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IMPURITY EFFECTS ON ELECTRICAL CONDUCTIVITY OF Ce-TZP BY IMPEDANCE SPECTROSCOPY

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1. INTRODUCTION

Oxides of the fluorite structure, when doped with aliovalent cations, are oxygen-ion conductors over a wide range of temperatures and oxygen partial pressures, and therefore have been of interest for technologically useful devices such as oxygen sensors and solid oxide fuel cells. Fully- and partially-stabilized zirconia ceramics have been studied for these purposes [1].

Over the last few years a growing interest has been observed on tetragonal zirconia polycrystals stabilized with Y_2O_3 (Y-TZP) and CeO_2 (Ce-TZP) mainly due to their improved thermomechanical properties. Ce-TZP shows high toughness (6-30 $MPa.m^{1/2}$), low mechanical strength (7-10 GPa) and better stability compared to Y-YZP [2]. Concerning electrical properties, ceria-doped zirconia is a mixed conductor unlike most stabilized zirconia-systems which are ionic conductors. However, results obtained by different authors are not always consistent [3-6]. It was suggested [7] that silicon, a normally found impurity in this system, may produce the observed scatter in the conductivity results. In a recent study [8] it was shown that in the low ceria (up to 20 mol%) concentration range, the electrical conductivity is independent on the oxygen partial pressure. In addition, conductivity values do not greatly differs with composition, and thus, the dominant defect is not a function of dopant concentration. Moreover, the activation energy for conduction is about 1 eV, a value usually found in most zirconia-based ionic conductors.

In this study, ZrO_2: x mol% CeO_2 ($8 \le x \le 20$) have been prepared by the powder mixing technique to verify the effect of dopant concentration and aluminum impurity on the electrical conductivity measured by impedance spectroscopy. This technique is most suitable for a detailed study of impurity effects because it allows for separating the grain and grain boundary contributions to the total conductivity. For comparison purposes, specimens with a more homogeneous microstructure containing 12 mol% ceria have also been prepared by the coprecipitation technique.

2. EXPERIMENTAL

ZrO_2 (DK-1 type, Zirconia Sales) and CeO_2 (>99%, IPEN) were mechanically mixed (Turbula model T2C) in ethanol using alumina as milling media. Cylindrical pellets have been prepared by uniaxial and cold isostatic pressing. Sintering has been carried out in air at 1500 °C for 1 h.

For coprecipitated specimens, $ZrOCl_2.8\ H_2O$ (99.9%, BDH) and $Ce(NO_3)_3.6\ H_2O$ (>99.5%, IPEN) were used as starting materials. Calcination of the dried powder has been accomplished at 600 °C for 1 h. Pressing has been carried out in a similar way as for the mixed powder. Sintering has been performed at 1500 °C for 2 h.

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Several techniques have been used for powder and sintered ceramics characterizations. Metallic impurity contents have been obtained by inductively coupled plasma (ICP). Apparent densities have been determined by the water displacement method. Phase composition was verified by X-ray diffractometry (Philips model 3710, X'Pert MPD) using a Ni filtered Cu K_α radiation. Lattice parameters have been calculated using Si as internal standard. Impedance spectroscopy measurements have been carried out in a HP 4192A LF impedance analyzer. Pt paste (Demetron 308A) has been applied on opposite faces of specimens and baked at 800 °C to be used as electrode material. Measurements have been done in the 340 °C to 580 °C temperature range.

3. RESULTS AND DISCUSSION

Metallic impurity contents determined in the precursor materials are similar to those found in most commercial powders. Cerium nitrate presents a relatively high (0.15 wt%) silicon content.

The apparent densities lie between 92% and 96% of the theoretical density (T. D.) for samples prepared by the powder mixing technique and 98% T. D. for coprecipitated specimens.

X-ray diffraction patterns show both monoclinic and tetragonal reflections for specimens with up 10 mol% CeO_2 whereas for higher ceria content it is observed only the tetragonal diffraction peaks. Lattice parameters determined in powder patterns using Si as internal standard are in close agreement with reported values. For the ZrO_2 12 mol% CeO_2 specimen the tetragonality ratio is c/a=1.02.

