

Electrical conductivity of $(\text{ZrO}_2)_{0.85}(\text{CeO}_2)_{0.12}(\text{Y}_2\text{O}_3)_{0.03}$

D. S. PATIL, N. VENKATRAMANI, V. K. ROHATGI

Plasma Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

A number of zirconia-based materials show promise as electrode materials in magnetohydrodynamic (MHD) generators. As a part of an exploratory programme to find suitable materials for graded electrode applications in MHD generators, partially stabilized and fully stabilized sintered ceramic materials are prepared and characterized. The oxygen ion transference number $t_{\text{ion}}(\text{O}^{2-})$ and electrical conductivity of this material are measured up to 1670 K in the oxygen partial pressure range 1 to 10^{-6} atm. The activation energies for conduction are determined. The electrical properties of this material are characterized by mixed conduction, ionic and electronic. The observed conductivity data are explained in terms of the defect equilibrium reactions between tetravalent Ce^{4+} and trivalent Ce^{3+} ions.

1. Introduction

Zirconia is one of the most refractory oxides, however, it has a destructive phase transition from monoclinic to tetragonal at about 1400 K. To stabilize it against this destructive transition, a cubic MO or M_2O_3 oxide is added, usually at >10 mol %. A cubic fluorite structure is generally found, as the metal ion of the additive (M) takes the place of the Zr^{4+} ion and oxygen ion vacancies are produced in the lattice to maintain the charge balance. This causes the conductivity to be almost wholly ionic.

Over the last 15 to 20 years, zirconia with additives of certain oxides has been the major candidate for electrode applications [1, 2]. Both pure and mixed zirconia as referred to above are ionic conductors.

In the late 1960s French as well as English workers [3, 4] studied the ZrO_2 - CeO_2 system, hoping to avoid the above drawbacks. The expectation was that cerium being a transitional metal could change its valency at reduced oxygen pressure, thus giving rise to enhanced electrical conductivity. However, more than 50% electronic conductivity is produced above 1000 K when CeO_2 becomes a major constituent. Measurement of ionic transference numbers in this system by Gokhsteyn [5] and confirmed by Rossing [6] indicates that total electronic conduction at high temperatures is reached for the composition 75 mol % CeO_2 -25 mol % ZrO_2 . The conductivity is due to hopping of electrons between Ce^{3+} and Ce^{4+} ions. It is necessary to consider the possible structure changes in the ZrO_2 - CeO_2 system at high temperatures. The phase diagram is given by Rossing and co-workers [6], and shows that single-phase binary solid solutions are obtained for compositions containing more than 75 mol % CeO_2 .

At high temperature the material loses a considerable amount of oxygen. The degrees of non-stoichiometry depends both on ZrO_2 : CeO_2 ratio and temperature. Due to the problems of CeO_2 evaporation the use of

CeO_2 -rich material is inhibited for high-temperature requirements (>2000 K), and ZrO_2 -rich materials are potential candidates for such requirements. Sintering of pure ZrO_2 with less than ~ 20 mol % CeO_2 is not possible as is evident from the phase diagram. Small addition of Y_2O_3 makes it possible to sinter this material with amounts of CeO_2 around 15 mol %. $(\text{ZrO}_2)_{0.85}(\text{CeO}_2)_{0.12}(\text{Y}_2\text{O}_3)_{0.03}$ has been proposed as a non-volatile material for graded electrode application in magnetohydrodynamic (MHD) generation [7]. It is well known that Y_2O_3 -stabilized zirconia is an ionic conductor. In the case of Y_2O_3 -doped CeO_2 the electronic conduction which is due to $\text{Ce}^{3+}/\text{Ce}^{4+}$ equilibrium is noticeable beyond 1673 K under a pure oxygen atmosphere. Thus an intermediate character is expected for the ternary solid solution ZrO_2 - CeO_2 - Y_2O_3 . The purpose of this work is to explain the electrical behaviour of the solid solution $(\text{ZrO}_2)_{0.85}(\text{CeO}_2)_{0.12}(\text{Y}_2\text{O}_3)_{0.03}$. The structure of this material is of the cubic fluorite type (i.e. AX_2 type) which is defined as simple cubic packing of X ions with A ions occupying the body-centre position of the alternate cube. The unit cell consists of eight such cubelets. In the present case Ce^{4+} ions are substituted in the lattice in place of Zr^{4+} ions and hence do not create any charge imbalance. However, then Y^{3+} ions are substituted for Zr^{4+} ions there is a charge imbalance in the lattice. In order to maintain charge neutrality, oxygen ion vacancies are formed in the crystal structure. These vacancies become mobile at high temperature and contribute to the ionic conductivity of this material.

2. Sample preparation, characterization and conductivity measurements

The starting materials were ZrO_2 , CeO_2 and Y_2O_3 powders and were of high purity ($>99.9\%$) and mesh size -325 , obtained from Indian Rare Earth Ltd (Bombay). Zirconia contains a low amount of hafnia (HfO_2), about 2.4 wt %. However, this would not

