JOURNAL OF SOLID STATE CHEMISTRY **84,** 138–143 (1990)

Electrical Conductivities of $SrFeO_{3-\delta}$ and $BaFeO_{3-\delta}$ Perovskites

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Received March 13, 1989; in revised form September 15, 1989

The conductivities and the Seebeck coefficients of the $SrFeO_{3-\delta}$ and the $BaFeO_{3-\delta}$ perovskites were measured in air, O_2, and N_2 in the temperature range from 650°C to room temperature. The carrier densities and the mobilities were calculated by using a small polaron hopping model. All the samples of the $BaFeO_{3-\delta}$ show the hopping conduction, while the conductions of the $SrFeO_{3-\delta}$ in air and O_2 will be near metallic because the carrier densities and the mobilities are very large. The mobilities rather than the carrier densities decreased with the increase of the amounts of the oxygen vacancy, δ, in the range of $0 < \delta < 0.5$. The mobilities of $SrFeO_{3-\delta}$ in which the Fe–O–Fe average distance is about 3.86 Å were about 10^3 times those of $BaFeO_{3-\delta}$ with the Fe–O–Fe distance of 4.01 Å. Thus, the mobilities remarkably decreased with the increase of the Fe–O–Fe distance. It was concluded that the electrical conductivities of the $SrFeO_{3-\delta}$ and the $BaFeO_{3-\delta}$ at room temperature are mainly determined by the mobility which is affected by the oxygen vacancy and the Fe–O–Fe distance.

Introduction

The iron perovskite oxides and the related oxides with high electrical conductivity have been mainly investigated as the sensor (*1, 2*) and the electrode materials such as the electrocatalysts and the photoelectrodes (*3–5*). These conductions are mainly determined by the interaction between the iron cation and the oxygen anion in the lattice (*6*), when the carrier density is relatively large. If the interaction is small, the carrier will move in the lattice by the hopping mechanism. Thus, the degree of the Fe–O–Fe interaction directly affects the carrier mobility, importantly controlling the conductivity. The degree of the Fe–O–Fe interaction will be directly influenced by the Fe–O–Fe distance and the presence of the oxygen vacancy in this chain. Therefore, we can expect some relationships between the mobility and both the Fe–O–Fe distance and the amounts of the oxygen vacancy in the perovskite and the related oxides.

In the case of $La_{1-x}Sr_xCoO_3$ perovskites which have high x values, Burren *et al.* (*7*) found that the expression for the Seebeck coefficient in a small polaron hopping model is very suitable for the calculation of the hole concentration. This success will indicate that the hopping model can be also used for other perovskite oxides with high conductivity such as $SrFeO_{3-\delta}$ and $BaFeO_{3-\delta}$ used in the present study. In this paper, we demonstrate the influences of the Fe–O–Fe distance and the oxygen vacancy on the mobility by using the above hopping model for $SrFeO_{3-\delta}$ and $BaFeO_{3-\delta}$ systems with high electrical conductivity.

0022-4596/90 $3.00

Experimental

Fe_2O_3, $BaCO_3$, and $SrCO_3$ were used as the starting materials. The stoichiometrical mixtures were heated at 1100°C ($BaFeO_{3-\delta}$) and 1300°C ($SrFeO_{3-\delta}$) for several hours in air. The samples were reground and then pressed into a tablet (1600 kg/cm^2), followed by sintering at 1100 and 1300°C for 7 hr in air. The crystal structures of the sintered samples were analyzed by an X-ray diffraction method. $SrFeO_{3-\delta}$ (80% sintering density) consisted of the single phase of the tetragonal perovskite, while $BaFeO_{3-\delta}$ (66% sintering density) consisted of the hexagonal perovskite phase with trace amounts of the triclinic perovskite. The thermogravimetric analysis (TG) was carried out in O_2, air, and N_2 in order to determine the oxygen vacancy in the oxides. The conductivities were measured by the four-probe method. The conductivities and the Seebeck coefficients of the samples were measured in O_2, air, and N_2 in the temperature range from 650°C to room temperature. The measurements were carried out under a slow cooling rate (about 1°C/min) after heating for 1 hr at 650°C.

