

Electrical Conduction of New Compounds $(\text{Ca,Ce})_2\text{Sn}_2\text{O}_7$ and $(\text{Sr,Ce})_2\text{Sn}_2\text{O}_7$ with Pyrochlore Structure

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The electrical properties of sintered specimens of new compounds $\text{Ca}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$ ($0.35 \leq x \leq 0.43$) and $\text{Sr}_{0.7}\text{Ce}_{1.3}\text{Sn}_2\text{O}_7$ with cubic pyrochlore structure were measured as functions of temperature and oxygen partial pressure. These compounds showed semiconductive behavior. The negative Seebeck coefficient indicates these compounds to be n-type, and the dominant carrier is the electron. In these compounds, almost no oxygen nonstoichiometry was detected in the range of oxygen partial pressure ($p\text{O}_2$) from 1 to $10^{-3.5}$ atm with thermogravimetric analysis. Moreover, the electrical conductivity slightly increased as $p\text{O}_2$ decreased from 1 to 10^{-15} atm. Since it was required that part of the Ce ions should be trivalent to maintain the electrical neutrality in the whole crystal from the point of view of the chemical composition, the formation of the carriers was explained by the substitution of trivalent Ce ion for Ca. The Seebeck coefficient increased as temperature increased from 780 to 1273 K, so the conduction mechanism of these new compounds is probably small polaron hopping. © 1993 Academic Press, Inc.

Introduction

A new compound, $\text{Ca}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$ ($0.35 \leq x \leq 0.43$), was prepared and its crystal structure was found to be pyrochlore (1). $\text{Sr}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$ ($0.345 \leq x \leq 0.365$) was also prepared as an isostructural compound. These compounds can be classified as mixed-cation-type at the A site of $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore. Ce ions were found to be tri- and tetravalent in the crystal (1).

Electrical conductivity of nonstoichiometric cerium dioxide, $\text{Ce}_{1+x}\text{O}_2$, has been

well investigated (2–7), especially by Blumenthal *et al.* (8). According to them, $\text{Ce}_{1+x}\text{O}_2$ is an n-type semiconductor. From the measurement of electrical conductivity and thermogravimetric analysis (TGA), Blumenthal and Palner (9) calculated the electron mobility in $\text{Ce}_{1+x}\text{O}_2$ and concluded that the mechanism of electrical conduction was small polaron hopping.

In order to clarify the electrical conduction mechanism in $\text{Ca}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$ and $\text{Sr}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$, electrical conductivity of these compounds was measured as a function of temperature and oxygen partial pressure ($p\text{O}_2$). The Seebeck coefficient was measured to obtain the information about

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the carrier type and concentration in these compounds.

Experimental

We have previously investigated the synthesis of single-phase powder specimens with composition of $(\text{Ca,Ce})_2\text{Sn}_2\text{O}_7$ and $(\text{Sr,Ce})_2\text{Sn}_2\text{O}_7$. Starting materials of these compounds are reagent grade CaCO_3 , SrCO_3 , CeO_2 , and SnO_2 . Phase analysis was carried out with powder X-ray diffraction (XRD). Rectangular pellets were isostatically pressed at 1.0×10^2 MPa, then sintered at 1450°C for 12 hr in air. After sintering, the specimens were polished with fine emery paper (#2000). Electrical conductivities were measured with four probe dc method as a function of temperature and oxygen partial pressure in the range from 700 to 1273 K and from 1 to 10^{-15} atm, respectively. Four platinum wire electrodes were attached to the sample with platinum paste. In order to subtract any thermoelectric effect, measurements were performed twice with opposite current directions. For $1 \text{ atm} > p\text{O}_2 > 10^{-4} \text{ atm}$, oxygen partial pressure was controlled by mixing N_2 and O_2 gas, and for $10^{-4} \text{ atm} > p\text{O}_2 > 10^{-15} \text{ atm}$, by trapping oxygen from N_2 gas with TiN as

