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Yttrium-Oxide-Doped Single-Crystal Zirconium Oxide\***

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## Pressure Effect on Ionic Conductivity in Yttrium-Oxide-Doped Single-Crystal Zirconium Oxide

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### ABSTRACT

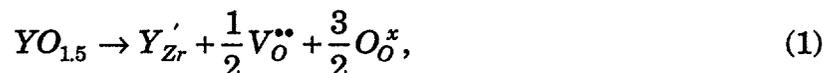
In this study, we investigated the effect of pressure on the ionic conductivity of a 9.5 mol% yttria-stabilized zirconia (YSZ) single crystal. The experiment was conducted in the elastic region, and the oxygen ion transport number was unity ( $t_{\text{ion}} > 0.99999$ ). A conventional four-probe DC method was used to measure the ionic conductivity of the rectangular-shaped sample under uniaxial pressures up to 600 atm at 750°C in air. Measured ionic conductivity decreased as applied pressure increased. Based on Henry Eyring's absolute reaction rate theory, which states that the calculated activation volume has a positive value ( $\Delta V^\ddagger = 2.08 \text{ cm}^3/\text{mol of O}^{-2}$ ) for oxygen ion transport in the fluoride cubic lattice, we concluded that the results we obtained could be explained by an oxygen ion transport mechanism. This mechanism can explain the fact that the interionic distance increases during oxygen ion transport from one unit cell to neighboring unit cells.

## 1. INTRODUCTION

### 1.1. Defects in Yttria-Stabilized Zirconia

Yttria-Stabilized Zirconia (YSZ) has a stable fluorite cubic structure consisting of  $Zr^{+4}$  at outer face-centered-cubic positions and  $O^{-2}$  at inner simple-cubic positions. Because the proposed defect model in metal oxide systems is similar, YSZ was chosen for our experiments.

When  $ZrO_2$  is doped with yttrium oxide ( $Y_2O_3$ ), a doubly ionized oxygen vacancy ( $V_O^{**}$ ) is produced. The defect reaction can be represented as<sup>1</sup>

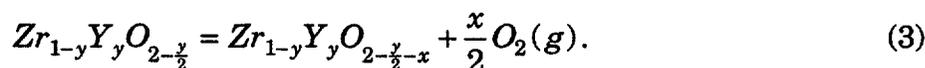


where  $Y'_{Zr}$  indicates yttrium on the zirconium site with a formal charge of -1, and  $O_O^x$  indicates normal oxygen on an oxygen site.

The formula for YSZ that contains  $y$  moles of yttria is  $Zr_{1-y}Y_yO_{2-y/2}$ . The electroneutrality condition is

$$[Y'_{Zr}] = 4[V_O^{**}], \quad (2)$$

where the bracket indicates the site fraction of each species. When the YSZ is in equilibrium with the surrounding oxygen, the overall solid/gas reaction is



Park and Blumenthal<sup>1</sup> have reported the temperature and oxygen partial pressure ( $P_{O_2}$ ) dependence of ionic and electronic conductivity for YSZ. The isothermal ionic conductivities are essentially constant over a wide range of  $P_{O_2}$

( $1-10^{-22}$  atm). The ionic transference numbers over this range are unity; therefore, the measured total conductivities are essentially ionic conduction in the YSZ.

## 1.2. Thermodynamics of Activated Process

The motion of ions can be described as an active jump process in the lattice, which can be described by adapting the absolute reaction rate theory proposed by Glasston and Eyring.<sup>2</sup> The Gibbs free energy  $G$  is most useful for describing an imperfect crystal, which can be regarded as a system whose state is defined by thermodynamic variables of the usual type (e.g.,  $P$ ,  $T$ , and chemical composition) plus a variable  $N$ , which represents the number of imperfections in the crystal. Thus,  $G$  has the form

