



Change in Properties of $(\text{Ba}_{1-x}\text{La}_x)\text{Fe}^{3+}_{1-t}\text{Fe}^{4+}_t\text{O}_{3-y}$ System Depending on Heat Treatment Conditions

Eun-Seok Lee[†]

Department of Chemistry, Cheongju University, Cheongju 28503, Korea

Seo-Jin Lee

Department of Materials Science and Engineering, Chungnam National University, Daejeon 34134, Korea

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The perovskite system $(\text{Ba}^{2+}_{1-x}\text{La}^{3+}_x)\text{Fe}^{3+}_{1-t}\text{Fe}^{4+}_t\text{O}_{3-y}$ ($y = (1 - x - t)/2$) having a composition of $x = 0.0, 0.1, 0.2,$ and 0.3 showed an increase in Fe^{4+} mole ratios with an increase in oxygen partial pressure ($\text{N}_2 \rightarrow \text{air} \rightarrow \text{O}_2$), and with an increase in s , the Fe^{3+} quantity decreased and oxygen content ($3-y$ value) increased. For each N samples heat-treated in N_2 gas, a considerable weight gain, i.e.g a steady increase in oxygen content, was observed in the TGA data on the cooling process. The conductivity values at a constant temperature were in the order of $\text{N}_2 < \text{air} < \text{O}_2$; the respective $\log \sigma$ values ($\Omega^{-1} \cdot \text{cm}^{-1}$) at 323 K of the BL0 sample were -5.75 (BL0-N), -3.39 (BL0-A), and -0.53 (BL0-O). The mixed valencies of Fe^{3+} and Fe^{4+} ions in each sample were also confirmed by both the oxidation curve above 350 mV and the cathodic reduction curve below 200 mV from cyclic voltammetry.

Keywords : Perovskite, TGA, Oxygen content, Electrical conductivity, Mixed valency

1. INTRODUCTION

Oxide materials with perovskite-type structures [1-7] are of significant importance for a variety of electrical and catalytic applications because they form solid solutions with many cations. This permits variation of their chemical and physical properties, some of which include electronic and mixed oxygen ionic conductivity. For ABO_3 -type oxides with $A = \text{Ln}$ (lanthanides), Ca, Sr, and Ba and $B = \text{Fe}, \text{Ti}, \text{Cr}, \text{Mn},$ and Co , there have been numerous studies [8-11] regarding the relationships between their compositions and physical or chemical properties.

As has been verified in several studies, the introduction of aliovalent metals (M) in perovskite materials including $(\text{Sr}, \text{M})\text{FeO}_{3-y}$ ($M = \text{Ba}, \text{La}$) [8] and K_2NiF_4 -type materials like SrMFeO_{4-y} ($M = \text{Dy}$)

[9] cause not only the formation of considerable quantities of Fe^{4+} (instead of Fe^{3+}) but also changes in the oxygen content [10,11] of the materials. The physical and chemical properties of these materials may change with the metal quantity (M), preparation conditions, and heat-treatment conditions. Also, many studies regarding the application of these materials as electrodes [12-15] for electrolytes in solid oxide fuel cells [16-18], additives for electrical conducting inorganic adhesives (ECIA) [4], partial oxidation of hydrocarbons, and oxygen separation membranes [19] have been carried out.

In searching for electrode materials, perovskites of the $(\text{Ba}^{2+}_{1-x}\text{M}^{3+}_x)\text{FeO}_{3-y}$ system ($M = \text{Nd}, \text{La}$) were found to be good candidates for oxygen evolution [1]. In particular, the $(\text{Ba}^{2+}_{1-x}\text{La}^{3+}_x)\text{FeO}_{3-y}$ system has improved stability in an alkaline bath and finer characteristics for electrochemical applications. Therefore, in this study, samples of the $(\text{Ba}^{2+}_{1-x}\text{La}^{3+}_x)\text{Fe}^{3+}_{1-t}\text{Fe}^{4+}_t\text{O}_{3-y}$ ($y = (1 - x - t)/2$) system with $x = 0.0, 0.1, 0.2,$ and 0.3 were synthesized in air and heat-treated in various atmospheres [2,3] to develop electrodes for oxygen evolution in the electrolysis of water. For each sample, a chemical analysis to determine the mixed valencies of iron, a TG/DTA thermal analysis, electrical conductivity measurements, and cyclic voltammetry were performed.

