CHEMISTRY LETTERS, pp. 377 - 380, 1985. © 1985 The Chemical Society of Japan

# PEROVSKITE-TYPE OXIDES HAVING SEMICONDUCTIVITY AS OXYGEN SENSORS

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Among the perovskite-type oxides examined, $SrTiO_3$ showed a high sensitivity to oxygen in the "lean-burn" region. The resistivity characteristics of the specimen were also investigated in the exhaust gas of propane-oxygen combustion. $SrSnO_3$ is promising for a combustion monitoring sensor.

The combustion of hydrocarbon fuels is widely used to obtain useful energy in various industries. As for an engine or a furnace, it is necessary to control the air to fuel ratio from the viewpoints of fuel conservation and pollution control.[1-3] Among oxygen sensors, some elements capable to detect the stoichiometric air to fuel ratio are required for pollution control[1-3] and other elements capable to detect the "lean-burn" region are required for enhancement of an energy efficiency.[3] In the past several years, there have been increasing interests in the semiconductive oxygen sensor, because of small size and simple structure. This type of sensor utilizes electrical conductivity changes due to oxygen adsorption or desorption. The conductivity is proportional to oxygen partial pressure with the following equation : $\sigma \propto P_{O_2}{}^{1/m}$. The m value depends both on the semiconductive nature of metal oxides and on the surrounding oxygen partial pressure in which they are placed. In order to use semiconductive metal oxides as an oxygen sensor, both thermal stability at elevated temperatures and stability under reductive environments are required for reproducibility and accuracy of the sensor. It is well known that redox properties of oxides can be modified by the formation of mixed oxides.[4] In fact, a mixed oxide of CoO and MgO is used for an oxygen sensor to improve a stability toward reduction in a "rich-burn" region where oxygen partial pressure is usually below $10^{-15}$ Pa. These consideration prompted us to investigate the oxygen sensor consisting of mixed oxides. The perovskite-type oxides were chosen by the following reasons : 1) The electronic properties of these oxides can be modified easily by selecting appropriate combination of the cation constituents. 2) They are stable under reducing environment at high temperature.

Perovskite-type oxides were prepared by calcining the mixtures of $TiO_2$, $SnO_2$, and alkaline earth carbonates in a desired proportion at 800 - 1000 °C for 2 - 5 h. The calcined powders were again ground with a ball mill and then pressed into discs of 10 mm in diameter and 1 mm in thickness. The disc was covered with powder of the same composition and was sintered at 1200 °C for 6 h. The Pt paste was applied on both side of these discs and was fired at 900 °C for 10 min. The semiconductive nature of the specimens was determined by the thermoelectromotive

Table 1. Characteristics of sintered specimens used for electrical measurements

| Specimen | Thermoelectromotive coefficient in air $d\theta/dT$ (mV·K$^{-1}$) | T/K | Semiconductive type[a)] | Relative density % | Surface area $m^2 \cdot g^{-1}$ | Conductivity[a)] S·cm$^{-1}$ | m value[a)] |
|---|---|---|---|---|---|---|---|
| $SrSnO_3$ | 0.41 | 983 | p | 69 | 2.7 | $9.1 \times 10^{-8}$[b)] | — |
| $SrTiO_3$ | 0.47 | 833 | p | 70 | 1.0 | $1.8 \times 10^{-4}$[c)] | 4.2[c)] |
| $Sr_{0.9}La_{0.1}SnO_3$ | -0.20 | 773 | n | 63 | 0.6 | — | — |
| $BaSnO_3$ | -0.08 | 745 | n | 65 | 5.9 | $2.4 \times 10^{-3}$ | -5.1 |
| $BaTiO_3$ | 0.50 | 953 | p | 57 | 0.4 | $4.6 \times 10^{-6}$ | — |
| $Ba_{0.97}Na_{0.03}TiO_3$ | 0.32 | 743 | p | 63 | 0.9 | $8.0 \times 10^{-6}$ | 4.8 |
| $CaSnO_3$ | 0.65 | 973 | p | 54 | 1.8 | — | — |
| $CaTiO_3$ | 0.21 | 873 | p | 55 | 1.5 | $6.9 \times 10^{-6}$ | 4.4 |

a) At 973 K in air. b) At 995 K. c) At 873 K.

coefficient. The D.C. conductivity of specimens was measured using a constant voltage supply and an electronic picoammeter in the temperature range from 400 °C to 800 °C under oxygen partial pressure between $10^2$ and $10^5$ Pa, which was established by a continuous flow of a mixed gas of nitrogen and oxygen of a total pressure of $10^5$ Pa. The resistivity characteristics of the specimen were also investigated in the exhaust gas of propane-oxygen combustion. Propane and oxygen were mixed at an appropriate ratio and then a flow rate of 200 $cm^3$/min with a total pressure of $10^5$ Pa was established by balancing with nitrogen. The mixture was burned over a $Pt/Al_2O_3$ catalyst and the exhaust gas was introduced into a quartz vessel in which the specimen had been installed. A stoichiometric point is defined as air excess ratio $\lambda = 1$, for which there is just enough oxygen to convert all of propane to $CO_2$ and $H_2O$. The resistivity measurements were carried out near $\lambda = 1$ at 700 °C.