Results and Discussion

All the samples were preheated for 1 hr at 650°C in O_2, N_2, and air before the measurements of TG, conductivity, and the Seebeck coefficient, as stated above. In the case of $BaFeO_{3-\delta}$, the single phases of the hexagonal perovskite and of the triclinic perovskite were obtained in O_2 and in N_2, respectively, by this heat treatment. These changes in the crystal structure have already been observed for both types of systems (*8*, *9*). The relationships between the amount of the oxygen vacancy and the lattice constant have also been obtained for both systems (*8*, *9*). Therefore, we initially determined δ from the lattice constants for the present samples at room temperature, which were pretreated at 650°C in air. Since the lattice constants were a = 3.855 Å and c = 3.870 Å (tetragonal form) for $SrFeO_{3-\delta}$, and a = 5.678 Å and c = 13.942 Å (hexagonal form) for $BaFeO_{3-\delta}$, δ values were determined to be 0.13 and 0.16 for $BaFeO_{3-\delta}$ and $SrFeO_{3-\delta}$, respectively. Figure 1 shows the typical TG trace of $SrFeO_{3-\delta}$ measured stepwise, where the cooling rate was 3°C/min. From this figure, it was found that the sample attains equilibrium with oxygen at each temperature higher than about 350°C, because its weight immediately reached a constant value after the temperature became constant. On the other hand, the composition in oxygen content was fixed in the temperature range lower than 300°C. Similar results were also observed in O_2, and for $BaFeO_{3-\delta}$. Therefore, the above situations for the present samples will be kept in all the measurements, since their measurements were done under the cooling rate of about 1°C/min. Figure 2 shows δ values which were calculated from the TG curves. It is clear that the oxygen vacancy is formed in the temperature range higher than about 300–350°C even in O_2.

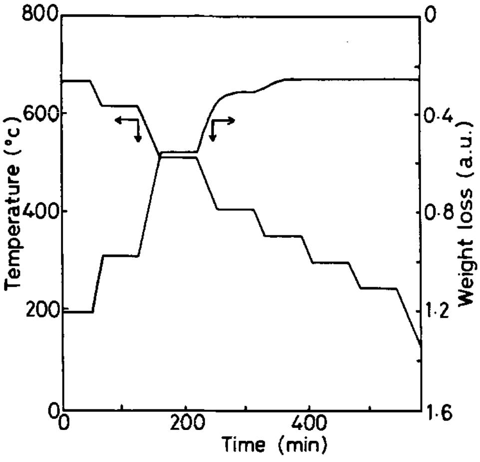

FIG. 1. TG trace of $SrFeO_{3-\delta}$ measured stepwise in air.

The conductivity, σ, as a function of T^{-1}, is shown in Fig. 3. The conductivities of

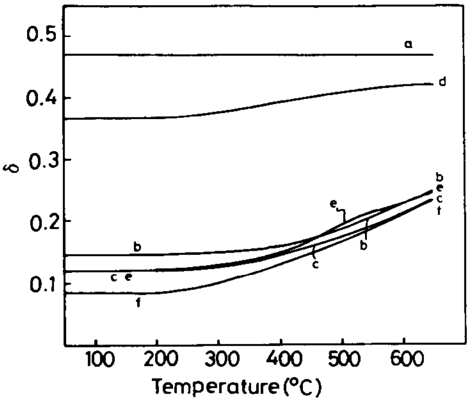

FIG. 2. δ in $SrFeO_{3-\delta}$ and $BaFeO_{3-\delta}$ as a function of temperature: (a) $SrFeO_{3-\delta}$ in N_2, (b) $SrFeO_{3-\delta}$ in air, (c) $SrFeO_{3-\delta}$ in O_2, (d) $BaFeO_{3-\delta}$ in N_2, (e) $BaFeO_{3-\delta}$ in air, (f) $BaFeO_{3-\delta}$ in O_2.

TABLE I

APPARENT ACTIVATION ENERGIES OF THE CONDUCTIVITY AND THE MOBILITY

Sample	Activation energy of conductivity (eV)	Activation energy of mobility (eV)[a]
$SrFeO_{3-\delta}$ in N_2	0.37 (~250°C)	0.35 (~250°C)
	0.65 (250–450°C)	0.69 (250–650°C)
$SrFeO_{3-\delta}$ in air	0.07 (~250°C)	0.07 (~250°C)
$SrFeO_{3-\delta}$ in O_2	0.03 (~350°C)	0.02 (~550°C)
$BaFeO_{3-\delta}$ in N_2	0.37 (~350°C)	0.38 (~350°C)
$BaFeO_{3-\delta}$ in air	0.30 (~350°C)	0.30 (~350°C)
$BaFeO_{3-\delta}$ in O_2	0.26 (~300°C)	0.26 (~300°C)

[a] Hole mobility except for $BaFeO_{3-\delta}$ in O_2.