$$G = \sum N_i \mu_i + N\mu, \quad (4)$$

where  $N_i$  and  $\mu_i$  are the number and chemical potential of atoms of type  $i$ , and  $\mu$  is chemical potential of the imperfection in question. When we assume that the system is ideal, Eq. 4 has the form<sup>3</sup>

$$\mu = RT \ln(N / N_a) + \Delta G^\ddagger, \quad (5)$$

where the first term on the right-hand side represents the entropy of mixing and  $N_a$  is the number of sites on which the atomic imperfection might be located. The second term on the right-hand side of Eq. 5 is called "free energy of activation;" it represents the increase in free energy of the crystal caused by the introduction of

an imperfection, not counting the entropy of mixing. The equilibrium concentration of defects in a simple case can be found by applying the condition  $\mu = 0$  to Eq. 5 to obtain:

$$N = N_a \exp(-\Delta G^\ddagger). \quad (6)$$

Equation 6 provides a link between theory and experiment. Diffusion and ionic conductivity, the commonly studied properties of solids that are sensitive to the existence of atomic defects, require not only that defects exist, but also that they move through the solid. The motion of defects is also an activated process because a defect has positions of minimum energy in the crystal lattice, and work is required to remove the defect from a position of minimum energy to the top of the energy barrier that separates it from another position of minimum energy. The thermodynamic description of the motion of a lattice defect over a free-energy barrier was given by Wert and Zener.<sup>3</sup> The rate for a defect to traverse a barrier is

$$1/\tau = \nu \exp(-\Delta G^\ddagger), \quad (7)$$

where  $\nu$  is the vibrational frequency of the defect in the direction that carries it over the barrier, and  $\Delta G^\ddagger$  is the free energy required to move the defect from a position of minimum energy to the top of the barrier. The expression for the diffusion constant of an interstitial or vacancy is  $D = fa^2/\tau$ , where  $f$  is a dimensionless geometrical factor,  $a$  is the lattice parameter, and  $\tau$  is given by Eq. 7.  $\Delta G^\ddagger$  can be derived from  $D$  by solving the relationships

$$\Delta G^\ddagger = RT \ln(D / fa^2\nu) \quad (8.1)$$

or

$$D = f a^2 v \exp(-\Delta G^\ddagger / RT), \quad (8.2)$$

and from the relationships  $\sigma_{ion} \propto Nz^2 D / RT$ , where  $z$  is electrical charge.<sup>4</sup> Therefore, the specific rate of ionic transfer is

$$\sigma_{ion} \propto \exp(-\Delta G^\ddagger / RT). \quad (9)$$

The free energy of activation  $\Delta G^\ddagger$  may be written as  $\Delta G^\ddagger - \Delta G_i$ , where these two quantities are the actual free energies in the activated and initial states, respectively. Substitution for  $\Delta G^\ddagger$  and differentiation with respect to pressure gives

$$d \ln \sigma_{ion} / dP = 1 / RT (\partial G_i / \partial P - \partial G^\ddagger / \partial P)_T \quad (10)$$

at constant temperature. It is known from thermodynamics that  $V \equiv (\partial G / \partial P)_T$  is equal to the volume, so that

$$d \ln \sigma_{ion} / dP = (V_i - V^\ddagger) / RT = -\Delta V^\ddagger / RT, \quad (11)$$

where  $\Delta V^\ddagger$  is an activation volume that can be obtained by measuring the dependence of the ionic conductivity of YSZ on pressure.

