Journal of the European Ceramic Society **19** (1999) 765–768
© 1999 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(98)00308-2 0955-2219/99/$ - see front matter

Structure and Electrical Behaviour in Air of TiO_2-doped Stabilized Tetragonal Zirconia Ceramics

Francisco Capel,[a] Carlos Moure,[a] Pedro Durán,[a]* Agustín R. González Elipe[b] and Alfonso Caballero[b]

[a]Instituto de Cerámica y Vidrio (CSIC), Departamento de Electrocerámica, 28500 Arganda del Rey, Madrid, Spain
[b]Instituto de Ciencia de Materiales de Sevilla (CSIC-Univ. Sevilla), P.O. Box 1115, 41080 Sevilla, Spain

Abstract

The data obtained from X-ray absorption (XANES and EXAFS) were used to provide information on the environment of Ti atoms in the TiO_2-doped stabilized tetragonal zirconia solid solutions. The electrical conductivity of the Ti–YTZP ceramics decreases with increasing TiO_2 content. From the EXAFS results, i.e. Ti–O and Ti–Ti distances, the decrease in conductivity was attributed to the formation of two kinds of cation–oxygen vacancy associations with different diffusion dynamics, leading to a decrease in the global concentration of moving oxygen vacancies. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: tetragonal zirconia, electrical properties.

1 Introduction

Ceramic oxides exhibiting both oxygen ionic and electronic conductivities are commonly known as mixed-conductors and are attracting interest as candidates to be used as electrodes (mainly anodes) in several applications as for example in SOFC, oxygen separation membranes and electrocatalysts for the partial oxidation hydrocarbons.[1–3] In the last decade the research efforts have been concentrated mainly in the TiO_2-doped stabilized cubic zirconia (TiO_2–YSZ), and several papers with contradictory results have been published.[4–7]

Although the TiO_2–YSZ solid solutions have been quite well studied, it cannot be said with respect to the TiO_2-doped stabilized tetragonal zirconia (TiO_2–YTZP) and, thus, only a few papers have appeared in the literature. For example, the stability range of the TiO_2–YTZP in the ZrO_2–Y_2O_3–TiO_2 system and the electrical behaviour of TiO_2 (1–30 mol%)-doped tetragonal zirconia (1–4 mol% Y_2O_3) compositions were reported.[8] Recently,[9] it was also reported that, contrarily to the above author results, the electrical conductivity of Y–TZP (2 mol% Y_2O_3) increased with TiO_2 content (4–13 mol%) in the temperature range 800 to 1000°C at an oxygen partial pressure of 0·1 Pa.

In the present work, using the X-ray absorption spectroscopy (XAS) and mainly the XANES and the EXAFS spectra, and the a.c. complex impedance spectroscopic electrical conductivity measurements in air, we attempt to achieve a better understanding of the role of titania (5 and 10 mol%) on the ionic conductivity of yttria-doped tetragonal zirconia (3 mol% Y_2O_3) solid solutions.

2 Experimental Procedure

The samples of Y–TZP containing 5 and 10 mol% TiO_2 were prepared as detailed elsewhere.[10] X-ray absorption spectra were collected at the LURE facility in Orsay (France) by using synchrotron radiation from the DCI storage ring at 1·85 GeV, with an average current of 250 mA. A double-crystal monochromator Si (111) and a total yield detector was used to collect the spectra. X-ray absorption spectra for Ti–YTZP samples were collected at liquid nitrogen temperature in the transmission mode. Spectra were taken within the energy range of primary photons between 4950 and 5050 eV, around the Ti–K absorption edge. The spectra were analyzed with the software package reported elsewhere.[11] The coordination numbers (CN), distances (R), and Debye-Waller values (σ) were extracted by a least-squares fitting procedure that makes use of the theoretical phases and amplitudes,[12] previously calibrated with the appropriate references.

---

*To whom correspondence should be addressed. Fax: +34-91-8700550; e-mail:pdurah@icv.csic.es

The temperature dependence of electrical conductivity measurements were carried out using an impedance analyzer (Hewlet Packard model 4192A) in the frequency range of 5 Hz to 13 MHz, in air in the temperature range of 200 to 800°C. For comparison, an undoped Y–TZP sample sintered in the same conditions as for TiO_2–YTZP ones, was used.

3 Results and Discussion

The XANES spectra of Ti–YTZP solid solutions (5 and 10 mol% TiO_2) are presented in Fig. 1 along with those of some reference compounds. The most informative features of the spectra are the pre-edge peaks below the energy of the Ti–K absorption edge. This was located at 4972·8 eV which is somewhat higher than that of metallic Ti. Thus, a relatively sharp pre-peak located at almost the same energy (4967·5 eV) but with different intensity for 5 Ti–YTZP and 10 Ti–YTZP samples, was present in the XANES spectra. Pre-peaks can be ascribed to 1s→3d transitions and can give information on the coordination environment of the absorbing Ti atom.