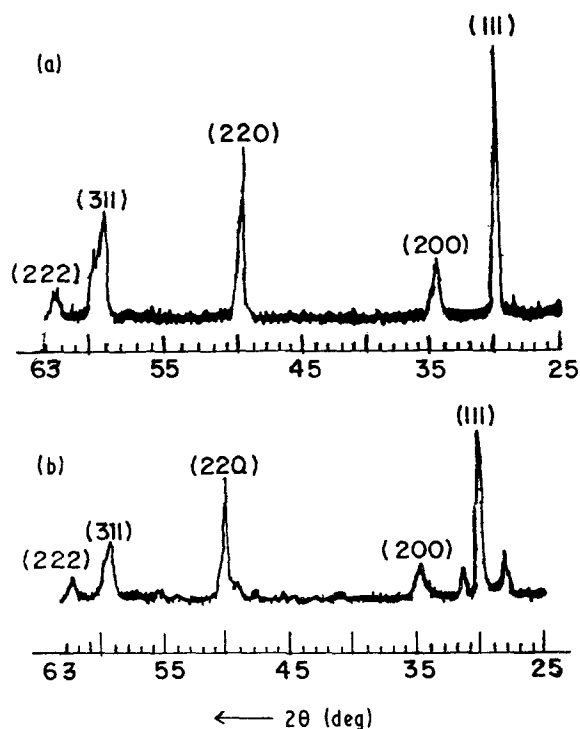


Figure 1 X-ray diffraction patterns of $(\text{ZrO}_2)_{0.85}(\text{CeO}_2)_{0.12}(\text{Y}_2\text{O}_3)_{0.03}$: (a) fully cubic, (b) partially stabilized.

affect the experimental results as the physical properties of the two oxides are quite similar [8]. The powders were accurately weighed, mixed in an agate mortar and were ball-milled for 24 h with ZrO_2 balls. A 1% polyethylene glycol solution was mixed to serve as a binder. The mixed powders were pressed into pellets of size 2.54 cm diameter \times 3 cm height at a pressure of 2 tonne cm^{-2} . Cap formation on the pellets was observed for pressures higher than this. The pellets were sintered at 1873 K for 4 h. For all specimens the porosity did not exceed 10%. The samples were characterized by the X-ray diffraction technique using $\text{CuK}\alpha$ radiation. Though it is stated that the addition of stabilizing Y_2O_3 ensures a cubic symmetry in the ternary solid solution $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3$ whatever the percentage of ceria [9], our observations indicate that formation of the fully stabilized structure depends on the processing parameters. From the X-ray diffraction pattern of the above sintered material it was found that it contains cubic solid solution and monoclinic zirconia, which can be called partially stabilized zirconia. Since the presence of the monoclinic phase in a stabilized zirconia enhances its hardness and thermal shock resistance [10, 11], which are very useful for various high-temperature applications, we have planned to study the electrical properties of this material also.

The prepared material was crushed, powdered, mixed, pelletized and further sintered at 1873 K for 30 h and again characterized by X-ray diffraction using $\text{CuK}\alpha$ radiation. It was found that it contained a single-phase cubic solution as shown in Fig. 1. The X-ray diffraction pattern was indexed and the cell constant was calculated from the high-angle line to minimize the error. It was found to be $a = 0.51623$ nm.

The electrical conductivity of both partially stabilized and fully stabilized zirconia samples cut from the sintered pellets was measured by the four-probe

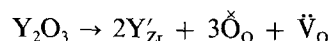
technique up to 1673 K and in the oxygen partial pressure range of 1 to 10^{-6} atm. In order to determine the contribution of the ionic part to the total conductivity, oxygen ion transport number measurements were done up to 1673 K on both partially and fully stabilized zirconia samples.

A platinum-rhodium furnace was used to provide a constant temperature zone of about 5 cm. The different oxygen partial pressure environments were provided using different gases like O_2 , N_2 and argon. The actual oxygen partial pressure of the gas flowing in the furnace was measured using a stabilized zirconia oxygen partial pressure gauge built in this laboratory. The temperature of the furnace was monitored using a Pt/Pt-13% Rh thermocouple kept at a distance of 2 to 3 mm from the sample. Measurements were taken at a temperature interval of 100 K. Readings were taken only after the sample attained equilibrium with its environment.

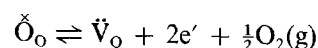
3. Theoretical considerations

The electrical conduction in $\text{ZrO}_2\text{-CeO}_2$ base systems can be explained in terms of various defect equilibrium reactions. To determine the defect structure, it is customary to write the possible defect equations, derive the P_{O_2} dependence of the conductivity and compare the measured pressure dependence with the predicted one. Thermodynamically each type of point defect is considered as an individual chemical species, and thus a defect equilibrium is represented by a form of chemical equation. Application of the law of mass action and the concept of the equilibrium constant together with the electrical neutrality condition enable one to calculate the equilibrium concentration of each type of defect as a function of the partial pressure of the components. For simplicity, infinitely dilute solutions of defects are considered so that activities can be equated to the concentrations. Kröger-Vink notations [12] will be used throughout this analysis.

The addition of Y_2O_3 to pure ZrO_2 provides oxygen vacancies in the crystal structure according to



The following equilibrium is always implied inside the crystal with the surrounding atmosphere:



The law of mass action can be applied to this equilibrium so that equilibrium constant is

$$k = [\dot{\text{V}}_{\text{O}}]n^2 P_{\text{O}_2}$$

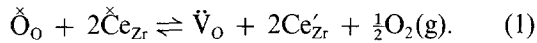
where [] denotes the concentration of the given species and n the electron concentration. In order to have electrical neutrality in the crystal the following relation between the concentration of defects is applicable.

$$p + 2[\dot{\text{V}}_{\text{O}}] = n + 2[\text{O}'_{\text{O}}] + [\text{Y}'_{\text{Zr}}]$$

where p is the concentration of holes.