[†] Author to whom all correspondence should be addressed:
E-mail: leees@cju.ac.kr

2. EXPERIMENTS

The $(\text{Ba}^{2+}_{1-x}\text{La}^{3+}_x)\text{Fe}^{3+}_{1-t}\text{Fe}^{4+}_t\text{O}_{3-y}$ ($y = (1 - x - t)/2$) ferrites with compositions of $x = 0.0, 0.1, 0.2,$ and 0.3 have been prepared from stoichiometric mixtures of La_2O_3 (99.99%), BaCO_3 (99.99%), and Fe_2O_3 (99.9%). To obtain homogeneous solid solutions, all of the mixtures were ground into a fine powder for 6 h using automatic mortar equipment (03-083-03, Samhwa, Seoul, Korea). The resulting mixtures reacted at 1473 K in air for 12 h and then cooled slowly with a reactor.

After the synthesis process, each sample was analyzed by X-ray diffraction (diffractometer: PW1710, Almelo, Netherlands, monochromatized $K\alpha$ radiation of a Cu target, $15\text{--}70^\circ$) to ensure the homogeneous phase of the solid solution and to determine the related parameters such as the crystal symmetry, cell parameters, and cell volume. The observed d values were compared with theoretical d values calculated by the least-square method; the Miller indices of each line were reasonably confirmed, and then the crystal systems, lattice parameters, and lattice volumes of the four samples were determined.

The chemical compositions were determined by the Mohr salt method [4,9] after annealing at 1273 K in N_2 (BL#-N series), air (BL#-A series), and O_2 (BL#-O series) for 20 h. To avoid probable errors from the existence of O_2 gas, N_2 gas flowed into the solution surface during the entire course of titration. For each composition, this experiment was carried out with great care and rapidity because the heat-treated samples may lose their characteristics when exposed to atmospheric pressure. Thus, the heated powder samples were directly weighed and dropped into solutions for chemical analysis that contain reagents such as Mohr salt ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) and acids (H_2SO_4 , HCl). Similar to the study [3], the end points were confirmed by two independent methods: Mohr salt analysis and zero-current potentiometry.

Referring to studies [4,8] on perovskites, TG/DTA experiments (TG/DTA 220, Seiko Instruments Inc., Japan, reference material: Pt wire (15.520 mg)) were executed in air. In this TG/DTA study, the temperature was raised at 40 K/min in the range of 293–1,073 K. The weight change data was converted [8,10] into the oxygen nonstoichiometric expression of $3-y$ values.

Pellets for electrical conductivity and electrochemical measurements were prepared by compressing the powdered oxides under 0.8 ton/ cm^2 , followed by sintering under the same conditions as those of the powder preparation process. All the powder samples (approximately 0.8 g) and pellets were finally annealed at 1,273 K in N_2 (BL#-N series), air (BL#-A series), and O_2 (BL#-O series) for 20 h and then cooled slowly (cooling rate = 20 K/h) to achieve equilibrium for each gas at low temperatures. Independent measurements of the currents with a constant voltage were performed using a model 236 SMU (KEITHLEY Co. Cleveland, Ohio, U.S.A.) at an interval of 50 K. The instrument used for the four-probe measurements was made of quartz and platinum for special usages such as high temperature conductivity measurements [4,7,12,14,16] in various oxygen pressures.

The electrochemical measurements (20°C in air) [5] were carried out under the following conditions: WPG 100 model (Potentiostat/Galvanostat, Won-A-Tech, Seoul, Korea), Init E: 0.0 V, High E: 0.6 V, Low E: -0.2V, Scan Rate: 10 mV/s, Init Direction: positive, Sweep Segment: 4, Current Range: auto, Sampling Interval: 0 mV, Quiet Time: 0 s. After being polished with alumina (particle size $\leq 0.5 \mu\text{m}$) and cleaned with distilled water, a pellet ($\phi = 10 \text{ mm}$ and thickness = 1.8 mm) of BL1-A was used as a working electrode. A platinum plate (15 mm \times 17 mm \times 1 mm) was used as an auxiliary electrode, and the reference electrode was a Ag/AgCl electrode ($E^\circ = +0.196 \text{ V/NHE}$), which was placed near the working electrode in the 0.1N-KOH solution.

