Crystal Structure and Electrical Properties of Magnesia

Co-doped Scandia Stabilized Zirconia

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Abstract

Mg-doping effects on the crystal structure and ion conduction properties of Scandia Stabilized Zirconia have been studied in the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0 \leq x \leq 0.07$) system. The materials have been prepared by a sol-gel method. Characterization of the crystal structure has been carried out by means of X-ray diffraction, Raman spectroscopy, synchrotron X-ray diffraction, selected area electron diffraction and high resolution transmission electron microscopy. Cubic phase-stabilization is observed in materials corresponding to $x \geq 0.03$ but single cubic-phase formation is achieved only in $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$. Ionic conductivity of the oxides has been determined by complex impedance spectroscopy. Stabilization of the cubic phase in the compounds with $x \geq 0.03$ values avoids rhombohedral-cubic phase transformation, improving the conductivity below 600 °C compare to the one of 11ScSZ.

Introduction

Reducing the operating temperature is the major challenge faced by solid oxide fuel cells (SOFCs). Development of intermediate temperature SOFCs (IT-SOFCs) requires, among different improvements in all fuel cell components, the use of new solid electrolytes with high ionic conductivity and negligible electronic conductivity at temperatures in the 600-800 °C range.

The cubic phase of scandia-stabilized zirconia (ScSZ) is an interesting candidate as electrolyte material for IT-SOFCs. ScSZ shows the highest conductivity at 1000 °C with scandia concentration of 11 mol% ¹. However, for ScSZ with more than 9 mol% of scandia, the material undergoes a cubic-rhombohedral phase transition at 600 °C, which significantly decreases the ionic conductivity below this temperature ^{1,2}. This phase transformation can be avoided by limiting the scandia content to 8-9 mol% but the material suffers from aging effects in annealing at high temperatures ². Co-doping with other metals is another mechanism for avoiding phase transformation in ScSZ and improving the conductivity at low temperatures ³⁻⁸. In this sense, stabilization of the cubic phase at room temperature of ScSZ by substitution of Al ⁵, Yb ⁴ or Bi ³ for Sc has been reported. Yttria co-doping has been investigated in the system $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{Y}_2\text{O}_3)_x$ ($0 \leq x \leq 0.11$) and found that compositions with 1 and 2 mol% yttria combine the best properties of both $\text{Sc}_2\text{O}_3\text{-Zr}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-Zr}_2\text{O}_3$ systems ^{6,8}. More recently, stabilization of the cubic phase at room temperature by substitution of 1-6 mol % Ga for Sc, also in the system $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{Ga}_2\text{O}_3)_x$, has been reported ⁷. The interesting point in $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{Ga}_2\text{O}_3)_x$, is that the doping of Ga^{3+} ion, with smaller radius than Sc^{3+} ion stabilizes the cubic phase of ScSZ and improves the electric conductivity more effectively than the system of the dopant ions like Y^{3+} or Yb^{3+} , suggesting that co-dopants with smaller radius than Sc^{3+} may dissociate the dopant-vacancy complexes.

The structural effects caused by the co-dopant atom and its influence on the O^{2-} ion conduction are complex and still under discussion. Variations of the activation enthalpy for the ion conductivity can be related to different processes of the conduction mechanism. Association between the dopant cations and the compensating anion vacancies usually takes place in stabilized zirconas. In this case, the conduction mechanism is explained by two processes: dissociation of the dopant cations and anion vacancies and oxygen migration⁹. The dissociation process takes place at the lower temperatures and therefore, the activation enthalpy of the O^{2-} conduction consists of the addition of the association enthalpy and the migration enthalpy. At the highest temperatures, the activation enthalpy only depends on the migration process. However, high activation enthalpies observed at low temperatures in some systems are explained by an additional process of short-range ordering of anion vacancies^{6,10}.

In this present work we have studied the effects of magnesia co-doping in the stabilization of the cubic phase and oxygen anion conduction mechanism of ScSZ. We have studied the crystal structure and ionic conductivity of the $(ZrO_2)_{0.89}(Sc_2O_3)_{0.11-x}(MgO)_x$ ($0 \leq x \leq 0.07$) system. The interest of Mg co-doping in ScSZs is that Mg^{2+} has same ionic radii than Sc^{3+} , avoiding tensions in the crystal structure. In addition to this, Mg co-doping increases the anion vacancy-concentration in the structure due to the lower formal oxidation

state of the Mg compare to the Sc, increasing the charge carrier concentration and hence the ionic conductivity.