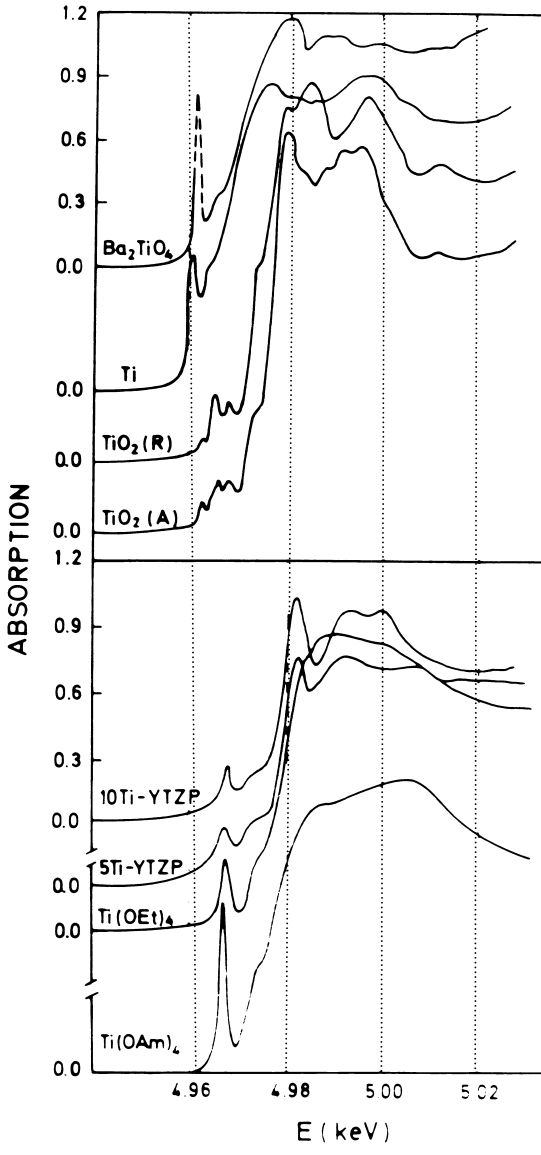

Fig. 1. Ti K-edge XANES spectra of the Ti–YTZP solid solutions along with those of reference compounds.

For example, the octahedrally-coordinated compounds (rutile or anatase) are characterized by several pre-edge peaks of low intensity, the central one at an energy of 4968 eV. Compounds with tetrahedrally coordinated Ti as Ba_2TiO_4 and Ti-$(OAm)_4$, exhibited a strong pre-edge peak at an energy of 4967 eV, and $Ti(OEt)_4$ with Ti ions five-fold coordinated in a square-pyramidal arrangement showed a relatively sharp pre-edge peak at 4967·5 eV. From Fig. 1 it seems reasonable to state that the intensity, shape and energy position of the pre-edge peak of the Ti–YTZP solid solutions matches well, in principle, with that of the $Ti(OEt)_4$ compound with Ti ions in a square-pyramidal environment.

On the other hand, the XANES spectra also display above the Ti–K absorption edge a prominent peak located at slightly different energies, 4983·6 and 4983·2 eV for 5 Ti–YTZP and 10 Ti–YTZP solid solutions, respectively. The characteristics of these post-edge peaks can also indicate a change in the geometrical arrangement of the scattered ions in the Ti environment. Such a suggestion is consistent with previous XANES studies on Ti–YTZP solid solutions.[13]

The normalized Ti–EXAFS for 5 Ti–YTZP and 10 Ti–YTZP solid solutions were plotted as χ(k), not shown here, and the Fourier transformation of such radial structure peaks yields a filtered χ(k) signal, which was used to study the local structure around Ti cations. Utilizing amplitude and phase shift derived from the TiO_2 model system, a quantitative analysis of the first Ti–O shell, as shown in Fig. 2 was performed. The decreasing of the amplitude of Ti–EXAFS with increasing TiO_2 indicates also an increased distortion of the cation network in the tetragonal zirconia lattice.

Quantitative fitting results, as shown in Table 1, for the Ti–O and the Ti–Ti shels and the Debye–Waller factors, can also indicate that Ti^{4+} ions do not randomly substitute Zr^{4+} lattice sites according to a statistical process. With these data, and assuming that Y^{3+} cations will not be associated with oxygen vacancies,[14] we assume a competition of Ti^{4+} and Zr^{4+} ions for the oxygen vacancies, leading to the formation of two cation–oxygen vacancy (Zr–Vö and Ti–Vö) associations with different vacancy diffusion dynamics. Given that the Zr–O distance is higher than Ti–O, then the oxygen vacancies associated to the Zr^{4+} cations will diffuse much faster.