3. RESULTS AND DISCUSSION

Solid solutions of the $(\text{Ba}^{2+}_{1-x}\text{La}^{3+}_x)\text{Fe}^{3+}_{1-t}\text{Fe}^{4+}_t\text{O}_{3-y}$ ($y = (1 - x - t)/2$) system for the compositions of $x = 0.0$ (BL0), 0.1 (BL1), 0.2 (BL2), and 0.3 (BL3) were successfully synthesized by the heating of the reactant mixtures at 1,473 K under atmospheric air pressure. By the examination of weight changes [10], it was possible to judge whether the target materials of each composition were synthesized. In this study, for example, BL1-N refers to the sample with a composition of $x = 0.1$ heat-treated in a N_2 stream at 1,273 K.

The solid solutions in which a Ba^{2+} ion is replaced by La^{3+} at $x = 0.0\text{--}0.3$ were found to be crystallographically homogeneous (Fig. 1). Similar to some studies [2,3,8] on perovskite-type compounds, after reasonable indexation by referring to the BaFeO_{3-y} system (JCPDS data, 14-0180, $a = 4.012 \text{ \AA}$), each sample was confirmed to have typical perovskite structures (cubic symmetries). The crystal symmetries, lattice parameters, and unit cell volumes for each composition are listed in Table 1.

As shown in Table 1, the lattice constants decreased steadily (BL0: 4.033 \AA , BL1: 4.009 \AA , BL2: 3.985 \AA , and BL3: 3.959 \AA) with an increase in the La content. When considering the explanations given by Yo et al. [11], three factors may affect the unit cell volumes: (1) the substitution of smaller La^{3+} ions ($r = 150 \text{ pm}$) for larger Ba^{2+} ions ($r =$

Table 1. X-ray powder diffraction data of the $(\text{Ba}_{1-x}\text{La}_x)\text{Fe}^{3+}_{1-t}\text{Fe}^{4+}_t\text{O}_{3-y}$ system.

Sample	Crystal symmetry	a (\AA)	Volume (\AA^3)	Standard deviation
BL0 ($x=0.0$)	Cubic	4.033	65.60	1.02×10^{-3}
BL1 ($x=0.1$)	Cubic	4.009	64.43	9.35×10^{-2}
BL2 ($x=0.2$)	Cubic	3.985	63.28	9.82×10^{-2}
BL3 ($x=0.3$)	Cubic	3.959	62.05	1.08×10^{-3}

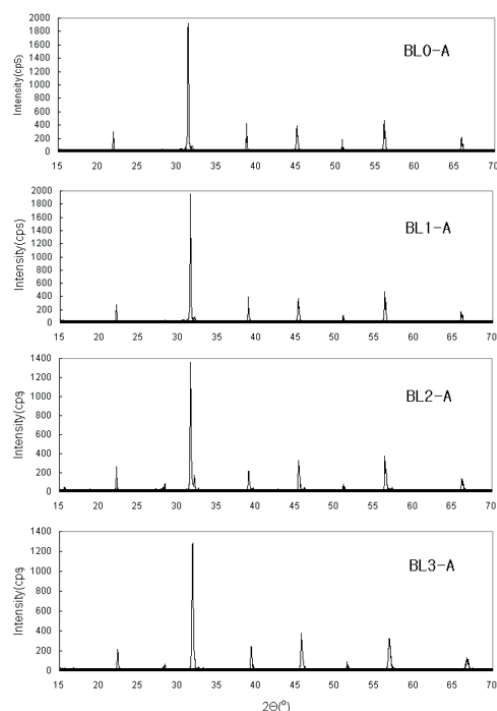


Fig. 1. X-ray diffractograms of $(\text{Ba}_{1-x}\text{La}_x)\text{Fe}^{3+}_{1-t}\text{Fe}^{4+}_t\text{O}_{3-y}$ powder samples prepared at 1,473 K in air.

175 pm), (2) the formation of oxygen vacancies (3-y values), and (3) the formation of mixed valence states of Fe³⁺ and Fe⁴⁺. In this system, with an increase in x, the unit cell volume decreased, and the (1) and (3) factors may be responsible for volume contraction.

To determine the nonstoichiometric compositions, redox titrations on Fe⁴⁺ content were performed using the Mohr salt method (Table 2).

As has been verified in several systems [4,5,9,11], it was presumed that the materials have not only oxygen vacancies but also mixed valencies of Fe including Fe³⁺ and Fe⁴⁺ due to the cation charge deficiency. For each composition, with an increase in the partial oxygen pressure (N→A→O), an increase in the Fe⁴⁺ mole ratios was observed (Fig. 2) [3].