Experimental

Polycrystalline samples of the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0 \leq x \leq 0.07$) system were synthesized by sol-gel method. Stoichiometric amounts of scandium nitrate (prepared by dissolving scandium oxide (Daichi rare element, 99%) in nitric acid (Kishida Chemical, GR) and magnesium acetate (Kishida Chemical, GR) were mixed with oxizirconium chloride (Kishida Chemical, 99%) and then added ethylene glycol (Kishida Chemical, 99.5%). Sol was obtained by evaporating the solvent at 80°C with stirring and gelation was induced by further heating. The obtained gels were dried at 110°C overnight and afterwards calcined at 700°C for 9 h. The obtained powders were isostatically pressed into a bar under a pressure of 120 MPa followed by sintering at 1600°C for 8 h.

Crystalline phase identification and purity of the samples were determined by powder X-ray diffraction (XRD) on a RIGAKU RU-200B diffractometer, using filtered $\text{CuK}_{\alpha 1, \alpha 2}$ radiation ($\lambda_1 = 1.5406 \text{ \AA}$, $\lambda_2 = 1.5443 \text{ \AA}$, $K_{\alpha 1}/K_{\alpha 2}$ ratio of 0.51) and equipped with scintillation detector. The atomic ratio of the metals was determined by X-ray energy dispersive spectroscopy (XEDS) analyses finding good agreement between analytical and nominal composition in all the crystals.

Raman spectra were obtained using a laser Raman system (Jasco NRS3300) with Ar ion laser (488 nm 0.1 W) in the wavenumber range of 200–800 cm⁻¹.

For transmission electron microscopy the samples were ground in *n*-butyl alcohol and ultrasonically dispersed. A few drops of the resulting suspension were deposited in a carbon-coated grid. Selected Area Electron Diffraction (SAED) and High Resolution Transmission Electron Microscopy (HRTEM) studies were carried out with a JEOL JEM 3000F microscope operating at 300 kV (double tilt ($\pm 20^\circ$)) (point resolution 1.7 Å), fitted with a XEDS microanalysis system (OXFORD INCA).

Synchrotron Radiation High Resolution Powder X-ray diffraction (SXRD) patterns were collected on the SpLine the Spanish CRG beamline BM25A at the European Synchrotron Radiation Facility (ESRF), Grenoble (France). The monochromator is a pseudo channel-cut with two fixed Si (111) crystals moved together by a simple goniometer circle, in the (-n,+n) configuration. The first monochromator crystal is Ethanol-cooled while the second crystal is kept at room temperature. The second crystal is equipped with a piezoelectric driver that allows changing very slightly the Bragg angle (pitch adjustment) in order to reduce the harmonic content of the beam, if necessary, and to keep the transmission of the monochromator constant during long-time intervals. Also, a bender curves sagittally the second crystal in order to focus the beam at the sample positions¹¹ The sample was finely ground and loaded into a 0.4 mm diameter capillary mounted in a spinning

goniometer. Room-temperature data were collected in a continuous 2θ -scan mode from 7 to 48 using an incident wavelength of 0.62100(6) Å (calibrated with NIST SRM 640c silicon powder; $a=5.431195(9)$ Å).¹² The counts from the different channels were rebinned to produce an equivalent normalized step scan of 0.01 step intervals, with a count time of 1 s per step. The powder diffraction data were analyzed by the Rietveld method, using the FullProf program¹³.

Scanning electron microscopy (SEM) experiments were performed using a FEI XL30[®] apparatus equipped with an EDAX[®] analyzer XEDS.

Ionic conductivity was determined from complex impedance diagrams at different temperatures. Impedance measurements were carried out using a frequency-response analyzer (Solatron 1255) over a frequency range 10^{-1} to 10^7 Hz with an applied potential of 0.2 V in the temperature range 250-1000°C under an open atmosphere.

Density of the sintered pellets was measured by means of the Archimedes method using specific gravity measuring instrument (Sartorius) at 23.5 °C under atmospheric pressure and density of water 0.99744 gcm^{-3} as a standard.

Results and Discussion

Figure 1 shows the XRD patterns of different compounds of the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0 \leq x \leq 0.07$) system. Single cubic phase is observed for the

materials with $x \geq 0.03$. However, reflections in agreement with rhombohedral phase ($x=0$), in addition to cubic one, are detected in the patterns of the compounds corresponding to $x = 0.01$.

SEM and XEDS analyses allow determining the metal distribution in the samples. Figure 2a shows the back-scattered electron (BSE) image of $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$. Since the contrast in BSE images is sensitive to the average composition light elements give dark contrasts, and vice-versa. Figure 2a suggests a homogeneous composition (dark zones in this figure correspond to holes in the sample surface due to poor sintering). This is confirmed by the elements distribution maps in $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$ shown in Figures 2b-2e, which demonstrate that all the elements are homogeneously distributed (the dark and bright zones observed are due to topological features, see Figure 2a). This supports the results of lab XRD which suggests that this sample is single-phase cubic stabilized zirconia highly homogeneous.

