Ionic conductivity of solid solution ceramics in the system of CaO–Y$_2$O$_3$–ZrO$_2$ prepared by SHS

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Abstract

The undesirable phase transformation of zirconium dioxide at high temperatures can be eliminated by stabilization of the cubic phase with an addition of a selected alkaline earth or rare-earth oxide. In this paper the ionic conductivity of cubic solid solutions in the stabilized ZrO$_2$ by CaO–Y$_2$O$_3$ system was examined. The higher ionic conductivity appears to be related to lower activation energy rather than to the number of oxygen vacancies dictated by composition. Those compositions of highest conductivity lie close to the cubic–monoclinic solid–solution phase boundary. Conductivity temperature data are presented that indicate a reversible order–disorder transition for ZrO$_2$–Y$_2$O$_3$ cubic solid solutions containing 20 and 25 mole % Y$_2$O$_3$.

Key Words: ionic conductivity, CaO–Y$_2$O$_3$–ZrO$_2$, SHS, refractory applications, activation energy.

I. Introduction

Zirconium dioxide has a melting point of 2700 °C and transforms from the monoclinic to the tetragonal form at about 1100 °C with a large, disruptive volume change. This unstable phase transformation can be eliminated by stabilization of the cubic phase with an addition of a selected alkaline earth or rare-earth oxide. Stabilized ZrO$_2$ has been widely utilized in various high-temperature refractory applications [1]. These stabilized ZrO$_2$–base solid solutions also possess rather unique electrical properties, and as a result have considerable potential as solid electrolytes in galvanic and fuel cells and, possibly, as heating elements in high-temperature furnaces. We are very interested in new materials as heating elements in high-temperature processes for natural gas decomposition. The present work was undertaken to determine if compositions in the binary system Y$_2$O$_3$–ZrO$_2$ or in the ternary system CaO–Y$_2$O$_3$–ZrO$_2$ would yield better anionic conductors than CaO–ZrO$_2$ binary compositions.

II. Experimental Procedure

CaO–Y$_2$O$_3$–ZrO$_2$ compositions were prepared by SHS method [2], then pressed into cylindrical specimens which were then sintered at 1800 °C for 3 hours in an oxygen–propane furnace. Specimen densities were calculated from weight and geometric measurements and the apparent densities of all specimens were in the range 90 to 95 % of theoretical density. Electrodes were applied to the circular faces of the specimens by spraying on a platinum–organic mixture and heating the coated specimens at 1,100 °C for 1 hour. Electrical conductivity versus temperature measurements was made at a test frequency using Impedance Bridge. Specimens were heated in a platinum–wound tube furnace to various
temperature levels up to 1,400 °C. As a check on the two-probe measurement method, several specimens were also measured using the four-probe method. The results obtained using these two methods agreed within experimental error.

III. Results and Discussion

a) Y$_2$O$_3$-ZrO$_2$ binary compositions

Yttria-zirconia compositions were prepared to span the range 5 to 50 mole % Y$_2$O$_3$. Nominal compositional increments were 5 mole % Y$_2$O$_3$ except in the region of the lower solid-solution limit. X-ray powder patterns showed the presence of two phases at 7.0 mole % Y$_2$O$_3$ and a single-phase cubic solid solution at 9 mole % Y$_2$O$_3$. The high cubic solid-solution phase boundary falls between 45 and 50 mole % Y$_2$O$_3$. The conductivity temperature data for 5, 10, 15, 20, 25, 30, 35 mole % Y$_2$O$_3$ compositions are presented in Fig.1. The data obtained for each composition can be expressed by an Arrhenius equation:

$$\sigma = A \exp \left( \frac{E}{kT} \right)$$

where, $\sigma$ is the electrical conductivity (Ohm$^{-1}$·cm$^{-1}$), $A$ the pre-exponential term, $E$ the activation energy, $k$ the Boltzmann constant, and $T$ the absolute temperature.

Fig. 2 shows conductivity composition isotherms at 800 °C, 1,000 °C, and 1,200 °C and corresponding activation energy.