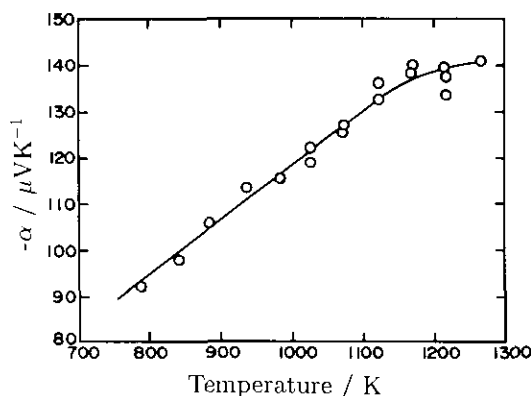


FIG. 1. Seebeck coefficient of $\text{Ca}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$ ($x = 0.43$) as a function of temperature.

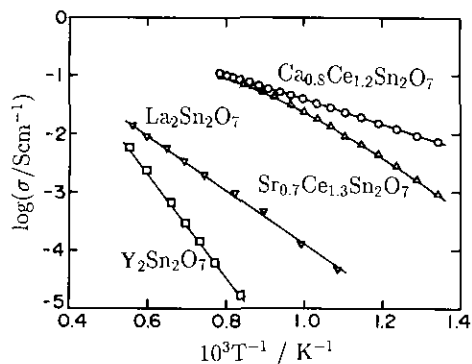


FIG. 2. Electrical conductivities of $\text{Ca}_{0.8}\text{Ce}_{1.2}\text{Sn}_2\text{O}_7$ and $\text{Sr}_{0.7}\text{Ce}_{1.3}\text{Sn}_2\text{O}_7$ as a function of temperature. The conductivities of $\text{La}_2\text{Sn}_2\text{O}_7$ and $\text{Y}_2\text{Sn}_2\text{O}_7$ (I_0) are also plotted for comparison.

an oxygen attractor. $p\text{O}_2$ was measured with two ZrO_2 sensors which were set upstream and downstream from the sample in the gas flow.

Seebeck coefficients were measured between 780 and 1273 K with a temperature gradient of about 10 K.

Oxygen nonstoichiometry was measured by thermogravimetric analysis (TGA) using a Cahn 1000 electro-balance.

Results and Discussion

In as-sintered samples, a slight change of the value of the electrical conductivity was recognized at 1273 K. This behavior may reflect that the valence states of as-sintered samples were slightly different from those at low temperature. Then all samples were annealed at 1273 K for 3 days. After annealing, no change in electrical conductivity was perceived.

Figure 1 shows the Seebeck coefficients of $\text{Ca}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$ ($x = 0.43$) versus temperature from 780 to 1273 K. The negative value of the Seebeck coefficients reveals that the major carrier of $\text{Ca}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$ is the electron.

Figure 2 shows the electrical conduc-

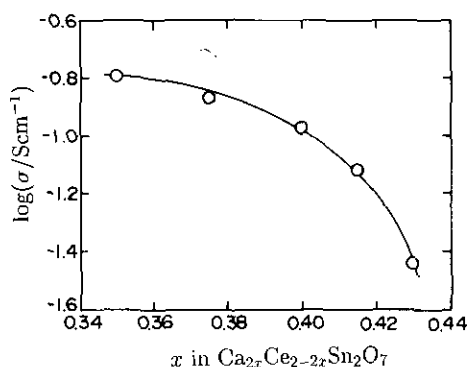


FIG. 3. Dependence of electrical conductivities on composition x in $\text{Ca}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$ at 1273 K.