$SrFeO_{3-\delta}$ were always higher than those of $BaFeO_{3-\delta}$, when the samples were measured in O_2 and air. The conductivities were saturated or decreased above the temperature of about 300–350°C for all the samples, except for the $SrFeO_{3-\delta}$ in N_2 as shown in Fig. 3. These phenomena are based on the formation of the oxygen vacancy, because the above temperature is in accord with the formation temperature of the oxygen vacancy as already stated. The apparent activation energies calculated in Fig. 3 are listed in Table I. The activation energies of $SrFeO_{3-\delta}$ in O_2 and in air were much smaller than those of the other samples, suggesting nearly metallic conduction.

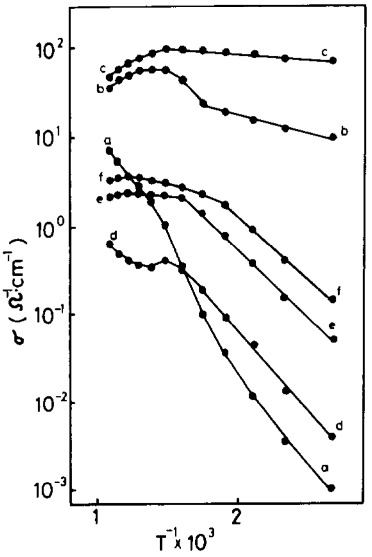

FIG. 3. Conductivity as a function of T^{-1}: (a) $SrFeO_{3-\delta}$ in N_2, (b) $SrFeO_{3-\delta}$ in air, (c) $SrFeO_{3-\delta}$ in O_2, (d) $BaFeO_{3-\delta}$ in N_2, (e) $BaFeO_{3-\delta}$ in air, (f) $BaFeO_{3-\delta}$ in O_2.

Figure 4 shows the Seebeck coefficient, Q, as a function of T^{-1}. The Seebeck coefficients were almost independent of the temperature in the range from 50 to about 300–350°C, except for $SrFeO_{3-\delta}$ in N_2, but increased at the temperatures above about 300–350°C. The increase in the Seebeck coefficient is also based on the formation of the oxygen vacancy, because of the same reason as that in the case of the conductivities. The temperature independence of the Seebeck coefficient suggests the hopping conduction mechanism, especially for the $BaFeO_{3-\delta}$ samples, because this temperature independence implies the temperature independence of the carrier density. The Seebeck coefficient was negative for the $BaFeO_{3-\delta}$ in O_2 in the low temperature range, but positive for other samples. These results indicate that the majority carrier is the electron for the former sample, but is the hole for the latter samples.

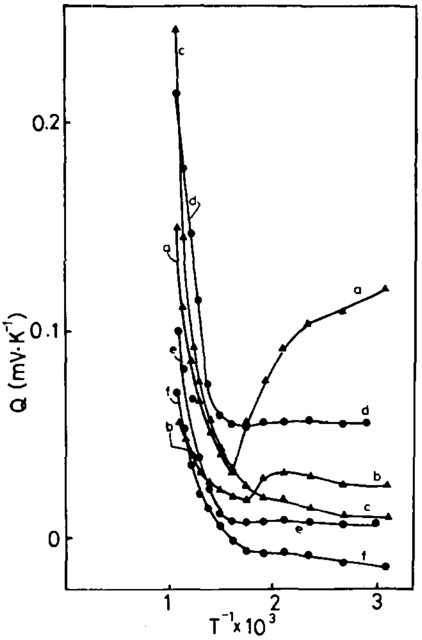

FIG. 4. Seebeck coefficient as a function of T^{-1}: (a) $SrFeO_{3-\delta}$ in N_2, (b) $SrFeO_{3-\delta}$ in air, (c) $SrFeO_{3-\delta}$ in O_2, (d) $BaFeO_{3-\delta}$ in N_2, (e) $BaFeO_{3-\delta}$ in air, (f) $BaFeO_{3-\delta}$ in O_2.