Nonstoichiometric formulas of the samples prepared in air can be expressed as follows: BL0-A: (Ba_{1.0}La_{0.0})Fe³⁺_{0.77}Fe⁴⁺_{0.23}O_{2.62}, BL1-A: (Ba_{0.9}La_{0.1})Fe³⁺_{0.69}Fe⁴⁺_{0.31}O_{2.71}, BL2-A: (Ba_{0.8}La_{0.2})Fe³⁺_{0.60}Fe⁴⁺_{0.40}O_{2.80}, and BL3-A: (Ba_{0.7}La_{0.3})Fe³⁺_{0.51}Fe⁴⁺_{0.49}O_{2.90}.

Generally, in a perovskite system, a partial substitution of higher valence ions (La³⁺) for lower valence ions (Ba²⁺) would (1) increase the mole ratios of Fe³⁺ and (2) increase the amount of oxygen. However, in this (Ba²⁺_{1-x}La³⁺_x)Fe³⁺_{1-t}Fe⁴⁺_tO_{3-y} (y = (1 - x - t)/2) system, with the increase of x values, the amounts of Fe³⁺ decreased and oxygen content increased.

$$[La_{Ba}^{3+}] = -p [Fe_{Fe}^{3+}] + ((1 + p)/2) [O_{O}^{2-}] \quad (1)$$

where, La_{Ba}³⁺, Fe_{Fe}³⁺, and O_O²⁻ represent La³⁺ ions at Ba²⁺ sites, Fe³⁺ at Fe ion sites, and oxygen at oxygen sites, respectively. Accordingly, the 3-y values of this system are in a wide range of 0.28 (2.62-2.90), and a similar tendency was observed in the (Ba²⁺_{1-x}Nd³⁺_x)Fe³⁺_{1-t}Fe⁴⁺_tO_{3-y} (y = (1 - x - t)/2) system [3]. This tendency is peculiar when we

Table 2. Nonstoichiometric data from mohr salt analysis of the (Ba_{1-x}La_x)Fe³⁺_{1-t}Fe⁴⁺_tO_{3-y} system.

Sample	Condition	Fe ³⁺	Fe ⁴⁺	3-y
BL0	BL0-N : in N ₂ , S.C.	0.95	0.05	2.53
	BL0-A : in air, S.C.	0.77	0.23	2.62
	BL0-O : in O ₂ , S.C.	0.62	0.38	2.69
BL1	BL1-N : in N ₂ , S.C.	0.95	0.05	2.58
	BL1-A : in air, S.C.	0.69	0.31	2.71
	BL1-O : in O ₂ , S.C.	0.57	0.43	2.77
BL2	BL2-N : in N ₂ , S.C.	0.96	0.04	2.62
	BL2-A : in air, S.C.	0.60	0.40	2.80
	BL2-O : in O ₂ , S.C.	0.53	0.47	2.84
BL3	BL3-N : in N ₂ , S.C.	0.97	0.03	2.67
	BL3-A : in air, S.C.	0.51	0.49	2.90
	BL3-O : in O ₂ , S.C.	0.48	0.52	2.91

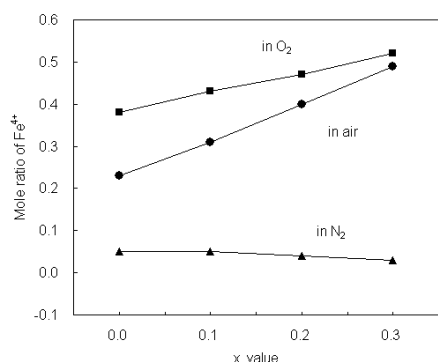


Fig. 2. Plot of t value change with composition (x) for the (Ba_{1-x}La_x)Fe³⁺_{1-t}Fe⁴⁺_tO_{3-y} system heat-treated in N₂, O₂, and air.

consider the properties of La_{1-x}Sr_xFeO_{3-y} [6] and the Sr_{1-x}Dy_{1-x}FeO_{4-y} [9] system, in which the substitution of ions with higher oxidation states caused a simultaneous increase in the amount of Fe³⁺ and oxygen content. All the samples heat-treated in N₂ had a small amount (Table 2 and Fig. 2) of Fe⁴⁺, i.e., a low oxygen partial pressure results mainly in a loss of oxygen. Conversely, when firing an O₂ stream, the Fe⁴⁺ quantities in all four samples were considerably larger, and the quantity of Fe⁴⁺ in BL3-O was larger (Fe⁴⁺:Fe³⁺ = 52:48) than that of Fe³⁺. The conversions of raw TG data into oxygen content values were carried out by the following equation,

$$3 - y = [FW \times (1 + \frac{\Delta m}{m \times 1000}) - W] \times \frac{1}{16} \quad (2)$$

where FW is the formula weight of each sample determined by the chemical analysis, Δm is the weight change in μg, m is the initial weight in mg, and W is the formula weight of each sample excluding O_{3-y}.