tivities σ of $\text{Ca}_{0.8}\text{Ce}_{1.2}\text{Sn}_2\text{O}_7$ and $\text{Sr}_{0.7}\text{Ce}_{1.3}\text{Sn}_2\text{O}_7$ as a function of reciprocal absolute temperature in 1 atm oxygen. This result shows that both $\text{Ca}_{0.8}\text{Ce}_{1.2}\text{Sn}_2\text{O}_7$ and $\text{Sr}_{0.7}\text{Ce}_{1.3}\text{Sn}_2\text{O}_7$ are semiconductors. It should be noted that the Sr-compound shows a considerable curve when plotted in this manner. This result is discussed later. Figure 2 also shows the electrical conductivities of $\text{La}_2\text{Sn}_2\text{O}_7$ and $\text{Y}_2\text{Sn}_2\text{O}_7$ after Champman *et al.* (10) for comparison. These two trivalent element stannates have the pyrochlore structure and are semiconductors, as are $(\text{Ca,Ce})_2\text{Sn}_2\text{O}_7$ and $(\text{Sr,Ce})_2\text{Sn}_2\text{O}_7$. However, the magnitude of the conductivities is from 10^2 to 10^4 times lower than that of the new compounds. For $\text{La}_2\text{Sn}_2\text{O}_7$ and $\text{Y}_2\text{Sn}_2\text{O}_7$, the carrier must correspond to the oxygen nonstoichiometry and valence change of Sn^{4+} because of the stable trivalence of La and Y elements. On the contrary, in $(\text{Ca,Ce})_2\text{Sn}_2\text{O}_7$ and $(\text{Sr,Ce})_2\text{Sn}_2\text{O}_7$, Ce ions can be either tri- or tetravalent. This seems to be the reason why these new compounds have higher conductivity.

Figure 3 shows the dependence of the electrical conductivity of $\text{Ca}_{2x}\text{Ce}_{2-2x}\text{Sn}_2\text{O}_7$ on x (the ratio of Ca to Ca + Ce) at 1273 K. This indicates that the electrical conductivity decreases as x increases.

Figure 4 shows the relations between the

electrical conductivities of $\text{Ca}_{0.8}\text{Ce}_{1.2}\text{Sn}_2\text{O}_7$ and $\text{Sr}_{0.7}\text{Ce}_{1.3}\text{Sn}_2\text{O}_7$ and oxygen partial pressure ($p\text{O}_2$). The electrical conductivities of both $\text{Ca}_{0.8}\text{Ce}_{1.2}\text{Sn}_2\text{O}_7$ and $\text{Sr}_{0.7}\text{Ce}_{1.3}\text{Sn}_2\text{O}_7$ are nearly constant and increase very slightly as $p\text{O}_2$ decreases (slope = 1/200). With the TGA of $\text{Ca}_{0.8}\text{Ce}_{1.2}\text{Sn}_2\text{O}_7$ at 1273 K in O_2 and N_2 atmosphere, no weight change was detected. These results suggest that oxygen nonstoichiometry is very small in these compounds at this temperature. The sudden decrease in the electrical conductivity of $\text{Sr}_{0.7}\text{Ce}_{1.3}\text{Sn}_2\text{O}_7$ below 10^{-15} is due to the decomposition of the pyrochlore phase, as shown by XRD analysis.

As discussed in the previous paper (1), part of the Ce ions should be trivalent to attain the electrical neutrality in the whole crystal. So the mechanism of the carrier generation in $(\text{Ca,Ce})_2\text{Sn}_2\text{O}_7$ is explained by the reaction



which means that a trivalent Ce ion substitutes for a divalent Ca ion as the dopant on the nondoped compound $(\text{Ca}^{2+}\text{Ce}^{4+})_2\text{Sn}_2\text{O}_7$. This consideration is in good agreement with the result shown in Fig. 3.