Figure 3 shows the Raman scattering spectra of some $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0 \leq x \leq 0.07$) compounds. For $x = 0$ and 0.01 , three scattering peaks at around 600 cm^{-1} and one at 300 cm^{-1} are observed, which are characteristic of the rhombohedral phase of ZrO_2 ^{14,15}. These results are consistent with those of the XRD measurements. The wide peaks from 400 to 500 appearing in some of the spectra must be related to some minor

phase in the sample. A single peak at around 620 cm^{-1} is assigned to cubic phase.^{14,16,17}.

These results indicate that the cubic is the main phase of the sample corresponding to $x =$

0.03. With increasing the content of MgO in ScSZ from $x=0.03$, weak peaks at about 260

and 480 cm^{-1} appear. Peaks at 260, 480, and 640 cm^{-1} are ascribed to the vibrations in the

tetragonal phase of zirconia.^{14,16,18,19} These results indicate that

$(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0.05 \leq x \leq 0.07$) includes tetragonal phase with the axial ratio

c/a equals to unity. This tetragonal phase, that is also observed in

$(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{Ga}_2\text{O}_3)_x$ system⁷, has been reported by many groups in similar

systems being denoted as t'' phase.^{15,16,18-20} The reason for the formation of t'' phase is

explained by the local ordering to oxide ions.¹⁵

We have carried out synchrotron radiation XRD measurement (and Rietveld analysis of these data) for $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$, which was identified as pure cubic phase by conventional XRD measurements and Raman spectroscopy. Figure 4 shows the fitting of the SXRD pattern to the calculated one using the structural model given in Table 1. The metal ratio determined by XEDS was confirmed, moreover SXRD data allowed to refine the oxygen content, suggesting the existence of a large concentration of oxygen vacancies undoubtedly related to the high ionic conductivity observed. The good

fitting obtained ($R_{wp} = 3.53\%$) strongly suggests that the average structure of this material is of cubic symmetry. As shown in Table 1 the lattice parameter of $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$ can be estimated to be $5.0882(2) \text{ \AA}$, whereas that for $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.10}(\text{Ga}_2\text{O}_3)_{0.01}$ is $5.0839(9) \text{ \AA}$ ⁷. These parameters seem to indicate introduction of magnesium ion into ScSZ. The larger lattice parameter for $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$ compares to that of $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.10}(\text{Ga}_2\text{O}_3)_{0.01}$ would be brought by the larger ionic radius of magnesium ion than that of gallium ion.

Figure 5 shows SAED patterns of three different zone axis of a crystal with composition $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$. The strong Bragg reflections are characteristic of the cubic phase of the fluorite structure. Only extremely weak extra reflections not consistent with the cubic symmetry are observed in the patterns of the $[-110]$ and $[-11-1]$ zone axes and diffuse scattering appears in the pattern along the $[112]$ zone axis. Reflections at $G_{F\pm}(11-2)^*$ and $G_{F\pm}(13-2)^*$ (F refers to cubic fluorite structure), indicated by arrows in the patterns, are characteristic of the tetragonal polymorph of ZrO_2 (t or t'' phases). Besides, reflections at $G_{F\pm}(110)^*$, $G_{F\pm}(001)^*$, and $G_{F\pm}(021)^*$ arise by a double diffraction effect. These extra lattice reflections are well observed in the SAED patterns of YSZ with yttria content of 8 mol% (8YSZ), indicating the formation of domains of t or t' phase in the average cubic crystals²¹. Figure 5 also shows a HRTEM image and the corresponding FFT of a crystal with composition $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$ along the

[-110] zone axis. The contrast differences of the image are characteristic of fluorite structure and the FFT does not show superlattice reflections. These results indicate that nano-domains of tetragonal phase are formed within the crystal, which are too small to be detected in the HRTEM images.

We have measured the temperature dependence of AC-impedance of dense sintered pellets of $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0 \leq x \leq 0.05$). As an example, that with $x=0.03$ presented a density of 5.31 gcm^{-3} , which corresponds to 90% of the crystallographic one.

The temperature dependence of the total (bulk + grain boundary) conductivity of $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0 \leq x \leq 0.05$) is shown in Figure 6. The materials present high ionic conductivity, comparable to that of 11ScSZ in the temperature region ($0.8 \leq 1000/T \leq 1.15$). The sharp drop of the conductivity at about 600 °C ($1000/T = 1.14$) of the 11ScSZ is associated to the cubic-rhombohedral phase transition. The transition is also clearly observed for the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ compound with $x= 0.01$. The materials corresponding to $x = 0.03$ and 0.05 do not undergo this decrease of the conductivity associated to phase transformation. Hence, the stabilization of the cubic phase in the Mg co-doped ScSZ improves the ionic conductivity bellow 600 °C. However, a careful analysis of the Arrhenius plots of the stabilized compounds above 600 °C shows that there is a change of slope, suggesting a variation of the activation energy of the conduction process. The activation enthalpies are lower for the high temperature region than for the