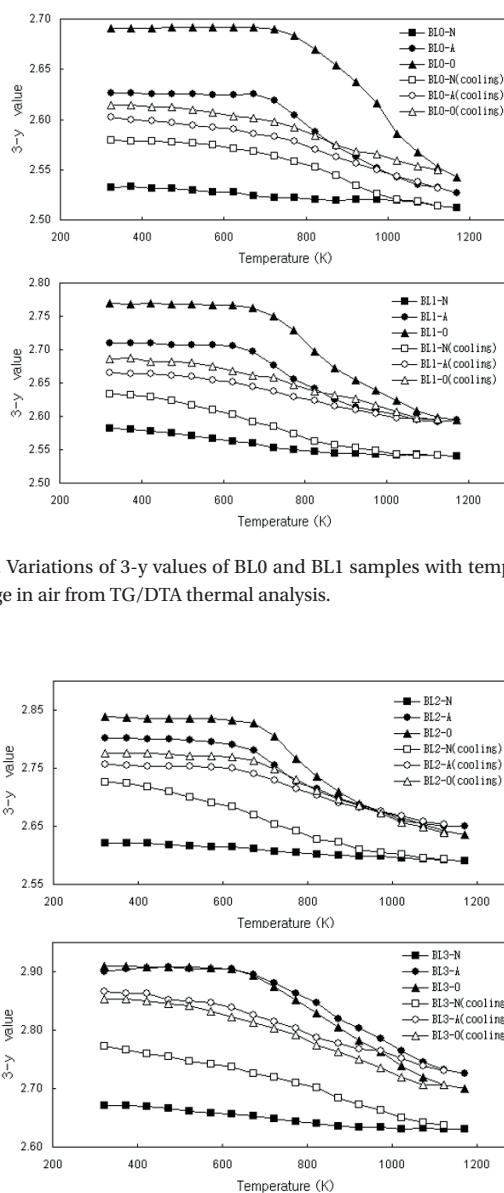


Fig. 3. Variations of 3-y values of BL0 and BL1 samples with temperature change in air from TG/DTA thermal analysis.

Fig. 4. Variations of 3-y values of BL2 and BL3 samples with temperature change in air from TG/DTA thermal analysis.

As has been observed in the TG/DTA study of various perovskite systems, all of the samples showed an abrupt decrease [3,8,14] in weight (loss of oxygen) at certain temperatures (Figs. 3 and 4).

The starting points of decreasing weight were in the range of 623–723 K, and unlike the Nd system [3], none of the samples showed a reversible weight gain.

It is very interesting that the four N samples heat-treated in N_2 showed a gradual and slight weight decrease in the heating process and a considerable weight gain (steady increase of oxygen) in the cooling process. Conclusively, from the TG/DTA study, we confirmed that by changing the annealing conditions including oxygen partial pressure and temperature, the mixed valency ratio and oxygen content could be controlled.

Figures 5 and 6 show that the relative conductivity values of each sample at a constant temperature are in the order of $N < A < O$.

As an example, for the BL0 sample, the respective $\log \sigma$ values ($\Omega^{-1} \cdot \text{cm}^{-1}$) at 323 K are as follows; BL0-N: -5.75, BL0-A: -3.39, and BL0-O: -0.53. A relative quantity of the Fe^{4+} ratio (Table 2) of the BL0 sample (BL0-N: 0.05 mole, BL0-A: 0.23 mole, and BL0-O: 0.38 mole) may explain these results. This tendency is explained by the fact that the sample with the Fe^{3+}/Fe^{4+} ratio ≈ 1 has the largest conductivity [8] value of all the samples.

