ELECTRICAL CONDUCTIVITY OF ALKALINE-EARTH METAL _-ALUMINAS AND THEIR APPLICATION TO A CO_2 GAS SENSOR

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Abstract: Sr and Ba_-aluminas in a single phase were synthesized in the MO-MgO-Al_2O_3 (M=Sr and Ba) system by a solid state sintering method. The electrical conductivity was measured at 873 K to 1473 K by an A.C. impedance method. The electrical conductivities of Sr_-alumina and Ba_-alumina were 1.2x10^{-2} S_m^{-1} and 6.7x10^{-4} S_m^{-1} at 1473 K, respectively. A CO_2 gas sensor using the Sr_-alumina was constructed. The sensor could be used at more than 1000 K.

1. Introduction

Monitoring and controlling of CO_2 partial pressures are important in environmental and industrial fields. Therefore, it is necessary to develop an inexpensive, stable, in-situ and convenient CO_2 gas sensor with high sensitivity and selectivity. A number of investigators have reported their work to develop CO_2 gas sensors using a solid electrolyte[1-17]. However, the most of the solid electrolytes used in the past were alkaline metal ionic conductors. The alkaline metals in the solid electrolytes would easily vaporize at high temperatures. In order to develop a CO_2 gas sensor with a solid electrolyte, we have used alkaline-earth metal aluminates with _-alumina type structure. The alkaline-earth metal _-alumina could be a candidate as a solid electrolyte at high temperatures because of their high chemical and physical stability. There are two ways to synthesize alkaline-earth metal _-aluminas; one is an ion exchange method using Na_-alumina [18-21] and the other is a solid state sintering method [22-35]. The alkaline-earth metal _-aluminas synthesized by the ion exchange method would often transform into a magnetoplumbite phase at high temperatures[26-27], which could cause micro-cracks and leakage of gases through the solid electrolyte in a gas sensor. Although there have been many reports on the synthesis of the alkaline-earth metal _-aluminas by the solid state sintering method [22-33], the detailed relationship between the composition and electrical properties has not been well understood.

In the present work, electrical properties of alkaline-earth metal _-alumina synthesized by a solid state sintering method have been investigated in SrO-MgO-Al_2O_3 and BaO-MgO-Al_2O_3 systems, and the _-alumina has been applied as a solid electrolyte to a CO_2 gas sensor.

2. Experimental Procedure

2.1 Synthesis of _-alumina

In order to synthesize alkaline-earth metal _-alumina from MO-MgO-Al_2O_3 (M=Ca, Sr and Ba) ternary system, MCO_3, $MgCO_3$, and _-Al_2O_3 powders were used as raw materials. The mixed powders were pressed into disks. The samples were calcined twice at 1573 K in an alumina crucible in an oxygen atmosphere for 24 hours. The calcined samples were ground to powder in an agate mortar. The powders(under #250 mesh) were pressed again into disks(10 mm in diameter and 3 mm in thickness). The disks were sintered in an alumina crucible at 2033 K or 2073 K in an oxygen atmosphere for 24 hours, and then either quenched in air or slowly cooled in the furnace. The structure and lattice constants of the sintered bodies were examined by X-ray powder diffraction (Ni-filtered, Cu K_).

2.2 A.C. impedance measurement

A.C. impedance spectra were measured by using an impedance analyzer (Solartron 1260, Schlumberger) in a frequency range between 0.05 Hz and 20 MHz. The measurements were performed in air using Pt electrode at 873 to 1473 K, after annealing at 1473 for 12 hours.

2.3 Application to CO_2 Gas Sensor

Figure 1 shows the schematic diagram of the CO_2 gas sensor which is expressed as the following cell(M : alkaline-earth metal),

$$Pt, O_2\_M\_\text{-alumina}\_MCO_3, CO_2, O_2, Pt.$$

Porous Pt electrodes were attached on the M_-alumina surface at first, and then a mixture of Pt paste and MCO_3 was placed on the Pt electrode as an auxiliary electrode. The auxiliary electrode was sintered at 1273 K in CO_2 atmosphere for 10 min. The electrode reactions of the cell may be given as Eqs. (1) and (2),

$$\text{the anodic reaction : } MO(\text{in\_-alumina, s}) = M^{2+} + 1/2\ O_2(\text{anode, g}) + 2e^- \quad (1)$$

$$\text{the cathodic reaction : } M^{2+} + CO_2(g) + 1/2\ O_2(\text{cathode, g}) + 2e^- = MCO_3(s) \quad (2)$$

The overall cell reaction could be expressed as Eq. (3).

$$MO(\text{in\_-alumina, s}) + CO_2(g) + 1/2\ O_2(\text{cathode, g}) = MCO_3(s) + 1/2O_2(\text{anode, g}) \quad (3)$$

When pure MCO_3 is used as the auxiliary electrode, the activity of MCO_3 is equal to unity. The EMF of the cell is given as

$$E = -\_G^o_{(3)}/2F - (RT/2F)\ln((P_{O2(anode)})^{1/2}/a_{MO(in\_-alumina)}\cdot(P_{O2(cathode)})^{1/2}\cdot P_{CO2}) \quad (4)$$

where $\_G^o_{(3)}$ is the standard Gibbs free energy change of Eq.(3), $a_{MO(in\_-alumina)}$ is activity of MO in the _-alumina, $P_{O2(anode)}$ and $P_{O2(cathode)}$ are CO_2 partial pressures in the anode electrode side and cathodic electrode side, respectively, and RT/2F have the usual meaning.