Several studies have investigated the cation transfer processes under applied pressure, such as alkaline cations in the  $\beta$ -alumina<sup>5</sup> and silver cations in silver ion conductors.<sup>6,7</sup> However, anionic conduction has not been investigated because of difficulties with the experimental method. In this study, we tried to

obtain information on the oxygen ion transfer process in an oxygen-ion conductor, a YSZ single crystal, by adapting Eyring's absolute reaction rate theory.<sup>2</sup>

## 2. EXPERIMENTAL APPROACH

The sample used in this study was single crystal of 9.5 mol % YSZ in the  $\langle 100 \rangle$  orientation. The sample was sliced from a single crystal boule and its surfaces were polished. The chosen experimental conditions were such that the ideal elastic region for mechanical behavior and an oxygen ion transport number of unity ( $t_{\text{ion}} > 0.99999$ ) should be present for oxygen ion-conduction. A conventional four-probe DC method was used to measure the ionic conductivity of a rectangular-shaped sample (13.55 mm x 4.00 mm x 4.42 mm) under uniaxial compression with a constant strain rate of  $1 \times 10^{-5} \text{ s}^{-1}$  up to 600 kg/cm<sup>2</sup> with a Model 1125 Instron (Instron, Canton, MA) at 750°C in air. The machine was fitted with a tungsten-mesh resistance furnace. The temperature was measured by a Pt/Pt+10% Rh thermocouple sheathed in Al<sub>2</sub>O<sub>3</sub> and positioned  $\approx 1$  mm from the surface of the sample. The experiment was performed at 750°C in air.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the potential drop voltages of YSZ as a function of applied load; it shows measured values, predicted values based on the geometry of the sample, and measured values corrected for geometry and calculated conductivity. The measured potential drop increased with applied load. If the ohmic values do not change, the measured values should decrease because length decreases as the

cross-sectional area becomes wider when load is applied, as shown by the dotted line in Fig. 1. The measured voltage drop values, corrected for the change in geometry with applied load are also shown in the figure. Poisson's ratio  $\nu$ , 0.3, was used in the calculation.<sup>8</sup> Figure 2 shows the load dependent fractional variation of the cell constant  $f_{K_{cell}}$ , length  $f_{length}$ , and cross-sectional area  $f_{area}$ , whereas Fig. 3 shows the conductivity values as a function of applied uniaxial pressure up to 600 atm. The ionic conductivity of the single-crystal YSZ decreased when applied pressure increased.

When we compare the effect of the present experimental conditions on the mechanical properties of 9.5 mol% YSZ of Cheong et al.,<sup>9</sup> we believe the present conditions should be in the pure elastic regime. Based on Henry Eyring's absolute reaction rate theory, which states that the calculated activation volume has a positive value ( $\Delta V^\ddagger = 2.08 \text{ cm}^3/\text{mol of O}^{2-}$ ) for oxygen ion transport in the fluoride cubic lattice, we concluded that the results we obtained could be explained by an oxygen ion transport mechanism. This mechanism can explain the fact that the interionic distance expands during oxygen ion transport from one unit cell to neighboring unit cells. When the oxygen ion moves from one position to another, the interatomic distance will be increased. According to the previous work on alkaline cations, such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ -substituted  $\beta$ -alumina, the  $\Delta V^\ddagger$  depends on ionic size; positive values for the large  $\text{K}^+$  ion, negative values are obtained for the small  $\text{Li}^+$  ion, and zero for the  $\text{Na}^+$  ion. This trend is consistent with the effect of steric hindrance during ionic transfer. The volume of activation for the  $\text{Ag}^+$  ion conductors, such as  $\text{Ag}_3\text{SBr}$ ,  $\text{b-Ag}_3\text{SI}$ , and  $\text{RbAg}_4\text{I}_5$ , is a negative value.<sup>6,7</sup>

The coulombic and elastic attractive forces between the individual  $Y'_{Zr}$  and  $V_{O}^{\bullet\bullet}$  defects lead us to postulate the existence of two associations, i.e.  $(Y'_{Zr}V_{O}^{\bullet\bullet})^{\bullet}$  and  $(Y'_{Zr}V_{O}^{\bullet\bullet}Y'_{Zr})^x$ . However, the expected random distribution of  $Y'_{Zr}$  suggests that the charged defect is more likely to occur. Recently, Manning et al.<sup>10</sup> determined the