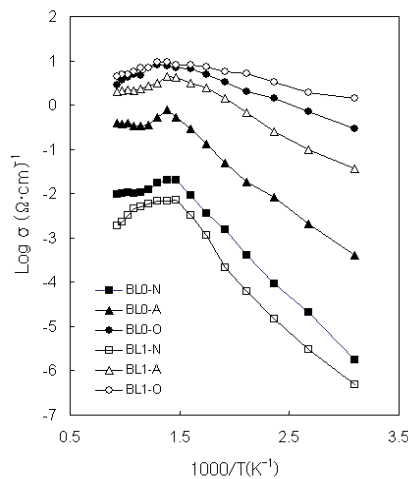


Fig. 5. Arrhenius plots of log conductivity of BL0 and BL1 measured in 283–1,173 K applying the four-point probe DC method.

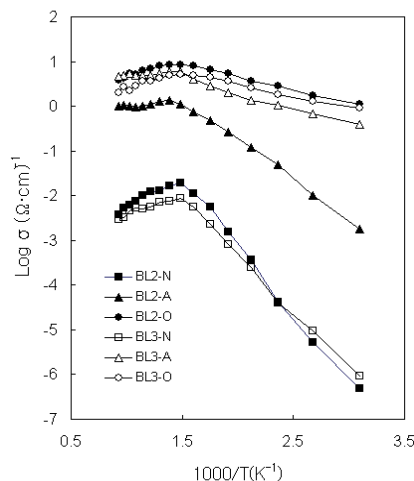


Fig. 6. Arrhenius plots of log conductivity of BL2 and BL3 measured in 283–1,173 K applying the four-point probe DC method.

In this study, we conclude that the control of the mixed valencies of transition metals (iron) may be carried out not only by variations in the amount of La but also by heat-treatment conditions. In other words, the conductivity values of the BL1 sample could be controlled by 6.4 orders ($0.15 \rightarrow -6.31$) of magnitude at 323 K only by the variation of heating conditions. The activation energies (Table 3) of all the samples consistently decreased with a variation in the Fe^{3+}/Fe^{4+} ratio; the activation energies of the N, A, and O samples are in the range of 0.49–0.59 eV, 0.14–0.38 eV, and 0.10–0.17 eV, respectively.

As has been observed in many perovskites, the conductivity characteristics of the A sample varied from semi-conductivity in the low temperature region to pseudometallic conduction in the high temperature region (Figs. 5 and 6). The break points are in the range of 672–723 K, and they seem to correlate with the starting points of the weight decrease (Figs. 3 and 4) (i.e., above a certain temperature, the energy is supplied to oxygen at lattice sites to move in bulk and even depart from the surface). Nowadays these properties are applied to devices such as electrodes for ceramic membranes [1] used in oxygen separation or fuel cell fields [16–19]. The O samples have the highest conductivities and lowest activation energies when compared to the N and A samples, and therefore, they appear to be good candidates for adhesive materials at high temperatures and oxygen evolving electrodes.

Figure 7 shows the voltammogram of BL0-O ($Ba_{1.0}La_{0.0}Fe^{3+}_{0.62}Fe^{4+}_{0.38}O_{2.69}$) from cyclic voltammetry ($-200 \text{ mV} \leq E \leq 600 \text{ mV}$).

The electrode potential data shown in Fig. 7 was referred to the Ag/AgCl electrode ($E^\circ = +0.196 \text{ V/NHE}$). During the cycle, both

Table 3. Activation energies from the electrical conductivity measurement of the $(Ba_{1-x}La_x)Fe^{3+}_{1-x}Fe^{4+}_xO_{3-y}$ system.

Sample	Measurement condition (temperature range (K))	Activation energy (eV) (temperature range (K))
BL0-N	in air (283–1173)	0.49 (283–673)
BL0-A		0.38 (283–673)
BL0-O		0.17 (283–673)
BL1-N	in air (283–1173)	0.52 (283–673)
BL1-A		0.27 (283–673)
BL1-O		0.10 (283–673)
BL2-N	in air (283–1173)	0.59 (283–673)
BL2-A		0.35 (283–673)
BL2-O		0.12 (283–673)
BL3-N	in air (283–1173)	0.50 (283–673)
BL3-A		0.14 (283–673)
BL3-O		0.10 (283–673)