3. Results and Discussion

3.1 Structure

Sr and Ba _-aluminas in a single phase were synthesized in the composition of MO:MgO:Al_2O_3=1:1:5 (M=Sr and Ba). Figures 2(a) and 2(b) show the XRD patterns of the Sr and Ba _-aluminas, respectively. The lattice constants and density of the_-aluminas are shown in Table 1. Iyi[29, 30] et al. synthesized the single crystals of Sr and Ba _-aluminas by a FZ method, and studied detailed crystal structures. The lattice constants of _-aluminas synthesized in the present work agreed well with those of the single crystals reported by Iyi et al. [29, 30]. On the other hand, the aluminate with_-alumina type structure could not be obtained in the CaO-MgO-Al_2O_3 system by the solid state sintering method. Kirchnerova et al.[26] indicated that the usual solid state synthesis from oxide powders could form a magnetoplumbite phase in the CaO-MgO-Al_2O_3 system. This is probably due to the low stability of Ca_-alumina at high temperatures. They found that Ca_-alumina has transformed to the magnetoplumbite phase at 1273 K. Iyi et al.[33] reported that the magnetoplumbite structure becomes more stable as the charge of the cation on the mirror plane increases, and the cation size decreases. Therefore, the _-alumina structure in the CaO-MgO-Al_2O_3 system may be less stable than that in the SrO-MgO-Al_2O_3 and BaO-MgO-Al_2O_3 systems.

3.2 Electrical Properties

Impedance plot of the Ba _-alumina measured at 1473 K is shown in Fig.3. An inclined spike was observed in a lower frequency region, as well as for Sr_-alumina[35]. The inclined spike is indicative of a diffusion process involved in an ionic conduction[36-38]. Figure 4 shows the temperature dependence of electrical conductivity of the Sr and Ba_-aluminas. The electrical conductivities of the slowly cooled Sr and Ba_-aluminas were 1.2×10^{-2} S_m^{-1} and 6.7×10^{-4} S_m^{-1} at 1473 K, respectively. It was found that the slowly cooled samples had greater electrical conductivities than those of quenched samples. The activation energies calculated from the lines in Fig.4 are 103.1 kJ_mol^{-1}(slowly cooled) and 101.3 kJ_mol^{-1} (quenched) for Sr_-alumina, and 173.8 kJ_mol^{-1} (slowly cooled) and 163.2 kJ_mol^{-1}(quenched) for Ba_-alumina.

The effect of MgO content in the _-alumina on the electrical conductivity was investigated. Samples with composition of MO:MgO:Al_2O_3=1:1:5 (M=Sr and Ba) had the greatest electrical conductivity as shown in Figs.5(a) and 5(b).

3.3 Application to CO_2 Gas Sensor

Figures 6 shows the relationship between EMF of the cell and temperature. The EMF increased with increasing temperature. The P_{CO2} dependence of the EMF for the cell is shown in Fig. 7. The EMF increased with increasing the ambient CO_2 partial pressure. In order to calculate the theoretical EMF value of Eq.(4) the activity of SrO(in _-alumina) and ionic transport number should be measured. This study is now in progress.

4. Conclusions

Sr and Ba_-aluminas in a single phase were synthesized in MO-MgO-Al_2O_3 (M=Sr and Ba) system by a solid state sintering method. Ca_-alumina could not be obtained in the present work. The electrical conductivity of slowly cooled Sr and Ba_-aluminas was greater than those of quenched samples. Sr_-alumina had greater electrical conductivity than Ba_-alumina. The activation energies of slowly cooled Sr and Ba_-aluminas are 103.1 kJ_mol^{-1} and 173.8 kJ_mol^{-1}, respectively. The EMF of the cell using Sr _-alumina increased with increasing temperature and CO_2 partial pressure. The cell with Sr_-alumina could be used as a CO_2 gas sensor at high temperatures.

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Captions

Table 1. Crystal indexes of _-alumina.
Fig.1 : Schematic diagram of the cell.
Fig.2 : XRD patterns of (a) Sr and (b) Ba_-aluminas.
Fig.3 : Impedance plot of Ba_-alumina at 1473 K(sintered at 2073 K, slowly cooled).
Fig.4 : Temperature dependence of the conductivity of Sr and Ba_-aluminas.
Fig.5 : Effect of MgO content on electrical conductivity of (a) Sr_-alumina at 1373 and (b) Ba_-alumina at 1473 K.
Fig.6 : Temperature dependence of EMF for the cell.
Fig.7 : CO_2 partial pressure dependence of EMF for the cell.