

Ionic Conductivity of Solid Solution Ceramics in The System of Stabilized ZrO₂ Prepared by Self-Propagating High-Temperature Synthesis

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Abstract

The ionic conductivity of cubic solid solutions in the systems of CaO-ZrO₂, Y₂O₃-ZrO₂ prepared by SHS was examined. The higher conductivity appears to be related to a lower activation energy rather than to the number of oxygen vacancies dictated by composition. Conductivity-temperature data was obtained at 1000 °C in atmosphere of low oxygen partial pressure ($\sim 10^{-40}$ atm) for Y₂O₃-ZrO₂ cubic solid solutions. The data indicated that these materials could be reduced, and the degree of reduction would be related with the measuring electric field.

Key Words : Ionic conductivity, CaO-ZrO₂, Y₂O₃-ZrO₂, SHS, Refractory applications, Activation energy

1. INTRODUCTUON

Oxide ionic conductors are very important functional materials for the application in oxygen sensors, solid oxide fuel cells, and so forth. In practice, materials with high oxide ion conduction can be obtained by introducing extrinsic oxide ion vacancies into some fluorite- or perovskite-type oxides. It is well known that the fluorite structured oxide consisting of tetravalent cations exhibits good oxide ion conductivity and Zr-based oxides are generally used as the oxide ionic conductor. However, 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. For example, fast oxide ion conductors are obtained by substituting fluorite-type ZrO₂ with an optimal amount of di- or tri-valent cations such as Ca²⁺ or Y³⁺. These stabilized ZrO₂-based solid solutions could possess rather unique electrical properties and have considerable potential of using as solid electrolyte in galvanic and fuel cells, and as heating element in high-temperature furnaces [1-3].

Self-propagating high-temperature synthesis (SHS) has been the subject of many analytical and experimental investigations because of its potentials for the synthesis of solid materials [2-4]. Demonstrated advantages of SHS include high purity products, low energy requirements, and relative simplicity of the process. However, high defect concentrations and nonequilibrium phases are likely to be present in the products caused by large temperature gradients and extremely high heating and cooling rates of materials during combustion [5].

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In the present work, the effects of the addition of di- or tri-valent cations for ZrO_2 upon the ionic conductivity were investigated for the compounds prepared by SHS. The factors that influence the magnitude of conductivity in the oxides have been clarified based on its observation.

2. EXPERIMENTAL PROCEDURE

Y_2O_3 - ZrO_2 (YZ), and CaO - ZrO_2 (CZ) compositions were prepared by SHS method from the mixture of solid powders (CaO -Aldrich, ACS, Zr -Aldrich, 99.9%, Y_2O_3 -Johnson Matthey, 99.99%, ZrO_2 -Aldrich, 99.9%, $NaClO_4$ -Johnson Matthey, ACS) pressed into 50~60% of the theoretical density. Ignition was initiated by electrical heating of a chemical match of $Al_2O_3 + Ti + BaO_2$. The combustion was conducted in air and with an internal oxygen supply from $NaClO_4$. A detailed synthesis procedure is described in [6-7]. The combustion temperatures were measured using an optical pyrometer (Promin-M1) and (Pt30%Rh - Pt6%Rh) thermocouple, which was more suitable than tungsten one due to the highly oxidizing environment. The phase composition and morphology of the samples were analyzed by X-ray diffraction (XRD : DRON 3M spectrometer using Ni filtered CuK_{α} radiation) and scanning electron microscope (SEM:JSM-35C). Then SHS product powder was pressed into cylindrical specimens which were sintered at $1750^{\circ}C$ for 3 hours in an oxygen-propane furnace. Electrodes were applied to the circular faces of the specimen by spraying on a platinum-organic mixture and heating the coated specimens at $1100^{\circ}C$ for 1h. The specimen was cut and polished to form a rectangular bar ($3 \times 3 \times 11$ mm), placed in a ceramic sample holder, and mounted in a programmable furnace. Those were heated in a platinum-wound tubular furnace with various temperatures levels up to $800 \sim 1400^{\circ}C$. The electrical conductivity was measured as a function of temperature and oxygen partial pressure ($1 \cdot 10^{-40}$ atm) using the conventional dc four-probe method. The electrical conductivity were measured isothermally, $P(O_2)$ was controlled by flow of O_2 , air, or Ar.