Obviously the carriers are trapped either

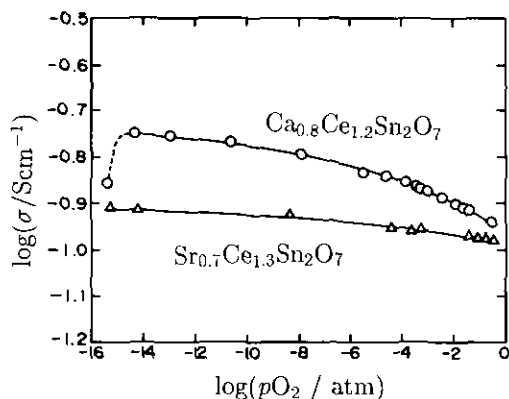
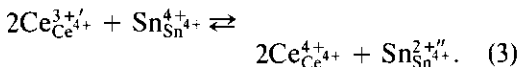
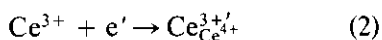


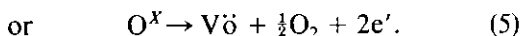
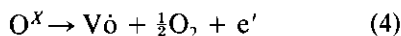
FIG. 4. The relation between electrical conductivities of $\text{Ca}_{0.8}\text{Ce}_{1.2}\text{Sn}_2\text{O}_7$ and $\text{Sr}_{0.7}\text{Ce}_{1.3}\text{Sn}_2\text{O}_7$ and oxygen partial pressure at 1273 K.

at the Ce^{4+} site or the Sn^{4+} site according to the following equations:

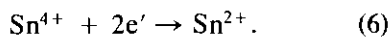


It is difficult to clarify which equation is realized in these compounds at the present time.

The slight increase of the electrical conductivity of $(Ca,Ce)_2Sn_2O_7$ as pO_2 decreases (Fig. 3) seems to correspond to the creation of carrier with oxygen nonstoichiometry. This is explained by either the reaction



The electrons seem to be trapped by the Sn ion with



Of course, the same discussion can be applied to the case of $(Sr,Ce)_2Sn_2O_7$.

$(CeO_2)_{1-x}(CaO)_x$ is known to be an intrinsic conductor having the same order of conductivities as those of $(Ca,Ce)_2Sn_2O_7$ and $(Sr,Ce)_2Sn_2O_7$ (11). The crystal structure of $(CeO_2)_{1-x}(CaO)_x$ is fluorite type and this ionic compound has 0.15 oxygen vacancies per formula unit. However, the crystal structure of $(Ca,Ce)_2Sn_2O_7$ and $(Sr,Ce)_2Sn_2O_7$ is pyrochlore and cannot have such a large amount of vacancies (1). Therefore the analogy cannot be used and we believe that the major carriers in the new compounds are electrons, which is in good agreement with the thermopower measurements result.

As mentioned in Fig. 2, the plot of electrical conductivity vs reciprocal temperature of $(Sr,Ce)_2Sn_2O_7$ showed a slight curve. This result would suggest that the conduction mechanism of this compound was small polaron hopping, since $La_{1-x}Sr_xCrO_3$ and $La_{1-x}Sr_xMnO_3$ showed the same result and their conduction mechanism was consid-

ered to be the small polaron transport mechanism (12, 13). Furthermore, in Fig. 1, the Seebeck coefficient of $Ca_{2x}Ce_{2-2x}Sn_2O_7$ increased as temperature increased from 780 to 1273 K. Such a behavior implies that the electron concentration is not thermally activated. Similar phenomena have been reported for semiconductive $Na_xTa_yW_{1-y}O_3$ (14), $Na_{1-x}Sr_xNbO_3$ (15), and Ni-doped CoO_3 (16). From the analogy of these reports, the carriers of $(Ca,Ce)_2Sn_2O_7$ and $(Sr,Ce)_2Sn_2O_7$ are localized and the mechanism of the conduction seems to be small polaron hopping, which supports the result in Fig. 2. To ascertain this prediction, Hall-coefficient measurement and XPS measurement are required. These measurements are now under investigation by us.

Conclusion

New compounds $Ca_{2x}Ce_{2-2x}Sn_2O_7$ ($0.35 \leq x \leq 0.43$) and $Sr_{0.7}Ce_{1.3}Sn_2O_7$ with cubic pyrochlore structure are semiconductors and the major carriers are electrons. This result is in good agreement with chemical composition and structural properties. The conduction mechanism of these new compounds seems to be small polaron hopping from the results of the Seebeck coefficient measurement.

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