The activation energy exhibits a minimum near the monoclinic cubic solid-solution phase boundary and, correspondingly, the conductivity is at a maximum.

b) CaO-ZrO$_2$ binary compositions

Calcia-zirconia compositions were prepared to span the range 10 to 25 mole % CaO with 3 mole % increments. The conductivity temperature data for 10, 13, 16, and 19 mole % CaO compositions are presented in Fig.3. The deviation from exponential behavior for the higher CaO compositions is similar to observed by other investigators and is attributed to an order-disorder transition of the oxygen vacancies which occurs at about 1,100 °C.
Fig. 3. Conductivity vs. temperature for various compositions in the CaO-ZrO$_2$ system. Numbers near the curves denote mole percent CaO.

c) CaO-Y$_2$O$_3$-ZrO$_2$ ternary compositions

In this paper we want to determine the evidence for a reversible order-disorder transition in Y$_2$O$_3$-ZrO$_2$ compositions containing 15 to 35 mole % Y$_2$O$_3$ which were annealed at 900 °C for 2 weeks. Conductivity temperature data were obtained for these specimens during heating from 600 °C to 1350 °C and during cooling to 800 °C. Only those compositions containing 20 and 25 mole % Y$_2$O$_3$ exhibited a conductivity anomaly at about 1100 °C, which is indicative of a transition from an ordered to a disordered state. Figure 5 presents typical data illustrating the conductivity anomaly observed for an annealed specimen of composition (Y$_2$O$_3$)$_{0.50}$(ZrO$_2$)$_{0.50}$. We suspect that the degree of ordering increases with increasing Y$_2$O$_3$ content, attaining a maximum (possibly 100 % ordered) at about 33.3 mole %.

Fig. 4. Conductivity isotherms (a) and activation energies (b) for the system CaO-ZrO$_2$.

Fig. 4 shows conductivity composition isotherms at 800 °C, 1,000 °C, and 1,200 °C and corresponding activation energy. Analogous to the system Y$_2$O$_3$-ZrO$_2$, the maximum conductivity occurs near the monoclinic cubic solid-solution phase boundary.

Fig. 5. Conductivity vs. temperature for a specimen of composition (Y$_2$O$_3$)$_{0.50}$(ZrO$_2$)$_{0.50}$ held at 900 °C for 2 weeks.

In low yttria compositions (10 to 15 mole % Y$_2$O$_3$) the degree of ordering is very low whereas for high yttria compositions (>30 mole % Y$_2$O$_3$) the degree of ordering is high. A conductivity temperature anomaly would not be detected for these extremes in ordering. Intermediate compositions hence would show the conductivity anomaly since annealing can vary the degree of ordering. The existence of an ordered phase, the degree of which is composition dependent, would explain why the activation energy increases as the cubic solid solution becomes richer in either Y$_2$O$_3$ or CaO.
It was known that a pyrochlore phase, \( Y_2Zr_2O_7 \), might exist in the \( Y_2O_3-ZrO_2 \) system. However, since \( Y^{3+} \) and \( Zr^{4+} \) have similar scattering factors, the detection of the pyrochlore phase by X-ray techniques would be most difficult. In the present paper, no pyrochlore lines were detected for any of the specimens. Therefore, if the ordered structure is a pyrochlore, it cannot be detected by X-ray method.

**Conclusion**

The ionic conductivity of cubic solid solutions in the system of \( CaO-Y_2O_3-ZrO_2 \) prepared by SHS was examined. For this system, the composition of highest conductivity was found to lie in the \( Y_2O_3-ZrO_2 \) binary at 9-mole \% \( Y_2O_3 \) near the low yttria cubic solid solution limit. The higher conductivity appears to be related to lower activation energy rather than to the number of oxygen vacancies dictated by composition. Annealed specimens of \( Y_2O_3-ZrO_2 \) compositions containing 20 and 25 mole \% \( Y_2O_3 \) exhibited an anomaly in conductivity temperature data at 1100 °C which is indicative of a reversible order–disorder transition analogous to that observed for \( CaO-ZrO_2 \) cubic solid solutions.

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**References**