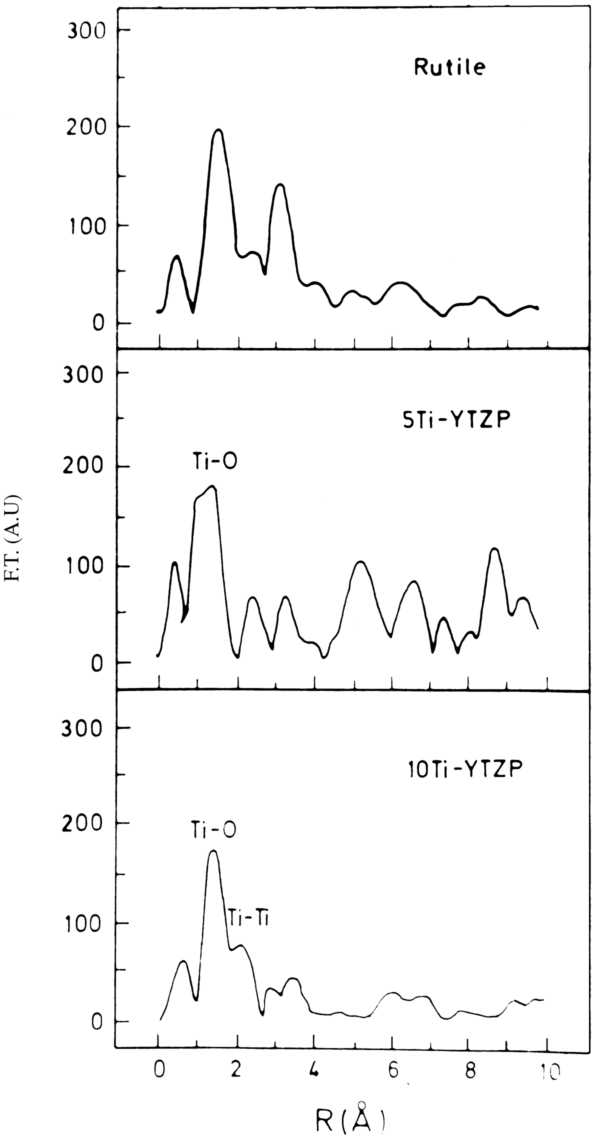

Fig. 2. Fourier transform magnitude for Ti in TiO_2, 5 Ti–YTZP and 10 Ti–YTZP.

Table 1. Fitting results of Ti EXAFS for Ti-doped tetragonal zirconia samples

First shell	*M–O*	*R (Å)*	*C N*	$\Delta\sigma^2$(Å$^2\times10^{-3}$)
STi–YTZP	Ti–O	1·73	2·6	0·1
	Ti-O	1·87	3·8	0·1
10 Ti–YTZP	Ti–O	1·88	2·2	0·1
	Ti–O	2·05	1·6	0·1
Second shell				
10 Ti–YTZP	Ti–Ti	2·81	2·2	0·1

Figure 3 shows the Arrhenius plot for the temperature dependence of the electrical conductivity for Y–TZP, 5 Ti–YTZP and 10 Ti–YTZP samples. A general trend to decrease the electrical conductivity with increasing titania content can be observed. These results can be explained on the basis of the Ti^{4+} ions local environments, and we state that the oxygen vacancy diffusion on the octahedrally coordinated sublattice (Zr^{4+}–Vö) is faster than on the square based pyramidal fivefold sublattice (Ti^{4+}–Vö). This gives rise to a lower global mobility of the oxygen vacancies, which is supported by a higher activation energy for the conduction process in TiO_2–YTZP solid solutions. Furthermore, the formation of Ti^{4+} clusters will give rise to the formation of more complex –Vö–Ti–Vö–Ti– associations in which the oxygen vacancies will be trapped, thus resulting in a decrease of the concentration of moving oxygen vacancies and, therefore, in a decrease of the ionic conductivity.