It is well known that CeO_2 can be reduced to Ce_2O_3 at high temperature in a reducing atmosphere. It is also established that the reduction reaction $\text{CeO}_2 \rightleftharpoons \text{Ce}_2\text{O}_3 + \frac{1}{2}\text{O}_2(\text{g})$ is biased to the right above 1700 K

even in the presence of oxygen and when in solution with ZrO_2 [13]. In a reducing atmosphere at high temperature Ce^{4+} ions are reducible to Ce^{3+} . The redox reaction is



which shows that reduction of the cerium ion is also associated with the formation of doubly charged anion vacancies (\dot{V}_O) by the oxidation of anions (\ddot{O}_O) to oxygen gas, i.e. $O_2(g)$. The defect equilibrium reaction can be written as

$$k_1 = \frac{[\dot{V}_O][Ce'_{Zr}]^2 P_{O_2}^{1/2}}{[\ddot{O}_O][\ddot{Ce}_{Zr}]^2}$$

The electroneutrality condition demands that

$$[\dot{V}_O] = 2[Ce'_{Zr}]$$

and the above equation can be written as

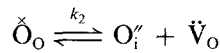
$$k_1 = \frac{2[Ce'_{Zr}][Ce'_{Zr}]^2 P_{O_2}^{1/2}}{[\ddot{O}_O][\ddot{Ce}_{Zr}]^2}$$

hence $[Ce'_{Zr}] \propto P_{O_2}^{-1/6}$.

Since the electronic part of the conduction is due to the hopping of electrons between \ddot{Ce}_{Zr} and Ce'_{Zr} ions

$$\begin{aligned} \sigma &\propto [Ce'_{Zr}] \\ &\propto P_{O_2}^{-1/6} \end{aligned} \quad (2)$$

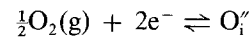
The following equations also hold inside the crystal:



$$np = k_3$$

$$e_v = e^- + e^+$$

where e^- is a valence electron and e^+ is an electron hole; also



$$[O'_i] = k_4 P_{O_2}^{1/2} n^2$$

For the oxygen-deficient zirconia material

$$[\dot{V}_O] = \frac{1}{2}[e^-] \gg [O'_i]$$

$$\frac{1}{2}[e^-] = \frac{1}{2}n = \frac{1}{2} \left(\frac{[O'_i]}{k_4 P_{O_2}^{1/2}} \right)^{1/2}$$

$$\frac{1}{2}n = \left(\frac{k_2}{4[\dot{V}_O]k_4 P_{O_2}^{1/2}} \right)^{1/2}$$

$$= \left(\frac{k_2}{4k_4(1/2)n P_{O_2}^{1/2}} \right)^{1/2}$$

$$\frac{1}{2}n = \left(\frac{k_2}{4k_4} \right)^{1/3} P_{O_2}^{-1/6}$$

$$n = \left(\frac{k_2}{2k_4} \right)^{1/3} P_{O_2}^{-1/6}$$

i.e.

$$n \propto P_{O_2}^{-1/6} \quad (3)$$

and hence

$$P \propto P_{O_2}^{+1/6} \quad (4)$$

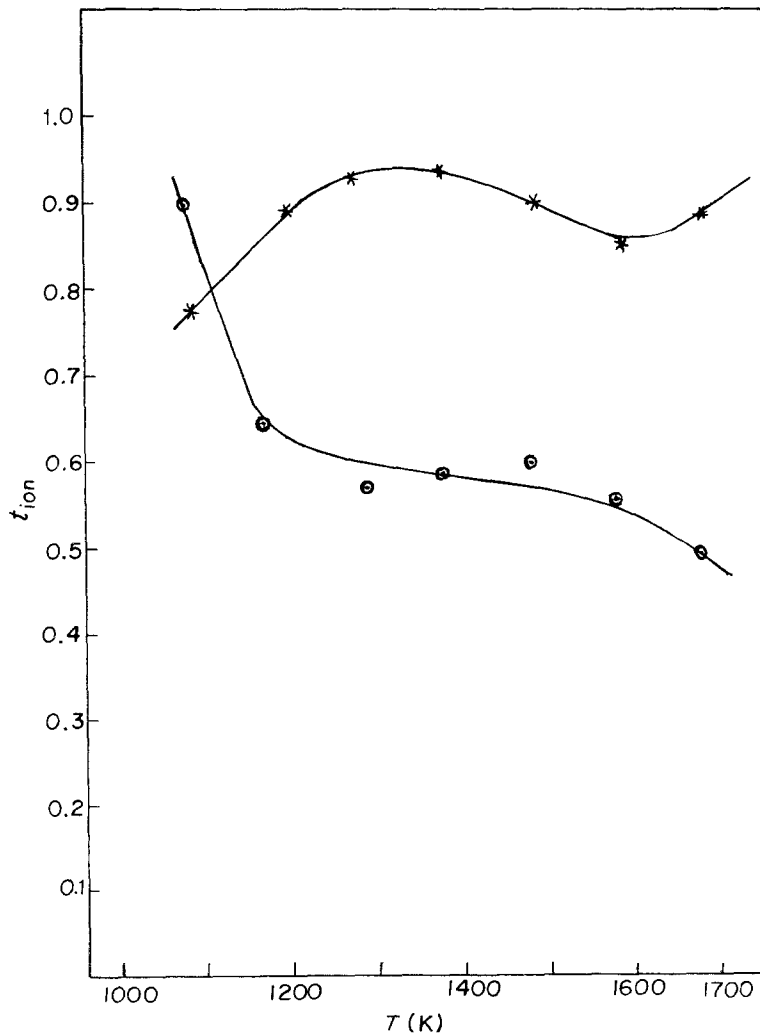


Figure 2 Variation of oxygen ion transference number with temperature for $(ZrO_2)_{0.85}(CeO_2)_{0.12}-(Y_2O_3)_{0.03}$: (*) partially stabilized, (⊙) fully stabilized.