3. RESULTS AND DISCUSSION

3.1 SHS synthesis of stabilized Zr dioxide

The highly exothermic reaction of powders raised the temperature to $1400^{\circ}C$. White smoke was generated during the combustion and pellet turned into a porous cake due to a partial melting in the pellet center (Fig.1). The combustion wave propagated at a velocity of about 1 mm/s. This produced a solid powder which was ground in a pestle and mortar, washed with distilled water (3×200 ml) filtered through a Buchner funnel and dried in air at $80^{\circ}C$ for 4 h.

Product yield was essentially quantitative. No traces of $NaCl$ were detected by XRD and electron probe microanalysis in the burned samples, indicating that it evaporated during the combustion due to the high reaction temperature.

In present work we used pre-heating the green pellet which enhanced the homogenization of the product. It was found two effects : (1) it increases the combustion temperature T_c , (2) it

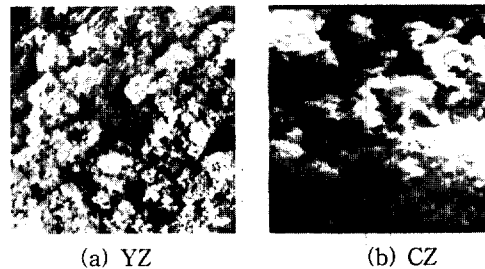


Fig. 1. Scanning electron micrographs of the surfaces of SHS-sintered specimens.

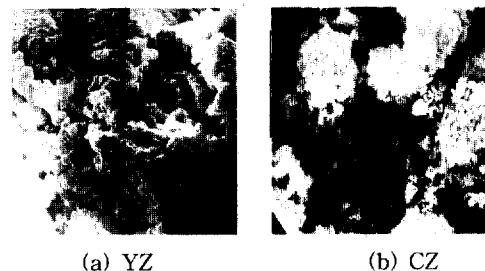


Fig. 2. Scanning electron micrographs of the surfaces of SHS-sintered specimens with preheating temperature to $500^{\circ}C$.

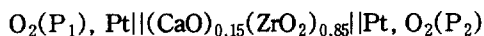
prolongs the exposure time of the burned sample to high temperatures. Both effects increase the homogeneity of the product. The pre-heating temperature to 500°C increased T_c almost 200°C higher than that of the sample ignited at room temperature (Fig. 2).

The wave propagation velocity through the pre-heated pellet was about 2~3 times faster than in the sample that was not pre-heated.

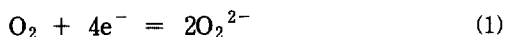
The higher combustion temperature increased the fraction of the pellet that was melted. The microstructure of the product was similar to that of the unheated sample, but with larger and more uniform spherical particles. The product density was higher than that of the sample without pre-heating.

3.2 Electrical conductivity

The electrolyte characteristic of oxide solutions of this type compound was first observed by Nernst, who detected the electrolytic evolution of oxygen from a specimen of composition $(Y_2O_3)_{0.15}(ZrO_2)_{0.85}$. Well-known Wagners postulates reported that oxide solid solutions of the type $(CaO)_x(ZrO_2)_{1-x}$ or $(Y_2O_3)_x(ZrO_2)_{1-x}$ are defect solid solutions. The defects being oxygen vacancies created to preserve lattice neutrality when either Ca^{2+} or Y^{3+} ions are substituted for Zr^{4+} ions in the fluorite type structure. He suggested that these oxygen vacancies should give rise to high oxygen ion mobilities. Kingery *et al* [5] have shown that the transference number for the oxygen ion in $(CaO)_{0.15}(ZrO_2)_{0.85}$ is near unity. Using a vacuum-tight single cell they confirmed that the type



have shown the electrode reactions at temperatures above 600°C correspond closely to the reversible reaction



and the voltage obtained was in good agreement

with the theoretical *emf* calculated from thermodynamic relations.

Since the prime conducting species in these oxides is the oxygen ion, a reasonable estimate of the oxygen ion transfer number might be obtained by measuring the decrease in dc conductivity of a specimen as the surrounding atmosphere is depleted with oxygen. The removal of oxygen from the surrounding atmosphere reduces the anionic conduction by elimination of the conducting species. The residual conductivity can then be attributed almost wholly to electronic and/or cationic conduction.

Thus, the approximate transference number for the oxygen ion would be

$$t_0^{2-} \cong (\sigma_0 - \sigma_t) / \sigma_0 \quad (2)$$

where σ_0 is the specimen conductivity in air and σ_t is the conductivity in an oxygen-depleted atmosphere. The oxygen depletion can be achieved by use of a vacuum or by flowing an inert gas over the specimen. Argon gas (99.9%) was passed through a dry ice-acetone cold trap, over titanium metal heated to 700°C, and into a tube furnace at 1000°C which contained the specimen to be measured. Since the free energies of TiO, TiO₃, and TiO₂¹⁸ at 700°C are of the same order of magnitude, this system would give an oxygen partial pressure of about 10⁻⁴⁰ atm regardless of the extent of oxidation of the titanium.