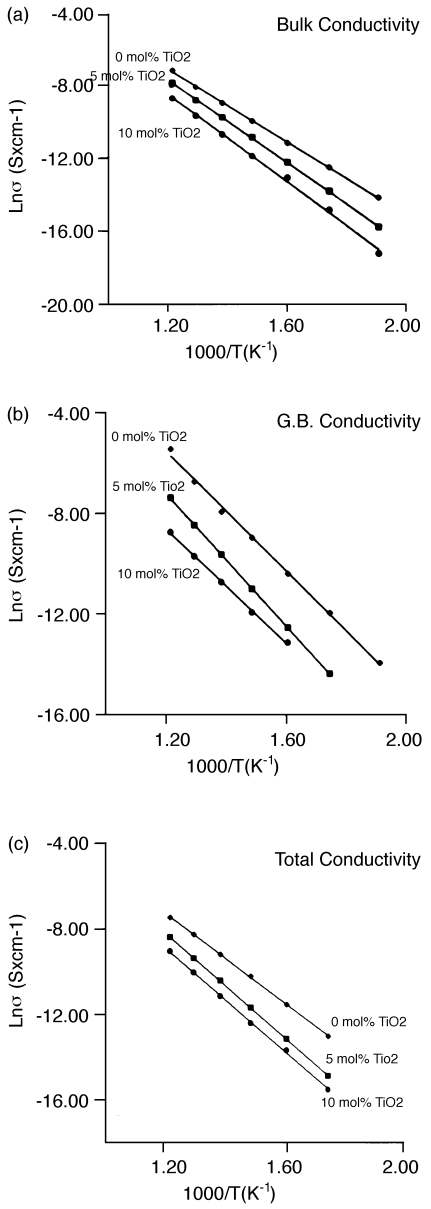

Fig. 3. Temperature dependence of the total conductivity in undoped and TiO_2-doped YTZP ceramics.

References

1. Han, P. and Vorrell, W. L., Mixed (oxygen and p-type) conductivity in yttria-stabilized zirconia containing terbia. *J. Electrochem. Soc.*, 1995, **141**, 2435–2446.
2. Burggraaf, A. J., Boukamp, B. A., Vinke, I. C. and de Vries, K. J., Recent developments in oxygen-ion conduct-

ing solid electrolytes and electrode materials. In *Adv. Solid. State Chem.*, Vol. 1, ed R. C. A. Catlow. J. A. Press Inc., 1989, pp. 259–294.

3. Tuller, H. L., Mixed conduction in nonstoichiometric oxides. In *Nonstoichiometric oxides*, ed. O. T. Sorensen. Mater. Sci. Series, Academic Press Inc., New York, 1981, pp. 271–332.
4. Lion, S. S. and Worell, W. L., Electrical properties of novel mixed-conducting oxides. *Appl. Phys. A.*, 1989, **49**, 25–31.
5. Naito, H. and Arashi, H., Electrical properties of ZrO_2–TiO_2–Y_2O_3 ceramic. *Solid State Ionics*, 1992, **53–56**, 436–441.
6. Traqueia, L. S. M., Pagnier, T. and Marques, F. M. B., Structural and electrical characterization of titania-doped YSZ. *J. Europ. Ceram. Soc.*, 1997, **17**, 1019–1026.
7. Colomer, M. T., Traqueia, L. S. M., Jurado, J. R. and Marques, F. M. B., Role of the grain boundaries on the electrical properties of titania-doped YSZ. *Mater. Res. Bull.*, 1995, 30-515-22.
8. Kopp. A., Nate, H., Weppner, W., Koutouros, P. and Schubert, H., Ionic and electronic conductivity of TiO_2–Y_2O_3 tetragonal zirconia polycrystals. In *Science and Technology of Zirconia V*. Technomic., Lancaster, P.A. 1993, pp. 567–575.
9. Rog, G. and Borchardt, G., Electrochemical properties of ZrO_2–Y_2O_3–TiO_2 ceramics. *Ceramics Intern.*, 1996, **22**, 149–154.
10. Capel, F., Ph.D. thesis. Complutense University of Madrid 1998.
11. Bonin, D., Kaiser, P., Freguy, C. and Desbarres, J. In *Structures fines d'absorption en chimie*, ed. H. Dexpert, *et al.* Orsay, 1989.
12. Rehr, J. J., de León, J. M., Zabinsky, S. J. and Albers, R. C., Theoretical X-ray absorption fine structure standard. *J. Am. Chem. Soc.*, 1991, **113**, 5135.
13. Zschech, E., Koutouros, P. N., Petzow, G., Behrens, P., Lessmann, A. and Frahm, R., Synchroton radiation Ti–K XANES study of TiO_2–Y_2O_3 stabilized tetragonal zirconia polycrystals. *J. Am. Ceram. Soc.*, 1993, **76**, 197–201.
14. Li, P., Chen, I. W. and Penner-Hahn, J. A., Effects of dopants on zirconia stabilization. An X-ray absorption study: I, Trivalent dopants. *J. Am. Ceram. Soc.*, 1994, **77**, 118–128.