According to Goodenough (*6*), the conduction band for $SrFeO_3$ is the π^*_β band, as illustrated in Fig. 5. This band mainly comprises the t^*_β orbital of the Fe cation, although the band is formed by the overlap between Fe–O–Fe. Therefore, the conduction of $SrFeO_{3-\delta}$ and $BaFeO_{3-\delta}$ perovskites will be mainly determined by the degree of the π^*_β band formation. If the π^*_β band is not formed, the t^*_β levels will be the hopping levels in the hopping conduction mechanism. The Seebeck coefficient is represented by the following equation (1) in the case of the hopping conduction:

$$Q = -(k/e)\ln(n_1/n_2), \qquad (1)$$

where n_1 and n_2 are the electron vacant and the electron occupied site numbers, respectively. If the hopping level is assumed to be the t^*_β level for the present oxides, the n_1 and n_2 are represented by δ as follows,

$$n_1 = 2 - 2\delta \qquad (2)$$

$$n_2 = 1 + 2\delta \qquad (3)$$

because three electrons can occupy the t^*_β level. For example, the values of n_1 and n_2 are two and one, respectively, for the Fe^{4+} ion ($\delta = 0$), since the total number of *d* electrons of this ion is four. (Three electrons occupy the t^*_α level in Fig. 5.) The majority carrier density, *p* or *n*, can be calculated by the following equations,

$$p = n_1/\mathrm{Vc} \quad \text{for } p\text{-type} \qquad (4)$$

$$n = n_2/\mathrm{Vc} \quad \text{for } n\text{-type}, \qquad (5)$$

where Vc is the volume of the unit cell which has one iron ion. If only the majority carrier is assumed to contribute to the conduction, the following equations are held,

$$\sigma = e \cdot \mu \cdot p \quad \text{for } p\text{-type} \qquad (6)$$

$$\sigma = e \cdot \mu \cdot n \quad \text{for } n\text{-type}, \qquad (7)$$

where μ is the mobility. The mobility and the majority carrier densities were calculated by using Eqs. (1), (3), (4), and (6) for the *p*-type oxides, while Eqs. (1), (2), (5), and (7) were used for the *n*-type oxides. Thus, we assumed that only the electron occupied number, n_2, is initially fixed by δ for the calculation of the hole density for the *p*-type oxides, while only n_1 is fixed for the electron density for the *n*-type oxide. This assumption will be reasonable, because all of the Fe^{4+} cations in the *p*-type oxides do not produce the hole as the majority carrier. That is to say, some of the

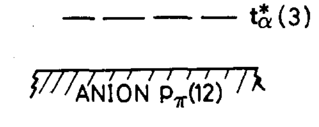

FIG. 5. Band structure of $SrFeO_3$.

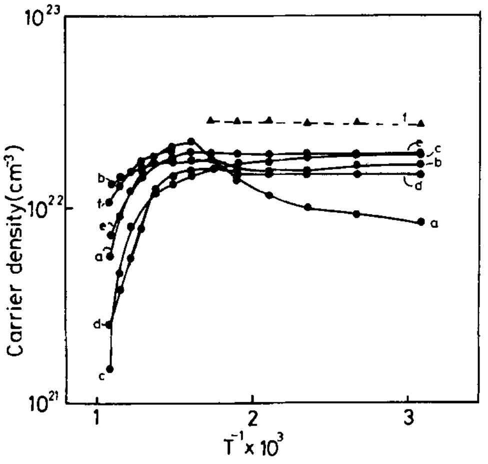

FIG. 6. Majority carrier density as a function of T^{-1}: (a) $SrFeO_{3-\delta}$ in N_2, (b) $SrFeO_{3-\delta}$ in air, (c) $SrFeO_{3-\delta}$ in O_2, (d) $BaFeO_{3-\delta}$ in N_2, (e) $BaFeO_{3-\delta}$ in air, (f) Ba$FeO_{3-\delta}$ in O_2. Triangle symbols denote the electron densities.

present oxides show the *p*-type conduction, even when the ratio of Fe^{4+}/Fe^{3+} in the concentration is in excess of one ($\delta < 0.25$).

Figures 6 and 7 show the majority carrier density and the mobility as a function of T^{-1}, respectively. The circle and the triangle symbols denote the cases of the hole and the electron majority carriers, respectively. The carrier densities of all the samples are about 10^{22} cm^{-3}, and decrease above 300–350°C. This decrease in the hole concentration is based on the formation of the oxygen vacancy. On the other hand, the mobilities largely increase with temperature except for $SrFeO_{3-\delta}$ in O_2 and in air. The mobilities of the latter oxides are in the range of $10^{-3} - 10^{0}$ V^{-1} sec^{-1} cm^2, suggesting near metallic conduction, although the values are not quantitatively accurate in the low temperature range, because the Seebeck coefficients are too small (= 10 μV) to assume the hopping conduction. The calculated activation energies of the mobility agree with the apparent activation energies of the conductivity very well, as listed in Table I. This indicates that the conductions below about 300–350°C are determined by the mobility for both of the oxide systems. Thus, the calculated carrier density and mobility are very reasonable in the values, in spite of the rough assumption of the hopping model.