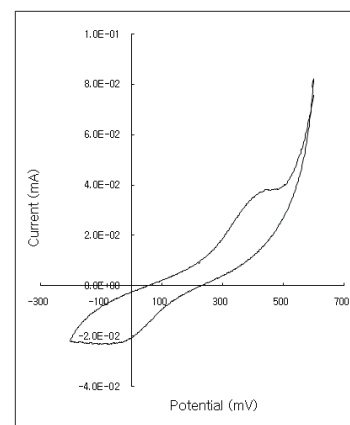


Fig. 7. Cyclic voltammogram of BL0-O ($Ba_{1.0}La_{0.0}Fe^{3+}_{0.62}Fe^{4+}_{0.38}O_{2.69}$) heat-treated in O_2 at 1,273 K (for 20 h and cooled slowly).

anodic oxidation (above 350 mV) and cathodic reduction (below 200 mV) confirm the mixed valency of iron (Fe^{3+} and Fe^{4+}) on the surface of BL0-O as previously observed for similar perovskites [5,12,13]. Thus, with an increase in voltage, the oxidation reaction proceeds in the E range of 350–500 mV (plateau).



When electrochemical oxidations are needed for this kind of perovskite, we generally choose the plateau as a starting point [12]. If reaction 3 continued on the surface, an increase in the amount of Fe^{4+} ions and a decrease in the concentration of anion vacancy would occur. This indicates that an appropriate electrochemical manipulation could change the surface composition as $\text{Ba}_{1.0}\text{La}_{0.0}\text{Fe}^{3+}_{0.00}\text{Fe}^{4+}_{1.00}\text{O}_{3.00}$. In the E range of ~600 mV, the following reaction [5] indicating oxygen evolution was also confirmed.



Conclusively, if the elimination of evolving oxygen on the surface is possible, it is possible to use perovskite materials as oxygen evolution electrode materials.

4. CONCLUSIONS

Solid solutions of the $(\text{Ba}^{2+}_{1-x}\text{La}^{3+}_x)\text{Fe}^{3+}_{1-t}\text{Fe}^{4+}_t\text{O}_{3-y}$ ($y = (1 - x - t)/2$) system for the compositions with $x = 0.0$ (BL0), 0.1 (BL1), 0.2 (BL2), and 0.3 (BL3) were confirmed to have typical perovskite structures (cubic symmetries), and their lattice constants decreased steadily: BL0: 4.03 Å, BL1: 4.009 Å, BL2: 3.985 Å, and BL3: 3.959 Å. The Mohr salt titration method gave the nonstoichiometric formulas of the samples prepared in air as follows: BL0-A: $(\text{Ba}_{1.0}\text{La}_{0.0})\text{Fe}^{3+}_{0.77}\text{Fe}^{4+}_{0.23}\text{O}_{2.62}$, BL1-A: $(\text{Ba}_{0.9}\text{La}_{0.1})\text{Fe}^{3+}_{0.69}\text{Fe}^{4+}_{0.31}\text{O}_{2.71}$, BL2-A: $(\text{Ba}_{0.8}\text{La}_{0.2})\text{Fe}^{3+}_{0.60}\text{Fe}^{4+}_{0.40}\text{O}_{2.80}$, and BL3-A: $(\text{Ba}_{0.7}\text{La}_{0.3})\text{Fe}^{3+}_{0.51}\text{Fe}^{4+}_{0.49}\text{O}_{2.90}$. The increase in x of the $(\text{Ba}^{2+}_{1-x}\text{La}^{3+}_x)\text{Fe}^{3+}_{1-t}\text{Fe}^{4+}_t\text{O}_{3-y}$ ($y = (1 - x - t)/2$) system caused the Fe^{3+} amount to decrease and oxygen content to increase. All the samples showed abrupt decreases in weight at certain temperatures, and the starting points of the weight decrease were in the range of 623–723 K. The relative conductivity values of each sample at constant temperature were in the order of $\text{N} < \text{A} < \text{O}$ (i.e., at 323 K, BL0-N: $-5.75 (\Omega^{-1} \cdot \text{cm}^{-1})$, BL0-A: $-3.39 (\Omega^{-1} \cdot \text{cm}^{-1})$, and BL0-O: $-0.53 (\Omega^{-1} \cdot \text{cm}^{-1})$). In the study of cyclic voltammetry ($-200 \text{ mV} \leq E \leq 600 \text{ mV}$) for BL0-O, both anodic oxidation (above 350 mV) and cathodic reduction (below 200 mV) confirm the mixed valency of iron (Fe^{3+} and Fe^{4+}) on the electrode surface.

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