vacancy trapping by the  $(Y_{Zr}'V_O^{**})^{\bullet}$  defect association at temperatures  $<500^{\circ}\text{C}$  by constructing Arrhenius plots of AC impedance data, in which the temperature dependence of oxygen ion conductivity was 0.26 eV. However, according to the Catlow et al.,<sup>11</sup> temperature below  $\approx 500^{\circ}\text{C}$  correspond to the region in which nearest neighbor Y-O and Zr-O peaks were formed in the magnitude of the Fourier transformed extended X-ray absorption fine structure (EXAFS) data for YSZ and monoclinic  $\text{ZrO}_2$ . Based on the EXAFS data, Catlow described the atomic distances between Y-O and Zr-O in the cubic YSZ and monoclinic  $\text{ZrO}_2$  as a function of temperature. The interatomic distance between Y-O and Zr-O in the YSZ becomes identical at temperatures above  $500^{\circ}\text{C}$ , and they claimed that the vacancies were more randomly distributed at high temperatures. Our experimental condition of  $750^{\circ}\text{C}$  is consistent with the interatomic distance proposed by Catlow et al. for single crystal YSZ.<sup>11</sup>

#### 4. CONCLUSIONS

The ionic conductivity of a single-crystal 9.5 mol% yttria-stabilized zirconia (YSZ) at uniaxial pressures up to 600 atm at  $750^{\circ}\text{C}$  in air decreased when applied pressure increased. Based on Henry Eyring's absolute reaction rate theory, which states that the calculated activation volume has a positive value ( $\Delta V^{\ddagger} = 2.08 \text{ cm}^3/\text{mol of O}^{2-}$ ) for oxygen ion transport in the fluoride cubic lattice, we concluded that the results we obtained could be explained by an oxygen-ion transport mechanism. This mechanism can explain the fact that the interionic distance expands during oxygen-ion transport from one unit cell to neighboring unit cells.

## ACKNOWLEDGMENTS

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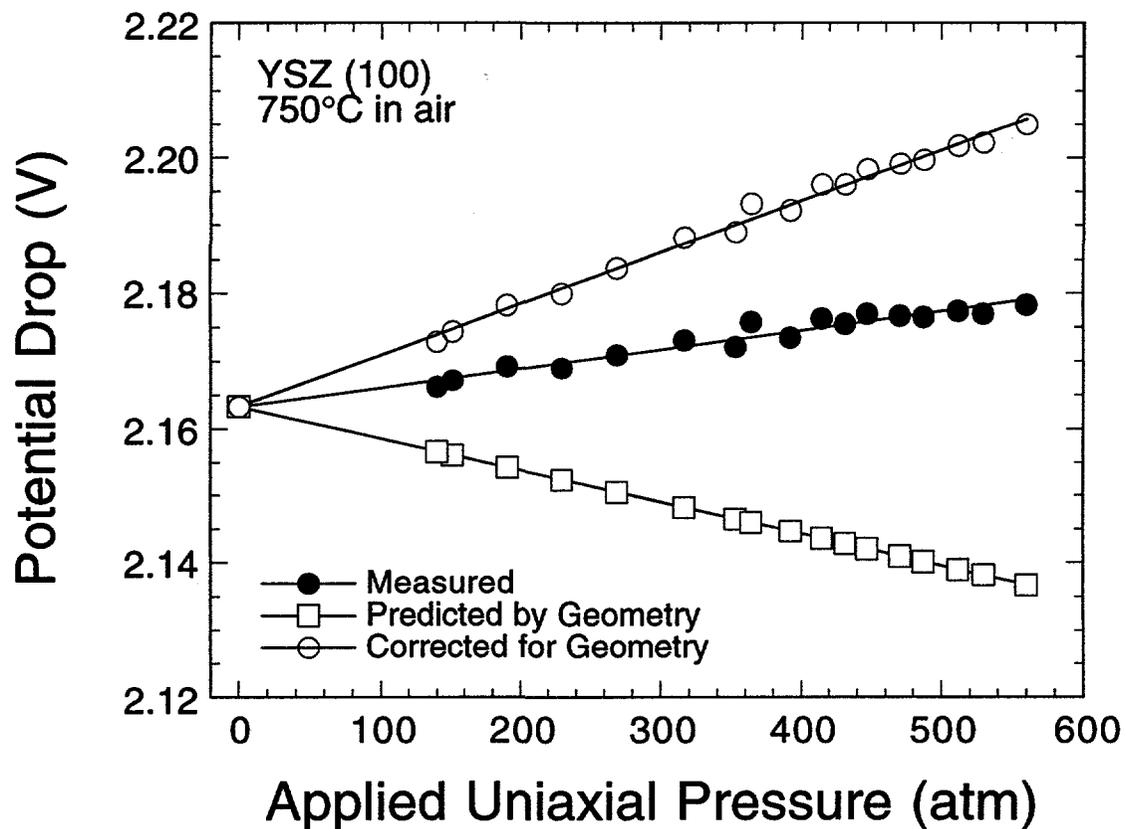