In the range of $\delta < 0.25$ of the present oxides, anomalous behavior is expected to occur in the carrier density, because the number of the electron vacant site (n_1) is nominally higher than that of the electron occupied site (n_2), leading to the change in the majority carrier from the hole to the electron. In Fig. 6, two anomalous behaviors are observed. One is the lowest hole density for $SrFeO_{3-\delta}$ in O_2 in this system at high temperature range, since the hole carrier in the *p*-type oxide semiconductor is believed to increase with oxidation. The other is that the majority carrier is the electron for the $BaFeO_{3-\delta}$ in O_2 at low temperature range. These behaviors will be mainly

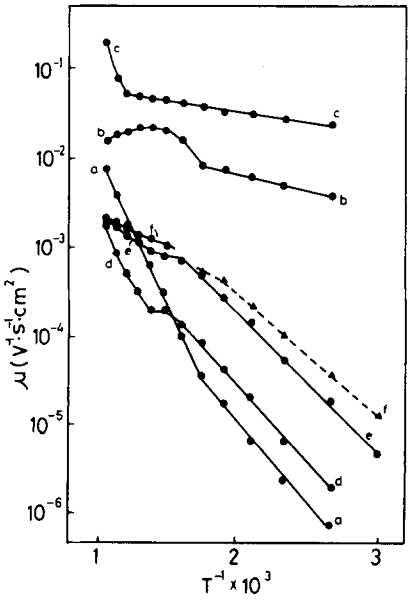

FIG. 7. Mobility as a function of T^{-1}: (a) $SrFeO_{3-\delta}$ in N_2, (b) $SrFeO_{3-\delta}$ in air, (c) $SrFeO_{3-\delta}$ in O_2, (d) Ba$FeO_{3-\delta}$ in N_2, (e) $BaFeO_{3-\delta}$ in air, (f) $BaFeO_{3-\delta}$ in O_2. Triangle symbols denote the electron mobilities.

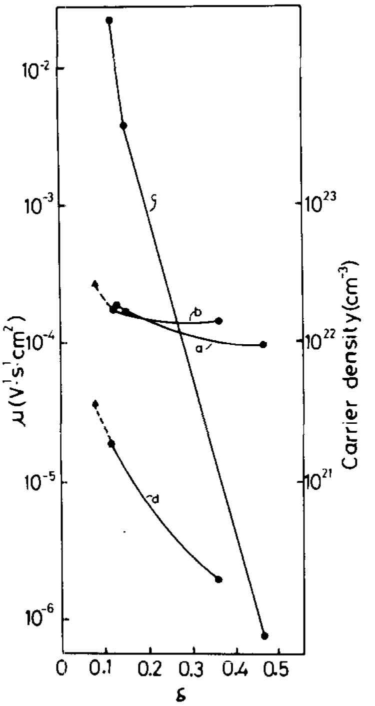

FIG. 8. Carrier density and mobility at 100°C as a function of δ: (a) Carrier density in $SrFeO_{3-\delta}$, (b) carrier density in $BaFeO_{3-\delta}$, (c) mobility in $SrFeO_{3-\delta}$, (d) mobility in $BaFeO_{3-\delta}$. Triangle symbols denote the electron density and the mobility.

based on the above nominal changes in n_1 and n_2.

Figure 8 shows the calculated majority density and the mobility at 100°C as a function of δ. The hole density slightly decreases with the increase in δ, but the mobility largely decreases with δ. The latter tendency is remarkable for $SrFeO_{3-\delta}$. Thus, the oxygen in the present perovskite type oxides strongly affects the mobility, indicating the importance of the Fe–O–Fe interaction in the conductivity. It should be noted that the mobility of $SrFeO_{3-\delta}$ is about 10^3 times that of $BaFeO_{3-\delta}$ at the same δ value in the range of $\delta < 0.2$, as shown in Fig. 8. This difference in the mobility is based on those in the Fe–O–Fe distance which are about 3.86 and 4.01 Å for $SrFeO_{3-\delta}$ and $BaFeO_{3-\delta}$, respectively. It is very interesting that the difference of about 0.15 Å in the distance determines the π^*_β band formation in the present perovskite type oxides. The conduction is near metallic if this band is formed, while the conduction is hopping if this band is not formed.

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