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Ionic conductivity of zirconia based ceramics from single crystals to nanostructured polycrystals

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Abstract

The ionic conductivity of yttria doped zirconia polycrystals was measured by impedance spectroscopy in the temperature range 240–800°C in air and compared to that of a single crystal. Polycrystals with 4% mol yttria and an average grain size of 300 nm have exhibited a grain boundary contribution to the ionic conductivity (value and activation energy) higher than the volume measured in the 9.5% mol yttria doped zirconia single crystal. The bulk conductivity of polycrystals with 9.5% mol yttria was found to be smaller than the single crystal one. The interpretation of the grain boundary contribution to ionic conductivity, measured by impedance spectroscopy, is revisited. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical conductivity; Grain boundaries; ZrO_2

1. Introduction

Stabilised zirconia has been actively investigated as an oxide ion conductor for application to oxygen sensors, solid oxide fuel cells (SOFC) and electrochemical oxygen pumps.[1,2] Consequently several approaches have been taken to improve the electrical properties of the stabilised zirconia in the last few decades. Although stabilisation of ZrO_2 with Y_2O_3 (the material is stabilised in the cubic phase and noted YSZ) does not yield the highest conductivities,[3] yttrium is the most frequently used dopant because of availability and cost. 9.5% mol Y_2O_3 doped ZrO_2 is generally considered as having an ionic conductivity close to the optimum.[3,6–8] In stabilised zirconia, oxygen–ion conduction takes place by the movement of oxygen ions via oxygen vacancies.

This work has been performed to try to increase the ionic conductivity of yttria doped zirconia at temperatures as low as 300°C. This material could be used to make oxygen pumps designed to purify gases unstables up to 300°C or oxygen sensors for motor cars.

It is well established that ionic conductivity of polycrystalline zirconia depends on the microstructure and grain boundaries have a large controlling importance for electrical properties.[3–5] For this reason we have used polycrystals doped with 9.5 and 4 mol% Y_2O_3, with different grain sizes (1 μm and 300 nm) and compared the results to those obtained on 9.5% mol Y_2O_3 doped ZrO_2 single crystals.

2. Experimental

The studied samples are noted M, P1, P2. M is monocrystalline zirconia $ZrO_2 + 9.5\%$ mol Y_2O_3, grown by skull melting, and provided by the Baikowski Chimie company. P1 is polycrystalline zirconia $ZrO_2 + 9.5$ mol% Y_2O_3, and P2 is polycrystalline zirconia $ZrO_2 + 4$ mol% Y_2O_3. P1 and P2 were prepared by sintering submicronic powders of ZrO_2 and Y_2O_3. After sintering, the average grain size was, 0.9 μm and 300 nm, respectively. P1 density was found around 84% of the theoretical density, P2 was close to the full density. The cubic phase has been identified by X-ray diffraction

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analysis in M and P1. P2 also contains a little of tetragonal phase.

Over a wide range of temperature the ionic conductivity of stabilised zirconia is independent of oxygen partial pressure over several orders of magnitude.[2,9] For that reason, the electrical conductivity has been measured under air by complex impedance spectroscopy. Because of the versatility of this method in the analysis of polycrystalline materials,[10,11] it has been used in the range 5 to 13×10^6 Hz, with a function analyser Hewlett Packard 4192A, in the temperature range 240–800°C.

The samples had either a parallelepipedic or a cylindrical shape. A layer of silver paint was deposited on the edges to assure good electrical contact between the sample and the Pt electrical junctions. The platinum wires and the sample are held in contact by a weak mechanical pressure controlled by a screw/spring system and transmitted by an alumina rod.

3. Results and discussion

3.1. Monocrystalline zirconia

A typical impedance spectrum obtained at the temperature $T=300$°C is represented in Fig. 1. It is an arc of circle, characteristic of the bulk conductivity. The values of the bulk conductivity as a function of the temperature have been plotted in Fig. 2.