Fig. 1. Potential drop voltages of YSZ as a function of applied pressure; it shows measured values, predicted values based on geometry of the sample, and measured values corrected for geometry and calculated conductivity.

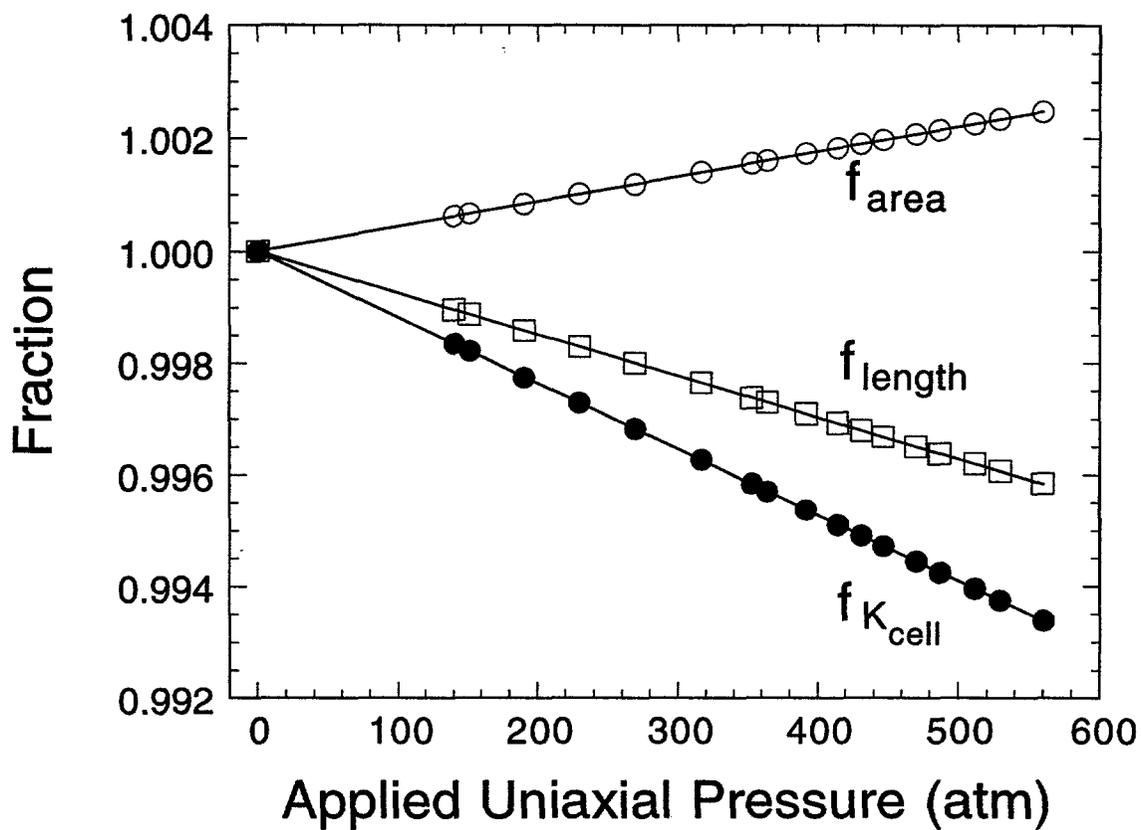