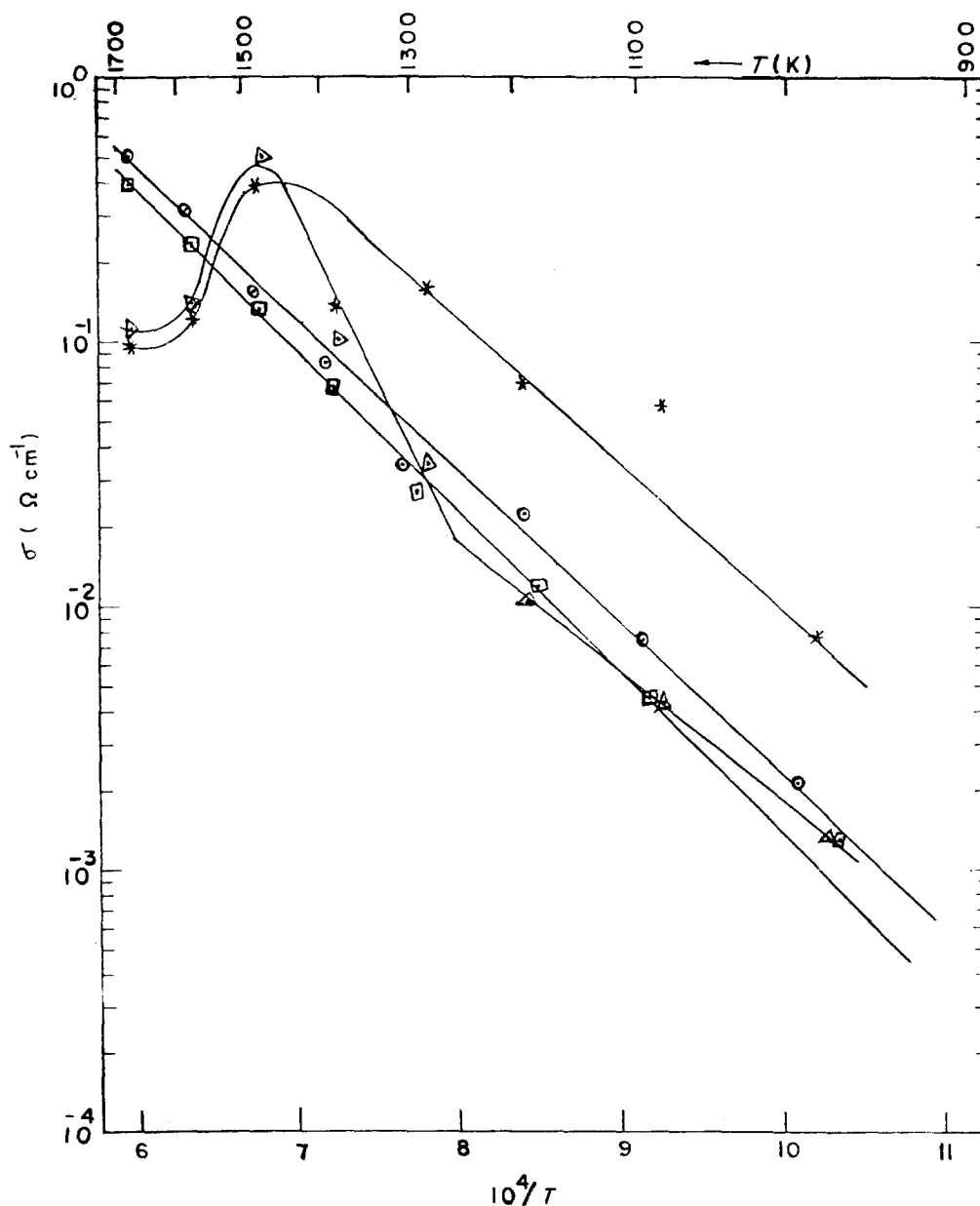


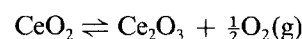
Figure 3 Electrical conductivity of partially stabilized $(\text{ZrO}_2)_{0.85}(\text{CeO}_2)_{0.12}(\text{Y}_2\text{O}_3)_{0.03}$. P_{O_2} (atm) = (*) 2.34×10^{-5} , (Δ) 1.26×10^{-4} , (\circ) 2.00×10^{-1} , (\square) 9.21×10^{-1} .

From the above derivation, it is clear that the various observed conductivity partial pressure dependences can be used to predict the sign of the charge carriers and also can be used to find out the various defects responsible for the conduction in that material.

4. Results and discussion

From Fig. 2 it is clear that the oxygen ion transference number t_{ion} for partially stabilized zirconia increases from a value of 0.77 at 1080 K to 0.93 at 1370 K and then decreases. The observed behaviour indicates that during the transition region (monoclinic \rightarrow tetragonal) the ionic transference number of the material increases. It is also evident that the material is predominantly ionic up to 1670 K. The observed transport number variations coincide with the conductivity variations as shown in Fig. 3 below. From Fig. 2 it is also clear that the oxygen ion transport number t_{ion} of the fully stabilized zirconia decreases from ~ 0.9 at 1073 K to ~ 0.5 at 1673 K. The decrease is systematic. Our results agree well with that of Akhopyov *et al.* [7], as they also got 50% electronic

conduction only above 1673 K. This can be explained on the basis of ceria reduction. At high temperature CeO_2 is reduced to Ce_2O_3 with the creation of oxygen vacancies [13]. The reduction reaction is



Because of this reaction Ce^{3+} ions are created in the lattice, and hence electronic conduction starts due to the hopping of electrons between Ce^{3+} and Ce^{4+} ions. Our observations confirm this, and also show that above 1673 K the conduction is likely to be predominantly electronic.