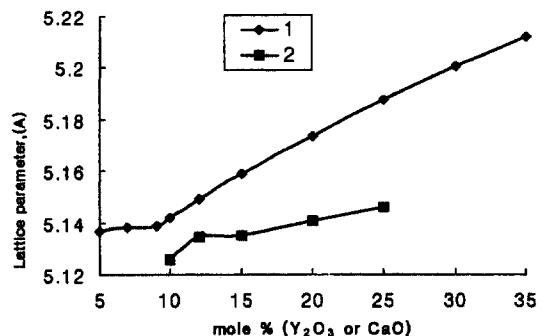


Fig. 3. Lattice parameter vs composition for solid solutions in the systems Y₂O₃-ZrO₂ (1), and CaO-ZrO₂ (2).

3.3 Y₂O₃-ZrO₂ binary compositions

Yttria-zirconia compositions were prepared to span the range 5 to 50 mole % Y₂O₃. Nominal compositional increments were 5 mole % Y₂O₃. X-ray powder analysis showed the presence of two phases: cubic with Space group Fm3m ($a = 5.1280 \text{ \AA}$) and tetragonal with Space group P42/nmc ($a = 5.1197 \text{ \AA}$; $c = 5.1732 \text{ \AA}$) at 7.0 mole % Y₂O₃ and a single-phase cubic solid solution ($a = 5.1389 \text{ \AA}$) at 9-mole % Y₂O₃ (Fig. 3).

It was found the presence of cubic and monoclinic phases over 9 mole % of yttria additions. To compare our data of low yttria-zirconia cubic phase boundary with Y₂O₃-ZrO₂ phase diagram of Duwez *et. al* [8] it was found slightly higher than 8 mole % of Y₂O₃. The high cubic solid-solution phase boundary falls between 45 and 50 mole% Y₂O₃, which agrees with the Duwez phase diagram [8]. The conductivity temperature data for 5 - 35 mole % Y₂O₃ compositions are presented in Fig. 4(a).

The data obtained for each composition can be expressed by an Arrhenius equation:

$$\sigma = A \cdot \exp^{-E/kT} \quad (3)$$

where σ is the electrical conductivity ($\text{Ohm}^{-1} \cdot \text{cm}^{-1}$). A pre-exponential term, E the activation energy, k the Boltzmann constant, and T the absolute temperature. Fig. 4(b) shows conductivity composition isotherms at 800°C, 1000°C, and 1200°C and 4(c) corresponding activation energy. The activation energy exhibits a minimum value near the monoclinic-cubic solid-solution phase boundary and, correspondingly to the equation (3), the conductivity is at a maximum.

3.4 CaO-ZrO₂ binary compositions

Calcium-zirconia compositions were prepared to span the range 10 to 25 mole % CaO in 3 mole % increments. Cubic phase with Fm3m space group and $a=5.1352 \text{ \AA}$ was found with 13 mole % of CaO addition, another ranges consisted of cubic and monoclinic phases (Fig. 3). The conductivity temperature data for 10, 13, 16, and 19 mole %

CaO compositions are presented in Fig. 5 (a).

The deviation from exponential behavior for the higher CaO compositions is similar to that of observed by other investigators [1,5] and is attributed to an order-disorder transition of the