Sintered specimens prepared by the powder mixing technique exhibit similar average grain sizes (~2 μm) and secondary phases rich in silicon, aluminum and calcium. The coprecipitated specimen, on the other hand, has a more homogeneous distribution of grain sizes with an average value of 500 nm and low porosity [9].

Impedance diagrams are shown in Figure 1 for 12 mol% CeO_2 specimens prepared by the powder mixing (a) and coprecipitation (b) techniques. Two semicircles are clearly seen in these plots. The high frequency is assigned to grain resistance and the intermediate frequency semicircle is a result of the blocking of charge carriers by grain boundaries. The segment of an arc in the low frequency region indicates that the electric conduction is predominantly ionic. The center of both semicircles lies below the real axis as usual for zirconia - based ceramics. All specimens prepared by the powder mixing technique exhibit similar impedance diagrams. The comparatively low contribution of grain boundaries in these specimens are probably related to a scavenger effect of Al impurity in analogy to that found in Y-doped ZrO_2 . These samples have been contaminated during the mixing step.

Arrhenius plots show no change in the slops in the temperature range of measurements. Activation energies calculated for grain and grain boundary contributions and conductivity values at 600 °C are shown in table 1.

Values of conduction activation energies are typical of ionic transport in zirconia-based solid electrolytes. Increasing ceria concentration resulted in a decrease in the grain conductivity.

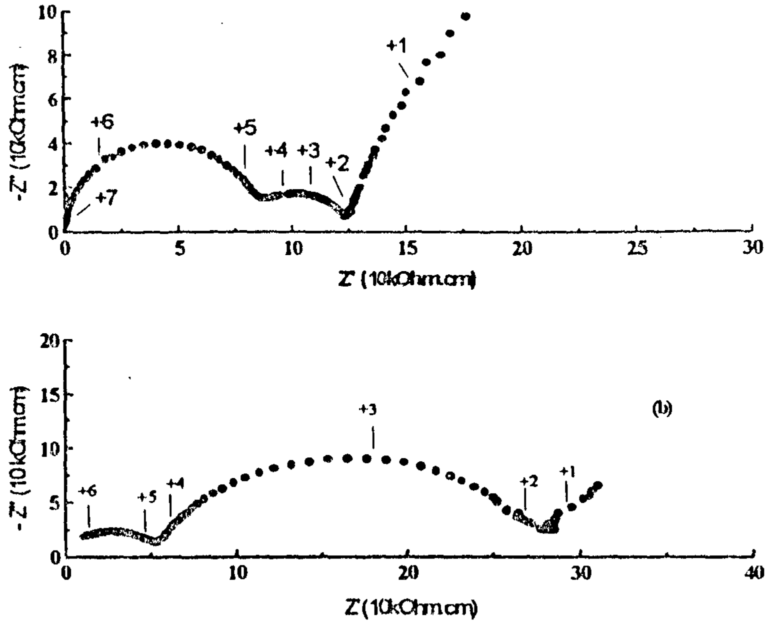

Fig. 1: Impedance diagrams for ZrO_2:12 mol CeO_2 prepared by the powder mixing (a) and coprecipitation (b) techniques. Measurement temperatures: (a) 500 °C and (b) 490 °C.

Table 1: Values of conduction activation energies for grain (E_g) and grain boundaries (E_{gb}). Estimated conductivity (σ) values at 600 °C. 12C=coprecipitated specimen.

mol% CeO_2	E_g(eV)	E_{gb}(eV)	σ (10^{-5} $S.cm^{-1}$)
10	1.00	1.33	9.10
12	1.01	1.28	7.00
15	1.01	1.31	5.32
20	1.04	1.30	4.21
12C	1.04	1.25	13.2

4. CONCLUSIONS

Zirconia-ceria ceramics present ionic conductivity in the tetragonal phase field. Grain and grain boundary components of the total conductivity decrease slightly with increasing ceria concentration. Aluminum contamination resulted in a scavenger effect reducing the grain boundary resistivity.

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