygen vacancy, because the peak temperatures are considerably in relation to the formation temperatures of the oxygen vacancy observed from TG analysis. Simple comparison of conductivity values of each A sample shows that at 283 K, conductivity value of the SB2-A is 1.04 $ohm^{-1}cm^{-1}$ which is larger than any other values of the other A samples (SB0-A : -0.64 $ohm^{-1}cm^{-1}$, SB1-A : -0.16 ohm^{-1} cm^{-1} and SB3-A : -0.30 $ohm^{-1}cm^{-1}$). Such a tendency can be explained by the chemical analysis data, *i.e.* Fe^{3+}/Fe^{4+} ratio of SB2-A is 0.96 which is the largest value of all the A samples. As has been clarified in some researches,[3,4] the mixed valency of iron plays an important role in perovskite oxides. Several researchers reported that the perovskite samples with Fe^{3+}/Fe^{4+} ratio $\fallingdotseq$ 1 usually has larger conductivity values than any other samples. On the other hand, the N samples in this study have little Fe^{4+} ion and the possibility of electrons hopping from Fe^{3+} to Fe^{4+} in the lattice can hardly be expected.[23] So every N sample of this system showed lower values than those of other A or O samples at constant temperature. For example, while the conductivity value of the sample SB0-N at 373 K is -4.02 $ohm^{-1}cm^{-1}$, those of SB0-A and SB0-O are -0.08 $ohm^{-1}cm^{-1}$ and -1.71 $ohm^{-1}cm^{-1}$ respectively. The activation energies (E_a) of each sample obtained by least-square data refinement[24,25] in the temperature range of 283~673 K are shown in Table 1 in eV unit. The activation energies of A and O samples are much smaller than those of the N samples.

All the specimens except ECIA-SB0-A were found to have strengths(tensile strength, KS standard method of M3734) enough to bear pressure of 8.71 Pa (2 kg of weights). Usually above that pressure, one of the two glasses of every specimen was broken. As expected, conductivities of the specimens were dependent on the conductivities and activation energies of their additives. ECIA-SB2-A had the highest conductivities of all the samples, *i.e.*, -0.543 ohm^{-1} cm^{-1} at 297 K and -1.432 $ohm^{-1}cm^{-1}$ at 673 K, which had been already expected from conductivity data of its additives, SB2-A. Each ECIA was found to have smaller conductivity values than those of its additives by 0.5~0.8 $ohm^{-1}cm^{-1}$. The electrical conductivity values of each ECIA at 297 K and 673 K are shown in Table 2 and all the conductivity values showed good linealities between the two temperature ranges. Conclusively speaking, the physicochemical properties of all the specimens such as electrical conductivities and their linealities, water-resistance and stability in alkaline solution were greatly improved compared with the ECIAs of the previous study.[12]

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