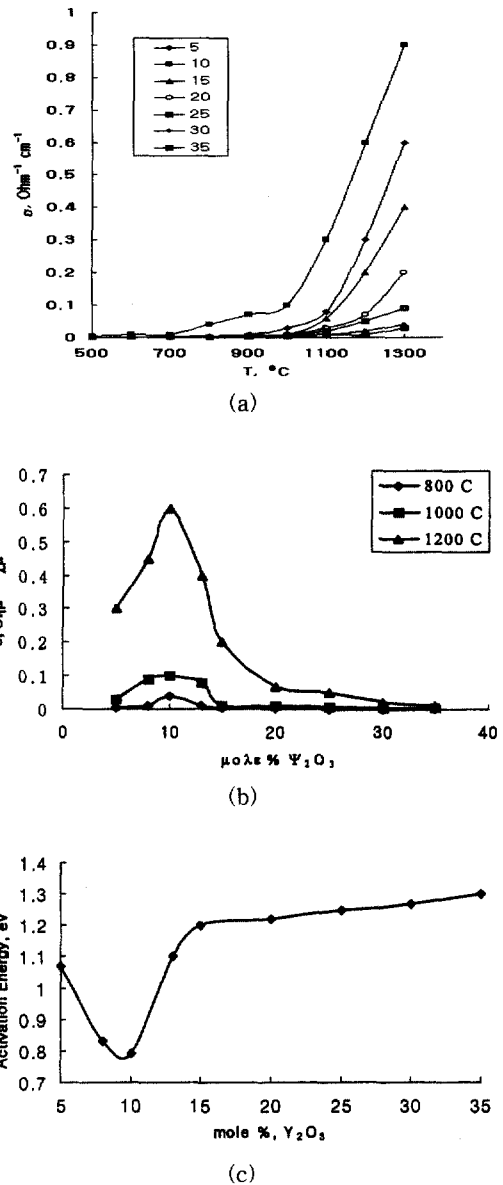
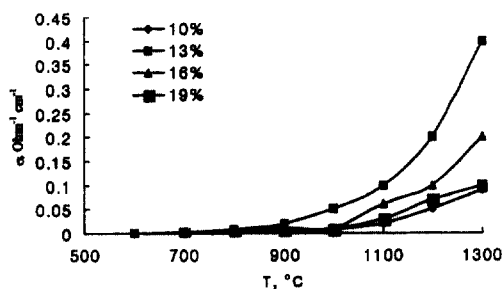
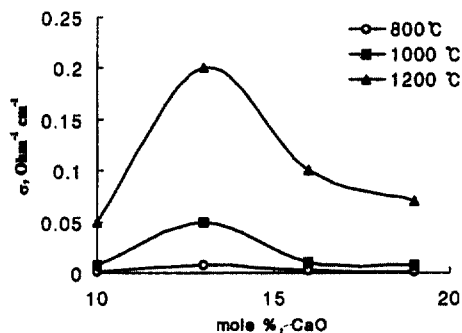


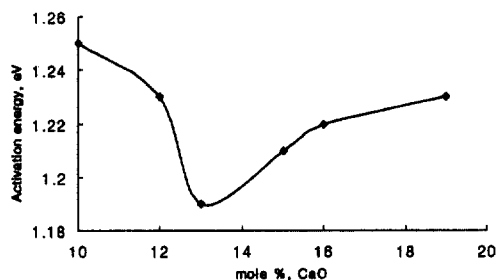
Fig. 4. (a) Conductivity vs. temperature for various compositions in the Y₂O₃-ZrO₂ system. Numbers near the curves denote mole percent of Y₂O₃. (b) conductivity isotherms, (c) activation energy.



(a)



(b)



(c)

Fig. 5. (a) Conductivity vs. temperature for various compositions in the CaO-ZrO₂ system. Numbers near the curves denote mole percent CaO, (b) conductivity isotherms, (c) activation energy.

oxygen vacancies which occurs at about 1100°C. Fig.5(b) shows conductivity composition isotherms at 800°C, 1000°C, and 1200°C, and 5(c) corresponding activation energy. Analogous to the system Y₂O₃-ZrO₂, the maximum conductivity occurs near the monoclinic-cubic solid-solution phase boundary.

3.5 Conductivity measurements at low oxygen partial pressure

Conductivity measurements were made by passing a constant current through the specimen and measuring the resistance with a bridge-type circuit. A specimen of composition with cubic phase structure (Y₂O₃)_{0.09}(ZrO₂)_{0.91} was tested at constant current levels of 0.50, 0.75, 1.0 and 10 mA dc. To eliminate thermoelectric effects, two measurements were obtained at each current level with the polarity being reserved in the second measurement. In each case, the original resistance value (~12 Ohms) was obtained.

The resistance vs. time data at the various current levels are plotted in Fig.6. Note that at currents of 0.75 mA or larger, the specimen resistance reaches a relatively constant value after a period of 1 h, whereas at 0.5 mA the resistance is still increasing. Extending the measurement period to 3 hours showed a continuously increasing resistance for a test current of 0.5 mA but a definite leveling of resistance for test currents of 0.75 mA or larger. The higher conductivities obtained with the larger currents are believed to be caused by reduction of Zr⁴⁺ to Zr³⁺, which would give rise to a mixed valence conduction mode. The oxidation potentials of Y³⁺ and Zr⁴⁺ indicate that Zr⁴⁺ would be more easily reduced than Y³⁺. The data presented in Fig. 6 were interpreted as follows.