The comparison of the two materials (partially stabilized and fully stabilized) indicates that the presence of the monoclinic phase affects the $t_{\text{ion}}(\text{O}^{2-})$ behaviour of the material drastically. Whereas the partially stabilized material is predominantly ionic up to 1673 K, the fully stabilized material becomes increasingly electronic at temperatures around 1673 K.

The electrical conductivity variations for partially stabilized zirconia with temperature and oxygen

TABLE I Activation energies for conduction in $(\text{ZrO}_2)_{0.85}(\text{CeO}_2)_{0.12}(\text{Y}_2\text{O}_3)_{0.03}$.

Partially stabilized			Fully stabilized		
P_{O_2}	Temperature range (K)	Activation energy (eV)	P_{O_2} (atm)	Temperature range (K)	Activation energy (eV)
9.21×10^{-1}	Up to 1673	1.21	9.08×10^{-1}	Up to 1670	0.72
2.00×10^{-1}	Up to 1673	1.14	2.00×10^{-1}	Up to 1670	0.87
1.26×10^{-4}	Up to 1250	0.97	1.61×10^{-4}	Up to 1670	1.07
	1250 < T < 1480	2.47			
2.34×10^{-5}	Up to 1430	1.09	3.46×10^{-5}	Up to 1670	1.33

partial pressure are shown in Fig. 3. The conductivity is expected to be mixed. In the temperature and oxygen partial pressure range studied here, for a given temperature interval the conductivity can be expressed as a function of the temperature and activation energy by

$$\sigma_T = \sigma_{0T} \exp - \left(\frac{E(P_{\text{O}_2})}{KT} \right)$$

where $E(P_{\text{O}_2})$ is the activation energy for conduction and can be a function of P_{O_2} . The data of the present study show that under a reducing atmosphere the conductivity goes through a maximum value and then decreases.

The activation energies at various partial pressures and temperature intervals for partially stabilized and fully stabilized cubic zirconia are shown in the Table I. It is possible to postulate an exclusively anionic representation arising from the thermal disorder at low temperature and redox reaction (Equation 1) at high temperature which promote the vacancy concentration dependence on P_{O_2} . The controlling factor will be the thermal equilibrium association of anion vacancies with Ce'_{Zr} defects. The measured activation energies can be identified as required for the motion of oxygen vacancies. For calcia-stabilized zirconia the value of activation energy is ~ 1.2 eV and is identified as energy for the motion of the oxygen