These results are in agreement with previous conductivity data[7,13] obtained for a single crystal ZrO_2 9.5 mol% Y_2O_3. The conductivities we have obtained are well represented by

$250 < T < 504$°C

$$\sigma(\mathrm{Scm}^{-1}) = \frac{1.65\ 10^7}{T}\exp\left(-\frac{104.21\mathrm{kJ/mol}}{\mathrm{RT}}\right)$$

$504 < T < 800$°C

$$\sigma(\mathrm{Scm}^{-1}) = \frac{1.11\ 10^6}{T}\exp\left(-\frac{83.95\mathrm{kJ/mol}}{\mathrm{RT}}\right)$$

The fact that the activation energy depends on the temperature range has been already observed[7,13] and is consistent with the assumption that two different oxygen diffusion mechanisms act in the material. Oxygen vacancies ($V_O^{\bullet\bullet}$) are the majority defects in zirconia ; they are created by charge compensation with yttrium, according to the reaction

$$Y_2O_3 \xrightarrow{ZrO_2} 2Y'_{Zr} + V_O^{\bullet\bullet} + 3O_O^x$$

and form complexes $(Y_{Zr'}, V_O^{\bullet\bullet})^{\bullet}$.[12,14] As suggested by oxygen tracer selfdiffusion measurements,[12,13] at temperatures higher than about 500°C, many vacancies and complexes are free and mobile, while at lower temperatures they are interacting strongly, forming domains in which the migration enthalpy of vacancies and their local concentration are higher.

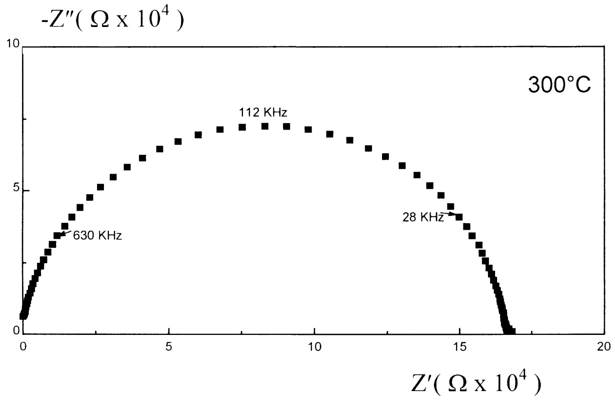

Fig. 1. Impedance spectrum at 300°C of the single crystal M ($ZrO_2+9.5$% mol Y_2O_3). It characterizes the volume.

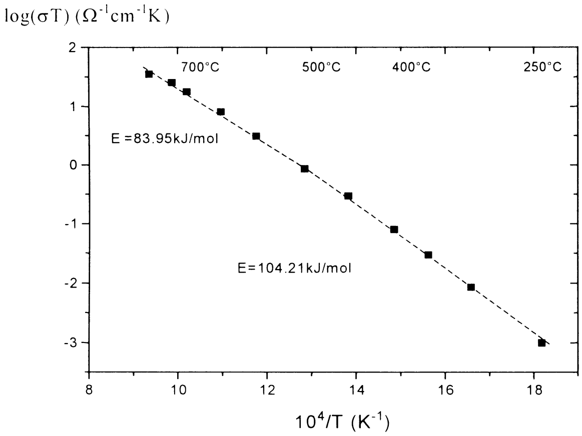

Fig. 2. Arrhenius diagram for the bulk conductivity of the sample M (single crystal of $ZrO_2+9.5$ mol% Y_2O_3).

3.2. Polycrystalline zirconia

Measurements have been performed between 240 and 800°C in air. Typical spectra of polycrystalline electrolytes were obtained by impedance spectroscopy measurements carried out in ZrO_2–Y_2O_3 samples as shown in Figs. 3 and 4.

Following the literature,[10,11,15] the bulk properties are associated with the semi-circular arc at higher frequencies, whereas the grain boundary properties are associated with the semi-circular arc at lower frequencies.