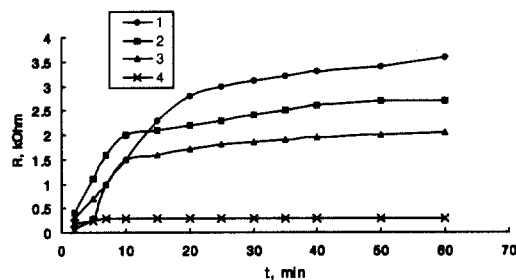


Fig. 6. Resistance vs. time at 1000 °C for a specimen of composition (Y₂O₃)_{0.09}(ZrO₂)_{0.91} at a low partial pressure of oxygen. Numbers above curve indicate direct current in milliamperes ; curve 1 - 0.5 mA, curve 2 - 0.75 mA, curve 3 - 1.0 mA, curve 4 - 10 mA.

Partial reduction of the specimen occurred in those tests which exhibited a resistance leveling and the degree of reduction in some manner associated with the impressed voltage which increases with increasing resistance to maintain a constant current level. The threshold voltage for reduction appears to be about 2.0 V. Thus, the resistance-time data for a constant current of 0.5 mA represents the case of negligible reduction. These data also suggest that the specimen had not attained equilibrium with surrounding atmosphere, since a static resistance level was not observed after a 4-hour test. However, a conservative estimate of the transference number for the oxygen ion can be obtained from the original specimen resistance (~12 Ohms) and the specimen resistance after a 1-hour test period (~3600 Ohms). Using these values and equation (2) gives an oxygen ion transference number ($t_{O^{2-}}$) greater than 0.99.

If reduction occurs in the high-current tests, it will manifest itself as both a weight loss and a change in specimen color. To have specimens

show these changes, several specimens were subjected to extreme reducing conditions of 50 mA in a depleted-oxygen atmosphere for a period of 2 hours. After this test, specimens were gray and on re-oxidation exhibited a weight gain of approximately 0.2%. This is too large weight loss to be attributed to reduction of impurities in the specimens and consequently must represent reduction of Zr^{4+} to Zr^{3+} .

Conductivity-temperature characteristics were measured in an inert atmosphere on a specimen, which had attained a constant conductivity level after subjected to a direct current of 10 mA for a period of 2 hours.

These data were shown in Fig. 7(a) along with the conductivity-temperature data obtained for the same specimen in air Fig. 7(b). The change in activation energy from 0.79 to 0.32 eV gives additional evidence for the presence of a different conduction mode.

4. CONCLUSION

The ionic conductivity of cubic solid solutions in the system $CaO-ZrO_2$ and $Y_2O_3-ZrO_2$ prepared by SHS was examined. For these systems, 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. Conductivity-temperature data obtained at 1000°C in atmosphere of low oxygen partial pressure (~ 10^{-40} atm) for $Y_2O_3-ZrO_2$ cubic solid solutions indicated that these materials could be reduced, and the degree of reduction would be related to the measuring electric field. At low impressed fields, no reduction was observed. Thus, these conductivity data give a transference number for the oxygen ion in $Y_2O_3-ZrO_2$ cubic solid solutions greater than 0.99.

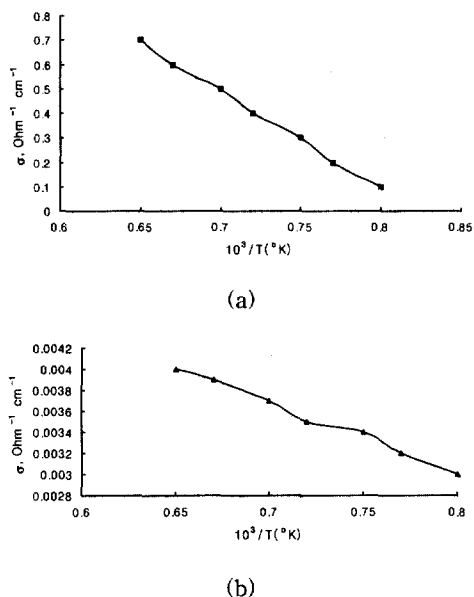


Fig. 7. Conductivity vs. reciprocal temperature for (a) 10 mA dc measurements in a low partial pressure of oxygen for a specimen of composition $(Y_2O_3)_{0.09}(ZrO_2)_{0.91}$, and (b) ac measurements in air.

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