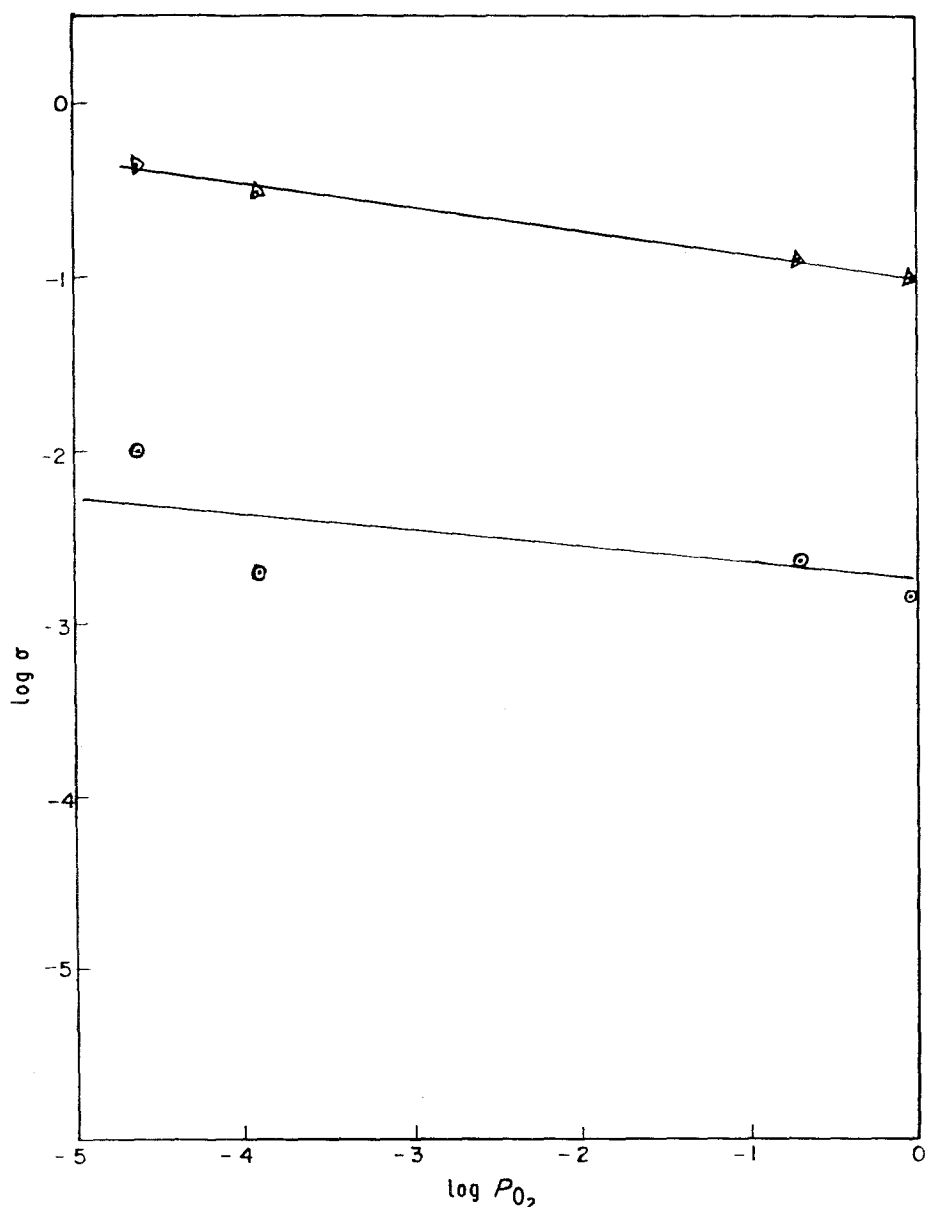


Figure 4 Log σ against log P_{O_2} plot for partially stabilized $(\text{ZrO}_2)_{0.85}(\text{CeO}_2)_{0.12}(\text{Y}_2\text{O}_3)_{0.03}$. (\odot) $T = 1000$ K (slope $-1/6.75$), (\triangle) $T = 1428$ K (slope $-1/5.44$).

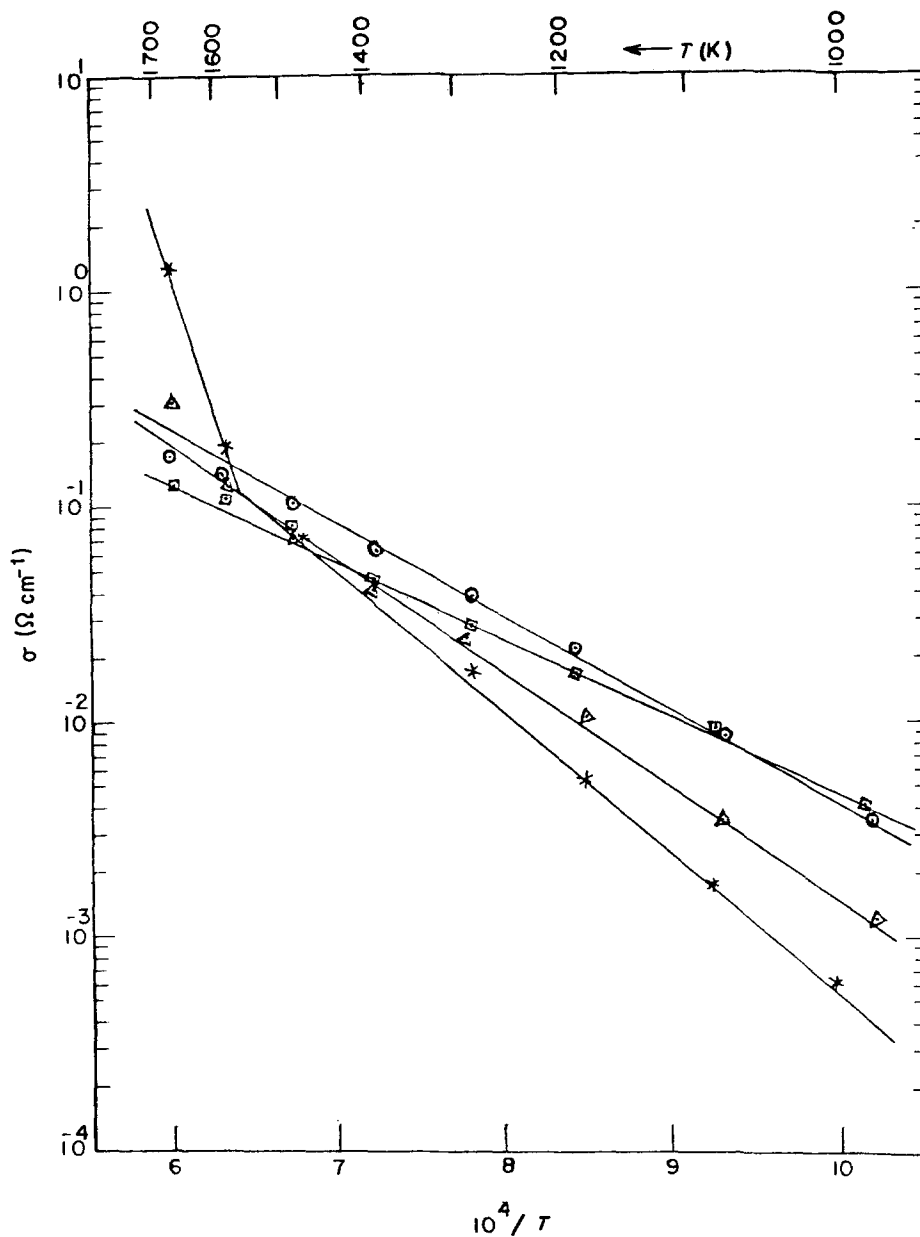


Figure 5 Electrical conductivity of fully stabilized $(\text{ZrO}_2)_{0.85}(\text{CeO}_2)_{0.12}(\text{Y}_2\text{O}_3)_{0.03}$. P_{O_2} (atm) = (*) 3.46×10^{-5} , (Δ) 1.61×10^{-4} , (\odot) 2.00×10^{-1} , (\square) 9.08×10^{-1} .

vacancies [14]. The measured activation energy is the sum of the dissociation energy and the energy for vacancy motion.