From the analysis of the impedance spectra, both the bulk and the grain-boundary contributions to the conductivity as a function of temperature (see Figs. 5 and 6) turned out to be reproducible. The results obtained are well represented by:

P1 (ZrO_2 + 9.5% mol Y_2O_3):

$340 < T < 520°C$,

$$\sigma(\mathrm{Scm}^{-1}) = \frac{4.36\ 10^6}{T}\exp\left(\frac{-107.10\mathrm{kJ/mol}}{\mathrm{RT}}\right)$$

$240 < T < 700°C$,

$$\sigma_{\mathrm{Gb}}(\mathrm{Scm}^{-1}) = \frac{1.30\ 10^6}{T}\exp\left(\frac{-110.96\mathrm{kJ/mol}}{\mathrm{RT}}\right)$$

$520 < T < 700°C$,

$$\sigma(\mathrm{Scm}^{-1}) = \frac{3.89\ 10^4}{T}\exp\left(\frac{-91.67\mathrm{kJ/mol}}{\mathrm{RT}}\right)$$

P2 (ZrO_2 + 4% mol Y_2O_3):

$240 < T < 455°C$,

$$\sigma(\mathrm{Scm}^{-1}) = \frac{1.25\ 10^6}{T}\exp\left(\frac{-89.74\mathrm{kJ/mol}}{\mathrm{RT}}\right)$$

$240 < T < 560°C$,

$$\sigma_{\mathrm{Gb}}(\mathrm{Scm}^{-1}) = \frac{1.37\ 10^8}{T}\exp\left(\frac{-104.21\mathrm{kJ/mol}}{\mathrm{RT}}\right)$$

$455 < T < 800°C$,

$$\sigma(\mathrm{Scm}^{-1}) = \frac{8.95\ 10^3}{T}\exp\left(\frac{-61.75\mathrm{kJ/mol}}{\mathrm{RT}}\right)$$

The volume conductivity of the polycrystalline 9.5% mol yttria doped zirconia (P1) and of the single crystal with the same composition (M), exhibit a similar change in the activation energies but the absolute values of the conductivity are different: $\sigma(P1) < \sigma(M)$. Thus, the same mechanism is controlling the oxygen transport in the single crystal and in the polycrystal bulk but the assumption that the microstructure is not influencing the bulk transport properties determined by the first circle is no longer valid. To describe the impedance behaviour of this sample it is necessary to consider that the volume resistance has increased. This change is probably due in this case to an increase of the real geometrical factor which is related to the microstructure (porosity here, reducing section).

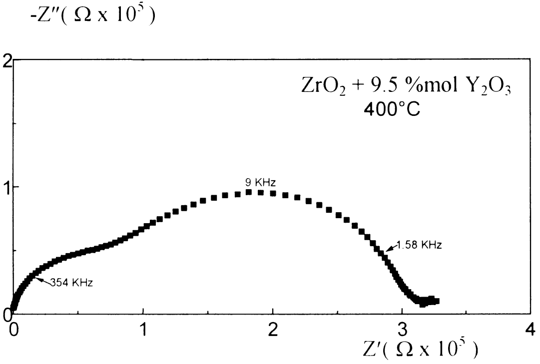

Fig. 3. Impedance spectrum of P1 at 400°C in air.

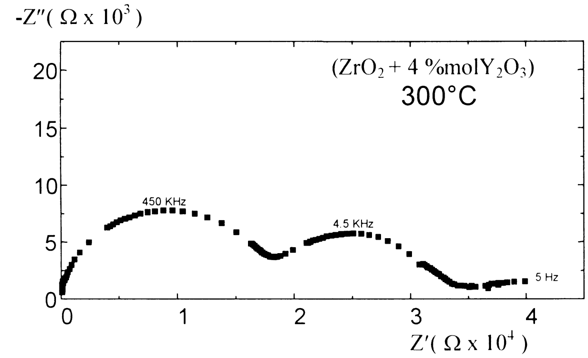

Fig. 4. Impedance spectrum of P2 at 300°C in air.

The grain boundary transport properties are expected to be controlled by the same type of point defects as those present in the bulk. Nevertheless, it may be pointed out that the grain boundary activation energy seems to be constant in the explored temperature range and higher than in the bulk. That leads to consider that only one mechanism is taking place in the grain boundaries. The concentration of defects being higher in the grain boundaries than in the bulk, they interact and form complexes in the whole temperature range explored and the mechanism found in volume at the lowest temperatures studied is probably also operating in the grain boundaries.