Fig. 2 Fractional variations of cell constant  $f_{K_{cell}}$ , length  $f_{length}$ , and cross sectional area  $f_{area}$  as a function of applied uniaxial load.

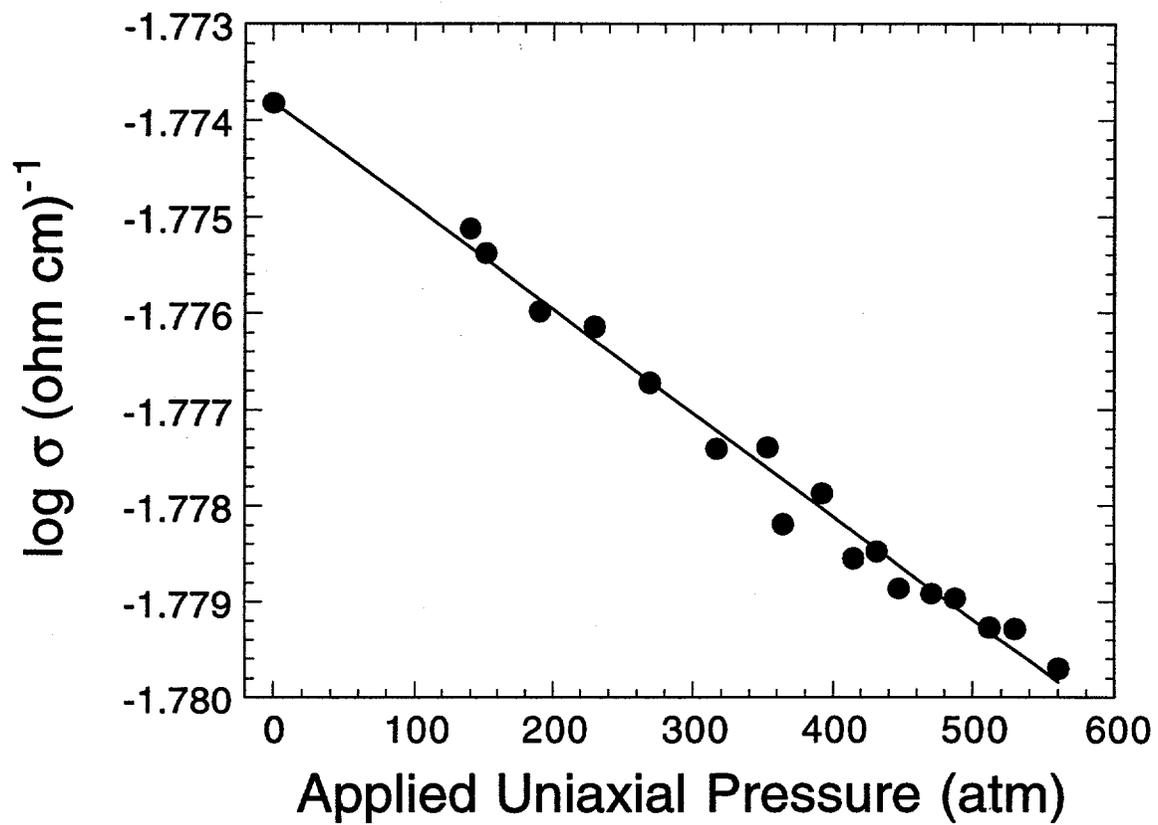


Fig. 3. Calculated conductivity values as a function of applied uniaxial pressure up to 600 atm.