Under a reducing atmosphere the conductivity goes through a maximum value and then decreases. At high temperature and when P_{O_2} decreases, according to Equation 1, $\check{\text{Ce}}_{\text{Zr}}$ is reduced to Ce'_{Zr} with the formation of $\check{\text{V}}_{\text{O}}$. Conduction is then by hopping of the electrons between $\check{\text{Ce}}_{\text{Zr}}$ and Ce'_{Zr} ions, the conductivity being simply proportional to $[\check{\text{Ce}}_{\text{Zr}}][\text{Ce}'_{\text{Zr}}]$. When P_{O_2} decreases Reaction 1 is displaced to the right and the product $[\check{\text{Ce}}_{\text{Zr}}][\text{Ce}'_{\text{Zr}}]$ increase rapidly. The slope of the curve in the reducing atmosphere $P_{\text{O}_2} = 1.26 \times 10^{-4}$ atm and in the temperature interval 1290 to 1430 K corresponds to an activation energy of 2.47 eV. In this range the material might be becoming an intrinsic electronic conductor with the activation energy for conduction as $\frac{1}{2}E_g$ [15]. This temperature interval also corresponds to the monoclinic-tetragonal phase transition region for zirconia. The observed data suggest that this transition affects the conductivity behaviour

only in the reducing atmosphere and has no effect on the high P_{O_2} region.

At still higher temperature and lower P_{O_2} , a larger fraction of $\check{\text{Ce}}_{\text{Zr}}$ is reduced to the Ce'_{Zr} state. It follows that the electronic part of the conductivity should go through a maximum just as $[\check{\text{Ce}}_{\text{Zr}}][\text{Ce}'_{\text{Zr}}]$. At the maximum condition

$$[\check{\text{Ce}}_{\text{Zr}}] = [\text{Ce}'_{\text{Zr}}]$$

since

$$[\check{\text{Ce}}_{\text{Zr}}] + [\text{Ce}'_{\text{Zr}}] = [\text{Ce}]_{\text{total}}$$

The maximum value of σ is indeed observed. The electronic part of the conductivity does not always increase when P_{O_2} decreases. For $P_{\text{O}_2} < P_{\text{O}_2\text{max}}$ the conductivity rapidly decreases as the product $[\check{\text{Ce}}_{\text{Zr}}][\text{Ce}'_{\text{Zr}}]$ does. The conductivity behaviour at lower P_{O_2} suggests a form of controlled valency compensation [16] for which two possibilities can be postulated.

(a) Autocompensation of $\check{\text{Ce}}_i$ by association with

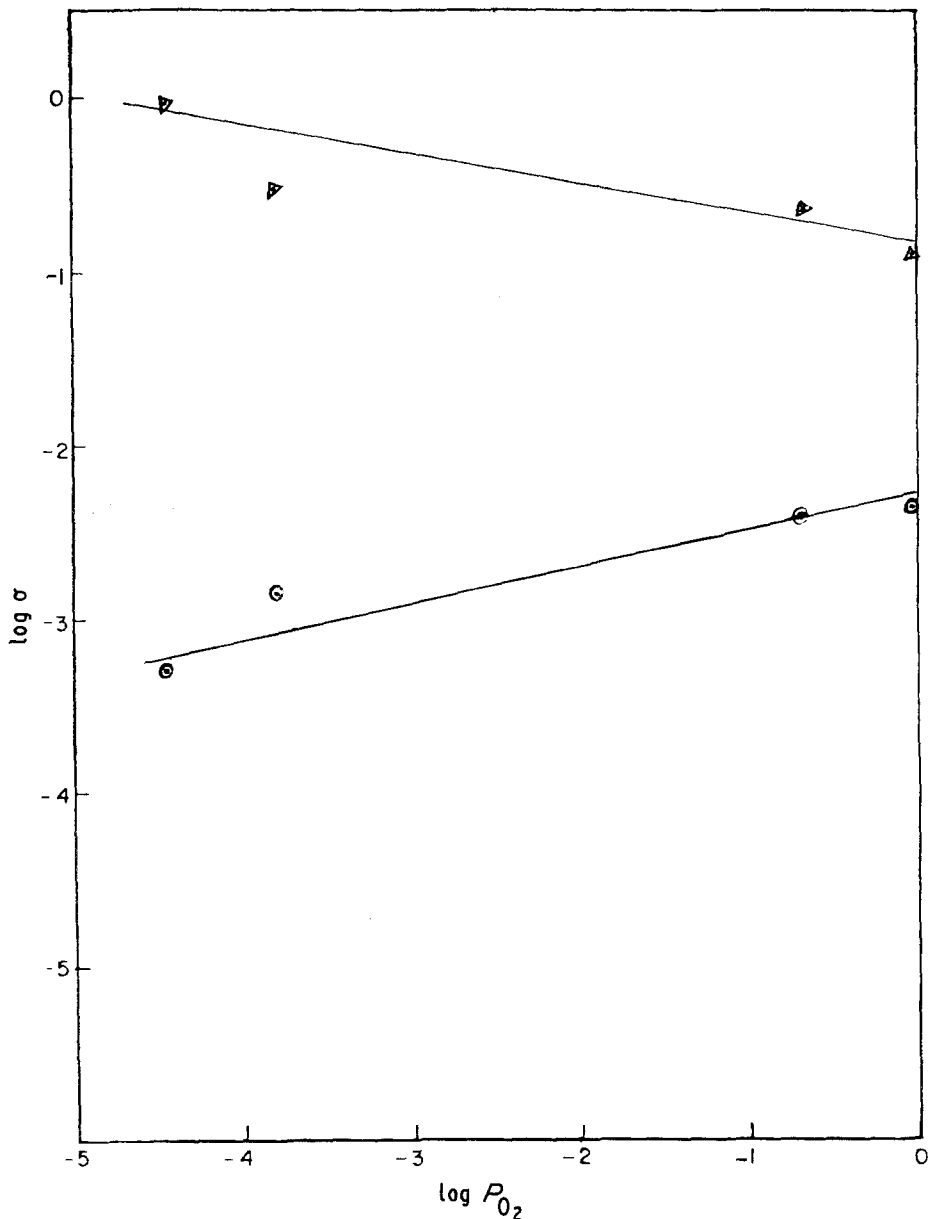
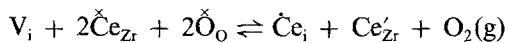
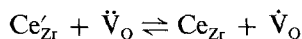


Figure 6 Log σ against log P_{O_2} plot for fully stabilized $(ZrO_2)_{0.85}-(CeO_2)_{0.12}(Y_2O_3)_{0.03}$. (○) $T = 1000$ K (slope 1/5.167), (△) $T = 1667$ K (slope -1/6.98).