An important result shown in Fig. 7 is that the sample P2 has the highest values of conductivity in both the bulk and the grain boundaries, in the main part of the investigated temperature range. It also exhibits the lowest values of the activation energy. This result is not easy to explain if one takes into account the composition of P2 does not correspond to the optimum dope concentration (8–10 mol% Y_2O_3) as shown by previous authors[3–5] (according to the electrical compensation by

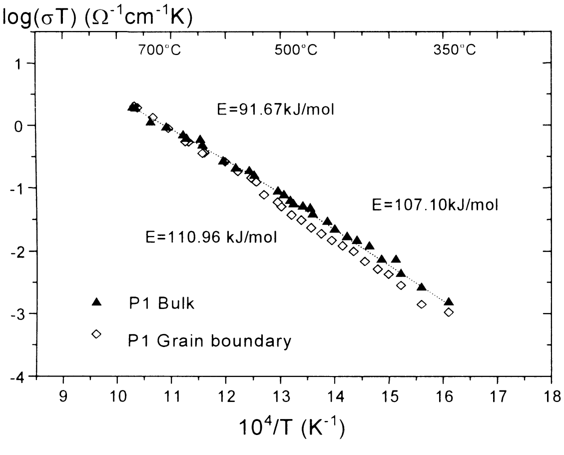

Fig. 5. Arrhenius diagram for ionic conductivity in P1 samples (ZrO_2 + 9.5 mol% Y_2O_3).

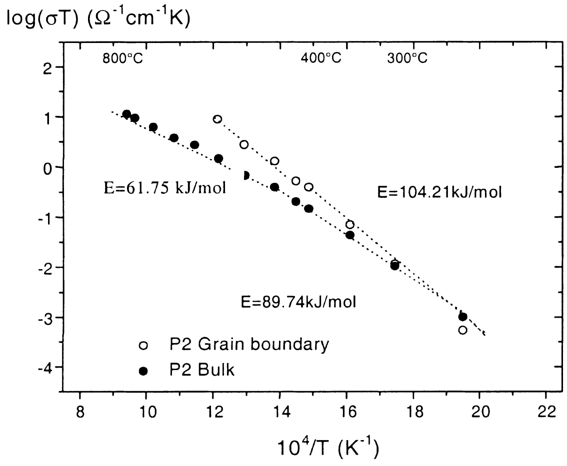

Fig. 6. Arrhenius diagram for ionic conductivity in P2 samples ($ZrO_2 + 4$ mol% Y_2O_3).

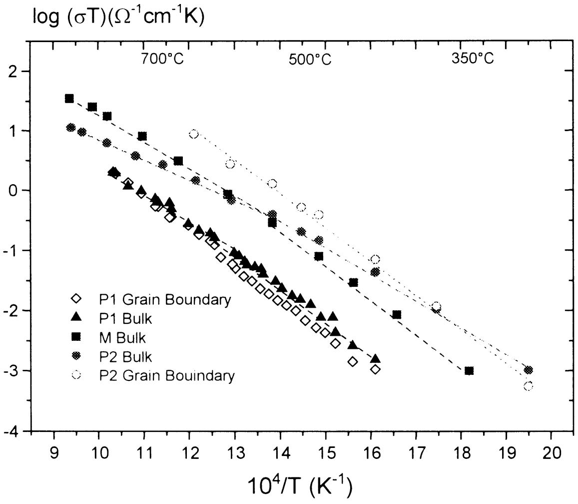

Fig. 7. Comparison of ionic conductivities of monocrystalline and polycrystalline samples of this study in an Arrhenius diagram.

yttrium, the concentration of oxygen vacancies is expected to be lower in P2 than in M and P1). An important feature comes from the fact that P2 is a nanomaterial (large value of interface area; due to the grain boundaries in the present case) and the influence of grain boundary diffusion in such a sample with small grain size, is specially important. The increase of the bulk conductivity of P1 compared to M could be due to a short circuit effect of the grain boundaries. The contribution of grain boundaries to the conductivity has indeed two components: one is detected by the second semi-circle in the impedance spectra and is mainly due to a "barrier effect" (in the P2 sample the resistance introduced by the barriers is less than the bulk resistance, perhaps due to the "sloping effect" proposed by Fleig and Maier[15]). The other component is included in the "bulk impedance semi-circle"; it corresponds to a short-circuiting effect (a resistance in parallel, leading to an apparently lower resistance of the bulk). A consequence is an effective lower activation energy of the bulk conductivity contrary to what is expected for such compositions.