low temperature region (the regions are indicated in Figure 6a). This is in agreement with a conduction mechanism based on two processes ⁹. In the low temperature region the activation enthalpy depends on both the enthalpy of association of the dopant cations and anion vacancies (H_a) and the anion migration enthalpy (H_m). However, in the high temperature region, the activation enthalpy of the conduction process is mainly related to the oxygen ion migration enthalpy. The association enthalpies have been calculated taking into account that $H_{act} = H_a + H_m$, where H_{act} is the activation enthalpy of the conduction process in the low temperature region. In the higher temperature region, H_a is equal to H_m . H_m can be estimated from the gradient in Figure 6 in high temperature region and H_a is also estimated from the increase of the gradient in the lower temperature region. Figure 7a shows the variation of the activation enthalpy in the high temperature region and Figure 7b shows the variation of the association enthalpy in the low temperature region with the Mg content of the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ system. There is not a clear trend on the variation of H_a with the co-dopant content of the materials. However, H_m (the activation enthalpy of the high temperature range) increases with increasing Mg content up to a value corresponding to $x=0.03$ and remains constant for higher Mg contents. This variation of H_m might be related to some differences in the crystal structure of the oxides or to strain introduced by a larger ion co-dopant than Sc, as it was suggested by Irvine for Y^{3+} co-doped ScSZ.⁸

Conclusions

Oxides of the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0.00 \leq x \leq 0.07$) system have been synthesized by sol-gel method. According to the XRD results, cubic phase is stabilized for $x \geq 0.03$ values but rhombohedral and cubic phase-mixtures are obtained for $x < 0.03$. However, Raman spectroscopy reveals that only the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$ material is single cubic phase and stabilization of tetragonal domains or particles is clearly observed for materials with $x > 0.03$ values. Stabilization of the cubic phase and single phase formation in $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$ are confirmed by synchrotron radiation XRD and Rietveld analysis of the results in combination with SAED and HRTEM.

The materials present high ionic conductivity, comparable to that of 11ScSz, at temperatures above 600 °C. Cubic-phase stabilization in the oxides corresponding to $x \geq 0.03$ avoids the cubic-rhombohedral phase transition at about 600 °C, improving the ionic conductivity below this temperature. The variation of the anion migration enthalpy with the Mg content of the compounds indicates possible strain-effects in the crystal structure of the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ system.

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Figure Captions

Figure 1: XRD patterns of different compounds of the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0 \leq x \leq 0.07$) system

Figure 2: (a) Backscattered electron micrograph taken at a magnification x4000 on the surface of a pellet of $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$, (f) topographic view, (b-e) elemental distribution maps.

Figure 3: Raman spectra of some $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0 \leq x \leq 0.05$) compounds.

Figure 4: Experimental (red points), calculated (black continuous line) SXRD pattern and its difference (blue line at the bottom) for $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$. Vertical bars indicate the positions of Bragg reflections corresponding to this phase.

Figure 5: SAED patterns a crystal with composition $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$ along the $[-110]$, $[112]$ and $[-11\bar{1}]$ zone axes. HRTEM image of a crystal with composition $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$ along the $[-110]$ zone axis and the corresponding FFT.

Figure 6: Temperature dependence of the electric conductivity for

$\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ ($0 \leq x \leq 0.05$).

Figure 7 : (a) variation of the activation enthalpy in the high temperature region, and (b) variation of the association enthalpy in the low temperature region with the Mg content of the $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.11-x}(\text{MgO})_x$ system.

Table 1: Structural parameters for $(\text{ZrO}_2)_{0.89}(\text{Sc}_2\text{O}_3)_{0.08}(\text{MgO})_{0.03}$ obtained from SXRD.

a (Å)	5.0882(2)
$V(\text{Å}^3)$	131.729(9)
$4a$	
Occ (Zr/Sc/Mg)	0.89(1)/0.08(1)/0.03(1)
$U*100$ (Å²)	0.24(1)
$8c$	
Occ O	1.94(2)
$U*100$ (Å²)	0.62(2)
Fm3m (#225): $4a$ (000), $8c$ ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$) $\chi^2 = 0.096$, $R_{\text{wp}} = 3.53\%$, $R_{\text{exp}} = 11.40\%$, $R_B = 3.90\%$,	

(a)

Fig.1(a) Ikeda et al.

(b)

(c)

Fig. 1 (c) Ikeda et al.

(d)

Fig. 2 Ikeda et al.

Fig. 3 (a) Ikeda et al.

(b)

Fig. 3(b) Ikeda et al.

Fig. 4 Ikeda et al.

Fig. 5 Ikeda et al.

Fig. 6 Ikeda et al.