Characteristics of the sintered specimens used for the electrical measurements were listed in Table 1. Among the perovskite-type oxides examined, $SrTiO_3$ showed a high sensitivity to oxygen as shown in Fig. 1. The conductivity of $SrTiO_3$ was found to be proportinal to $P_{O_2}{}^{1/4}$ above $10^2$ Pa of oxygen partial pressure in the temperature range from 550 °C to 800 °C. This trend in the electrical conductivity means a p-type semiconductive nature of $SrTiO_3$ under these conditions, as also expected from the result of thermoelectromotive coefficient. On the other hand, as for $SrSnO_3$, no significant changes in conductivity were observed, as shown in Fig. 2, while thermoelectromotive coefficient of this specimen indicated a p-type nature at $2.1 \times 10^4$ Pa. These results tell us that the change of the conduction mechanism of the specimen from p-type to n-type occurs in the oxygen partial pressure from $10^2$ to $10^5$ Pa. These results are quite similar to those reported in literatures.[5)] However, the values of the oxygen

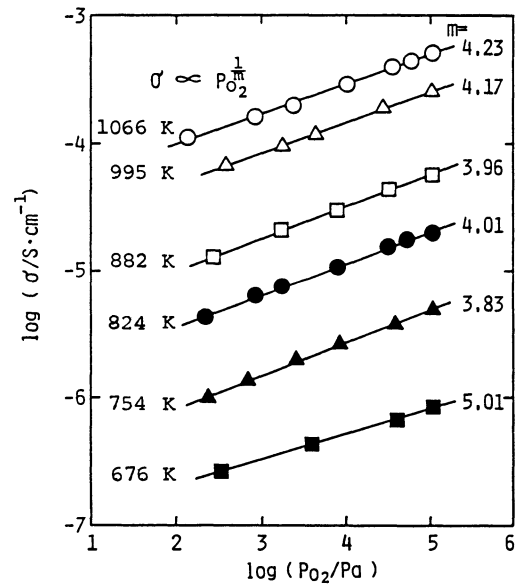

Fig. 1. Electrical conductivity of $SrTiO_3$ as a function of $O_2$ partial pressure.

partial pressure at which the change occurs are not the same as those reported, probably due to contribution of unknown impurities.

The resistivity characteristics of the specimens were also investigated in the exhaust gas of propane-oxygen combustion. As shown in Fig. 3, the resistivity of all specimens decreased dramatically at the stoichiometric point of combustion with a decrease in the air excess ratio λ. From these results, we can classify these specimens into three groups. In the first group of specimens, such as $SrTiO_3$ and $CaTiO_3$, the resistivity increased with decreasing λ at first, decreased dramatically at λ = 1, and then decreased with decreasing λ. The magnitude of the decrease in the resistivity at λ = 1 was, however, smaller than that of other specimens. In the second group, such as $SrSnO_3$ and $BaTiO_3$, the resistivity increased slightly with decreasing λ down to λ = 1, but, the magnitude of the change above λ = 1 was small compared with that of the first type specimens, and then the resistivity decreased dramatically at λ = 1. Finally, in the third group, such as $BaSnO_3$ and $Sr_{0.9}La_{0.1}SnO_3$ the resistivity decreased with decreasing λ and then decreased dramatically at λ = 1. These resistivity characteristics depend on the semiconductive nature of the specimens. As stated previously, $SrTiO_3$ showed the p-type conductivity in the oxygen partial pressure of $10^2$ to $10^5$ Pa and the change of the conduction mechanism into the n-type occurred below $10^2$ Pa. Thus a slight decrease in the resistivity is seen at λ = 1. On the other hand, as for $SrSnO_3$ and $BaTiO_3$, the conductivity change from p-type to n-type occurred in the oxygen partial pressure range from $10^2$ to $10^5$ Pa. In cases of $BaSnO_3$ and $Sr_{0.9}La_{0.1}SnO_3$, the n-type conduction mechanism was found to prevail even in a high oxygen partial pressure. Therefore, specimens whose conduction mechanism changes from p-type to n-type below $10^2$ Pa can not be used for monitoring of the stoichiometric air to fuel ratio. Among the perovskite-type oxides examined, $SrSnO_3$ was promising for a combustion monitoring sensor,

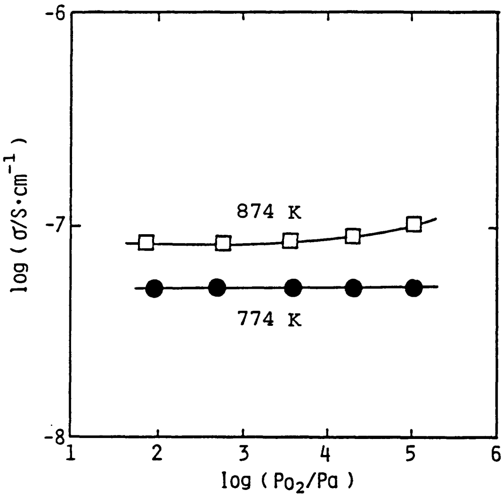


Fig. 2. Electrical conductivity of $SrSnO_3$ as a function of $O_2$ partial pressure.