4. Conclusion

The grain boundary contribution to the ionic conductivity has been found higher than the volume one in a typical case of 4% mol yttria doped zirconia with 300 nm grain size. Both are, in the main, part of the investigated temperature range, higher than the ionic conductivity measured on single crystals containing 9.5% mol Y_2O_3 which is generally considered as close to the optimum concentration.

Once again the electrical transport properties are demonstrated to be related to the microstructure. It seems that nanomaterials could exhibit an important increase in the ionic conductivity of the yttria doped zirconia at temperatures below 500°C. The competition between the grain boundary short-circuit effect, the sloping effect and the barrier effect is not easy to quantify to predict which is the best nanomaterial.

Acknowledgements

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References

1. Minh Nguyen, Q., Ceramic fuel cells. *J. Am. Soc.*, 1993, **76**(3), 563–588.
2. Science and technology of zirconia. *Advances in Ceramics*, vol. 3, ed. A. H. Heuer and L. W. Hobbs. American Ceram. Soc., Columbus, OH, 1981.
3. Baumard, J. F., Papet, P. and Abelard, P., Transport properties of ZrO_2-based solid electrolytes. In *Science and Technology of Zirconia III, Advances in Ceramics*, 1986, 24b, pp. 779–788.
4. Bonanos, N., Drennan, J., Stlotwinski, R. K., Steele, B. C. H. and Butler, E. P., Characterisation of grainboundaries in ceramic ionic conductors using A.C. electrical technics. *Silic. Ind.*, 1985, **9–10**, 127–132.
5. Miyayama, M. and Yanagida, H., Dependence of grain-boundary resistivity on grain-boundary density in yttria-stabilised zirconia. *J. Am. Ceram. Soc.*, 1984, **67**, C194–C195.
6. Kilner, J. and Steele, B. C. H. In *Nonstoichiometric Oxide, Materials Science Series*, ed. T. O. Sorensen. Academic Press, New York, 1981, pp. 233.
7. Filal, M., Petot, C., Mockchah, M., Château, C. and Carpentier, J. L., *Solid State Ionics*, 1995, **80**, 27–35.
8. Monty, C., Boussetta, H., Rouanet, A., Sibieude, F., Amdouni-Cheikh, A., Madani, A., Roucau, C., Snoeck, E., Brun, N., Georgescu, C., Lelievre, D., Piticescu, R. R., Carry, C. P., Begin-Colin, S., Gandhi, A. S. and Jayaram, V., Zirconia based

nanomaterials: elaboration, characterisation and transport properties. *Inzynieria Materialowa Journal,* 1999 al.

9. Patterson, J. W., Borgen, E. C. and Rapp, R. A., Mixed conduction in $Zr_{0.85}Ca_{0.15}O_{1.85}$ and $Th_{0.85}Y_{0.15}O_{1.85}$ solid electrolytes. *J. Electrochemical. Soc.*, 1967, **114**, 752–758.
10. Bauerle, J. E., Study of solid electrolytes polarisation by a complex admittance method. *J. Phys. Chem. Solids*, 1969, **30**, 2657–2670.
11. Macdonald, J. R., Interpretation of AC Impedance Measurements in Solids. In *Superionic Conductors*, ed G. D. Mahan and W. L. Roth. Plenum Press, 1987, pp. 81–97.
12. Solmon, H., *Autodiffusion de l'oxygène, du zirconium et de l'yttrium dans la zircone cubique stabilisée par l'yttrium.* Thèse, Univ. Paris VI, 1992.
13. Solmon, H., Monty, C., Filal, M., Petot-Ervas, G. and Petot, C., Ionic transport properties of yttria-doped zirconia. *Solid State Phenomena*, 1995, **41**, 103–112.
14. Schouler, E., Kleitz, M. and Desportes, C., *J. Chem. Phys. (Paris)*, 1973, **70**, 1309.
15. Fleig, J. and Maier, J., A finite element study on the grain boundary impedance of different microstructures. *J. Electrochem. Soc.*, 1998, **145**, 2081–2089.