Ce'_{Zr} , thereby inhibiting the conduction. Reduction of Ce_{Zr} is associated with the formation of univalent cerium interstitials [17] according to



(b) Trapping of the electrons from Ce'_{Zr} by anion vacancies according to



The log σ against log P_{O_2} curves at temperatures 1000 and 1667 K are shown in Fig. 4. The slopes of the curves are computed by the method of least squares and found to be -1/5.44 and -1/6.75, respectively. Since the conduction is mixed, it is doubtful whether the carrier concentration is high enough in the material studied to show strictly -1/6 dependence, as predicted by Equation 2. However, our computed values which are near to -1/6 confirm the tentative model described in the theoretical part.

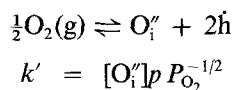
For fully stabilized zirconia the conductivity variation with temperature and oxygen partial pressures P_{O_2} is shown in Fig. 5. The activation energies for conduction are tabulated in Table I. The activation energies show a steep increase with reducing P_{O_2} . Since the conduction is mixed the calculated activation energy

represents the dissociation energy plus the energy for vacancy motion. The exhibited behaviour suggests that even a small amount of monoclinic phase changes the conductivity behaviour of the material.

For fully stabilized zirconia structure the increase in activation energy with reducing P_{O_2} can be explained as follows. At a given temperature, as P_{O_2} decreases, more and more Ce'_{Zr} sites are created and oxygen vacancies (\check{V}_o) agglomerate with (Ce'_{Zr}) as $\{(Ce'_{Zr})-(\check{V}_o)\}$. Since the concentration of Ce'_{Zr} increases with reducing P_{O_2} , it causes hindrance for the motion of \check{V}_o and hence the activation energy increases with reducing P_{O_2} . However, in a reducing atmosphere and at sufficiently high temperatures, there is a dissociation of agglomerates $\{(Ce'_{Zr})-(\check{V}_o)\}$ in addition to the formation of Ce'_{Zr} , and $[Ce'_{Zr}]$ exceeds $[\check{V}_o]$. Hence there is a steep rise in the conductivity. The conduction in this region is due to electron hopping between $\check{C}e_{Zr}$ and Ce'_{Zr} . The steep increase in the activation energy also suggests that the material might be becoming an intrinsic electronic conductor.

The log σ -log P_{O_2} plots at temperatures 1000 and 1670 K are shown in Fig. 6. The observed n values are 5.17 and -6.98, respectively, and according to Equations 3 and 4 suggest that at low temperature the

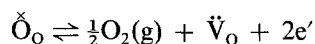
conductivity is p-type and at high temperature it is b-type. The observed behaviour can be explained in terms of defect equilibrium reactions. At lower temperature (i.e. ~ 1000 K) the material exhibits positive hole (p) conduction due to equilibrium between the oxygen in the surrounding atmosphere and interstitial oxygen ions O_i'' in the lattice. This can be shown as



where p represents the number of positive holes per unit volume. Electrical neutrality demands that $[O_i''] = \frac{1}{2}p$, so that

$$p \propto P_{O_2}^{1/6}$$

Since $P_{O_2}^{1/6}$ dependence of the conductivity is observed, it is clear that at low temperature the cubic structure encourages oxygen interstitials in the regular structure. However, since in partially stabilized zirconia this type of behaviour is not observed, it is clear that presence of the monoclinic phase does not allow oxygen interstitials as governed by the above equation. On the other hand at high temperature (~ 1670 K) oxygen vacancies are formed which are electrically compensated by electrons dissociated from vacant oxygen sites. The equilibrium reaction is



and

$$k'' = [\check{V}_O]n^2 P_{O_2}^{1/2}$$

where n is the number of excess electrons per unit volume. Again for charge balance

$$[\check{V}_O] = \frac{1}{2}n$$

and hence

$$n \propto P_{O_2}^{-1/6}$$

which explains the experimentally observed behaviour at higher temperature.

5. Conclusions

A study of the electrical conductivity of $(ZrO_2)_{0.85}-(CeO_2)_{0.12}(Y_2O_3)_{0.03}$ with temperature and oxygen partial pressure variations has allowed us to display the mixed conductivity (ionic and electronic) for this material. The conductivity depends on T as well as on P_{O_2} . The electronic character is due to the redox equilibrium between Ce^{3+} and Ce^{4+} ions at high temperature. Although the fully stabilized material becomes increasingly electronic at high temperatures, the par-

tially stabilized material remains predominantly ionic throughout the range studied.

From the above discussion, it can be concluded that in both partially stabilized and fully stabilized cubic zirconia, there is n-type conduction at high temperature. However, at lower temperatures the cubic structure gives p-type conduction as explained above; also a small amount of the monoclinic phase changes the conductivity behaviour drastically. The observed oxygen partial pressure dependences confirm the various defect equilibrium reactions inside the material as discussed earlier.

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