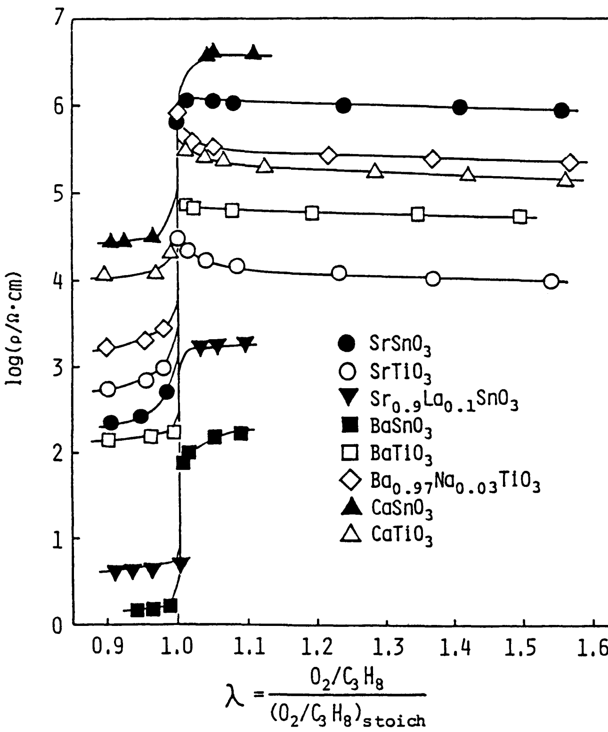


Fig. 3. Dependence of the resistivity of Perovskite-type oxides on the air excess ratio.

Table 2. The change of conduction mechanism of specimens

| Specimen | Air excess ratio $\lambda = 1$ $P_{O_2} \simeq 10^{-5} \sim 10^{-10}$ Pa | $n \rightleftharpoons p$ transition $P_{O_2}$ /Pa | Atmosphere $P_{O_2} = 2 \times 10^4$ Pa | Magnitude of the decrease in the resistivity at $\lambda = 1$ $\log(\sigma_{\lambda>1}/\sigma_{\lambda<1})$ |
|---|---|---|---|---|
| $SrSnO_3$ | n | $10^2 \sim 10^4$ | p | 3.7 |
| $SrTiO_3$ | n | below $10^2$ | p | 1.3 |
| $Sr_{0.9}La_{0.1}SnO_3$ | n | — | n | 2.6 |
| $BaSnO_3$ | n | — | n | 2.1 |
| $BaTiO_3$ | n | $10^2 \sim 10^4$ | p | 2.6 |
| $Ba_{0.97}Na_{0.03}TiO_3$ | n | below $10^2$ | p | 2.2 |
| $CaSnO_3$ | n | — | p | 2.2 |
| $CaTiO_3$ | n | below $10^2$ | p | 1.1 |

judging both from the magnitude of the decrease in the resistivity at $\lambda = 1$ and from excellent reproducibility of the resistivity characteristics. In general, the electrical conductivity of semiconductive metal oxides can be illustrated as a function of oxygen partial pressure. The oxygen partial pressure at which the change of the conduction mechanism is observed depends on the concentration of electrons n and electron holes p in the specimen which is closely related to that of fully ionized atomic defects. The oxygen partial pressure, the type of conduction mechanism both in the "lean-burn" and in the "rich-burn" region for these specimens, and the magnitude of the decrease in the resistivity are summarized in Table 2. The materials whose conduction mechanism is unchangeable in the oxygen partial pressure below $10^2$ Pa are useful for oxygen sensors to detect the stoichiometric ratio of air to fuel. From this point of view, $BaSnO_3$ and $Sr_{0.9}La_{0.1}SnO_3$ are suitble for detecting the stoichiometric ratio. However, judging from the magnitude of the decrease in the resistivity at $\lambda = 1$, $SrSnO_3$ was most suitable for a combustion monitoring sensor.

In conclusion, among the perovskite-type oxides examined, $SrTiO_3$ was most suitable for the "lean-burn" sensor because of the large slope in log-log plots of the conductivity and the oxygen partial pressure. On the other hand, $SrSnO_3$ was promising for a combustion monitoring sensor, judging from the magnitude of the decrease in the resistivity at $\lambda = 1$ and excellent reproducibility of the resistivity.

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(Received December 5, 1984)