

Ionic conductivity of solid solution ceramics in the system of CaO-Y₂O₃-ZrO₂ 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 ZrO₂ by CaO-Y₂O₃ 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 ZrO₂-Y₂O₃ cubic solid solutions containing 20 and 25 mole % Y₂O₃.

Key Words: ionic conductivity, CaO-Y₂O₃-ZrO₂, 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 1,100 °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 ZrO₂ has been widely utilized in various high-temperature refractory applications [1]. These stabilized ZrO₂-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 Y₂O₃-ZrO₂ or in the ternary system CaO-Y₂O₃-ZrO₂ would yield better anionic conductors than CaO-ZrO₂ binary compositions.

II. Experimental Procedure

CaO-Y₂O₃-ZrO₂ 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

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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) $Y_2O_3-ZrO_2$ binary compositions

Ytria-zirconia compositions were prepared to span the range 5 to 50 mole % Y_2O_3 . Nominal compositional increments were 5 mole % Y_2O_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_2O_3 and a single-phase cubic solid solution at 9 mole % Y_2O_3 . The high cubic solid-solution phase boundary falls between 45 and 50 mole % Y_2O_3 . The conductivity temperature data for 5, 10, 15, 20, 25, 30, 35 mole % Y_2O_3 compositions are presented in Fig.1. The data obtained for each composition can be expressed by an Arrhenius equation :

$$\sigma = A \exp \frac{E}{kT} \quad (1)$$

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

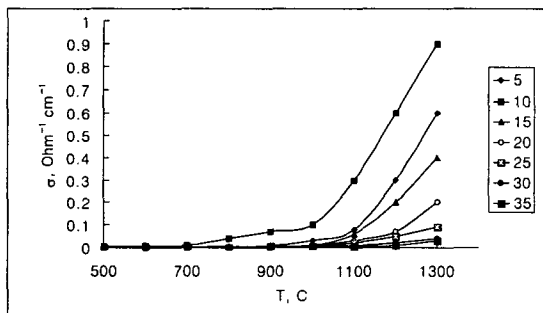
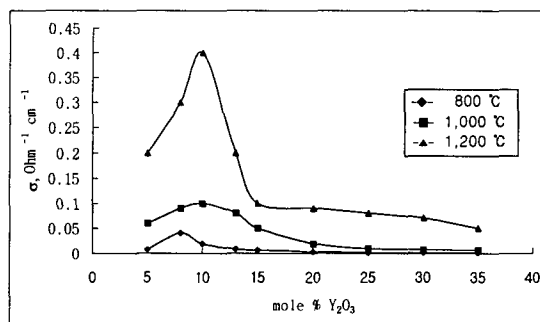


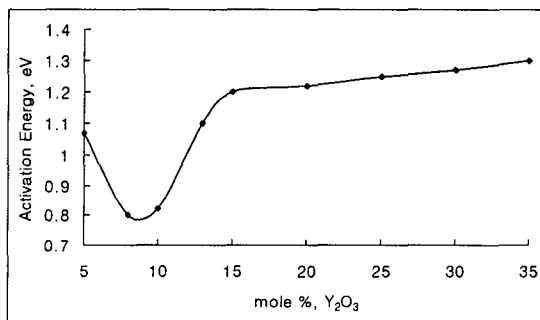
Fig.1. Conductivity vs. temperature for various compositions in the $Y_2O_3-ZrO_2$ system. Numbers near the curves denote mole percent Y_2O_3 .

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.



(a)



(b)

Fig.2. Conductivity isotherms (a) and activation energies (b) for the system $Y_2O_3-ZrO_2$.

b) $CaO-ZrO_2$ binary compositions

Calcium-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.

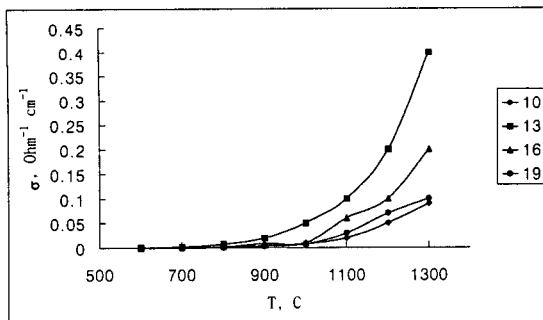
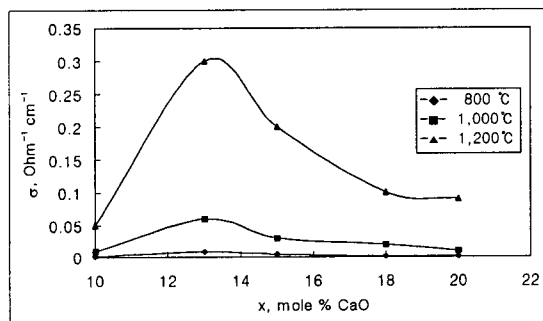
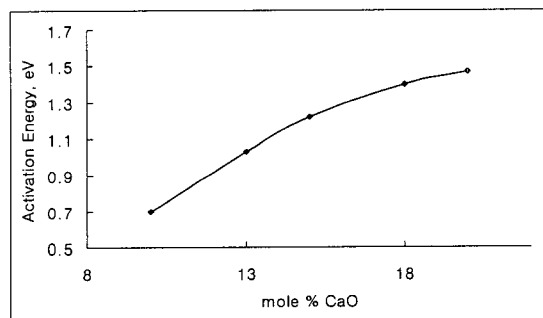


Fig.3. Conductivity vs. temperature for various compositions in the CaO-ZrO₂ system. Numbers near the curves denote mole percent CaO.



(a)



(b)

Fig.4. Conductivity isotherms (a) and activation energies (b) for the system CaO-ZrO₂.

Fig. 4 shows conductivity composition isotherms at 800 °C, 1,000 °C, and 1,200 °C and corresponding activation energy. Analogous to the system Y₂O₃-ZrO₂, the maximum conductivity occurs near the monoclinic cubic solid-solution phase boundary.

c) CaO-Y₂O₃-ZrO₂ ternary compositions

In this paper we want to determine the evidence for a reversible order-disorder transition in Y₂O₃-ZrO₂ compositions containing 15 to 35 mole % Y₂O₃ 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 % Y₂O₃ 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 (Y₂O₃)_{0.25}(ZrO₂)_{0.75}. We suspect that the degree of ordering increases with increasing Y₂O₃ content, attaining a maximum (possibly 100 % ordered) at about 33.3 mole %.

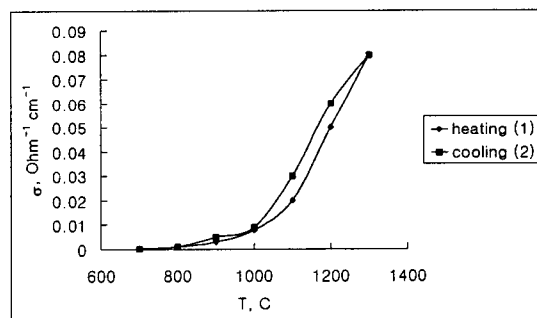


Fig.5. Conductivity vs. temperature for a specimen of composition (Y₂O₃)_{0.25}(ZrO₂)_{0.75} held at 900 °C for 2 weeks.

In low yttria compositions (10 to 15 mole % Y₂O₃) the degree of ordering is very low whereas for high yttria compositions (>30 mole % Y₂O₃) 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 Y₂O₃ 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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