Effect of the synthesis method and praseodymium on the electrical properties of Mg-Cubic Zirconia

J. BADENES, A. FORÉS, M. VICENTE, M. LLUSAR, J. CALBO, M.A. TENA, G. MONRÓS

Dpto. Química Inorgánica i orgánica, Universitat Jaume I, Campus Riu Sec s/n, 12080-Castellón

The synthesis of nanostructured Mg-FSZ fully stabilized zirconia by chemical methods such as colloidal gel, polyester resin and hydrolisis of alkoxides has been studied. The addition of praseodymium ion facilitates cubic stabilization avoiding the Mg-FSZ partitioning with temperature. Praseodymium improve the ionic conductivity of the material probably by the entrance of Pr^{3+} on the host lattice substituting Zr^{4+} and subsequently introduction of additional oxygen vacancies trapped near the zirconium ion.

Key words: cubic zirconia, synthesis, praseodymium.

Efecto del método de síntesis y del praseodimio sobre las propiedades eléctricas de Circonia-Mg cúbica.

En este trabajo se estudia la obtención de circona cúbica estabilizada con magnesio nanoestructurada por métodos químicos tales como el gel coloidal, resina poliéster de citrato así como hidrólisis de alcóxidos. La adición de praseodimio mejora la reactividad del sistema y evita la transformación a monoclinica con la temperatura. Asimismo el praseodimio mejora la conductividad iónica del material por un mecanismo de disolución sólida de modo que el Pr^{3+} introduce nuevas vacantes de oxígeno que podrían quedar asociadas a iones circonio en la red.

Palabras clave: circona cúbica, síntesis, praseodimio.

1. INTRODUCTION.

Stabilized zirconia has been the most important material recently studied as ionic conductors based in oxygen vacancies because it becomes a pure ionic conductor in a wide range of oxygen pressure. The main stabilizant cations of zirconia are trivalent because they induce higher conductivity than divalent ions. There are few studies on the electrical properties of the magnesium stabilized zirconia system. Muccillo et al (1,2,3) studied both FSZ and PSZ systems by complex impedance technique establishing a relationship between cubic zirconia decomposition and their electrical properties and microstructure.

The production of polycrystalline stabilized zirconias requires to attain a good sintered microstructure: this type of result can be obtained with nanostructured dense ceramics. Monodispersed nanoparticles are necessary in order to obtain nanostructured materials, but the ultrafine powders which are attractive for sintered microstructures and sintering kinetics, usually conflict with problems involved in its processing: nano-mono-size powders do not flow or pack well on pressed compacts; they can produce strenghtened agglomerates and they present enhanced problems associated with dispersion and with binder removal (4).

Sol-gel process has been widely used for the production of monosized nanoparticles (5) and in order to avoid processing limitations fluxing agents or rare-earth dopants can be added (6,7): liquid phase and doping agents presence migrating to the grain boundary enhance the sintering properties, in this sense is well known the solid solution of praseodymium ions in zirconia and zircon systems (8).

Praseodymium cations in air, at high temperature, usually share the oxidation states +3 and +4. $\text{Pr}^{3+}/\text{Pr}^{4+}$ redox equilibrium is well known in the ordered intermediate phases with composition $\text{Pr}_n\text{O}_{2n-2}$ which when fired produce Pr_6O_{11} which present fluorite structure similar to PrO_2 . The electrical transport properties of Pr_6O_{11} have been investigated by conductivity studies suggesting that the electrical conductivity is due to a mixed conduction process involving oxygen ion conduction, but with increasing temperature the oxide tends to lose oxygen, changing the ratio $\text{Pr}^{3+}/\text{Pr}^{4+}$ ions and promoting electronic conductivity. When Pr_6O_{11} is doped with La^{3+} the lattice parametes systematically increase, but conductivity studies show an ordering of the neighbour oxygen vacancies and above 20% of La doping the conductivity decrease due to the nucleation of vacancy clustering or domains (9). On the other hand, some authors suggested that Pr^{3+} is not present in Pr-doped circon where the Zr^{4+} triangular dodecahedral positions are substituted by Pr^{4+} (10).

The analysis of the influence of the synthesis method and the praseodymium oxide as dopant on the sinterability of powders and their electric properties in Mg-FSZ system is the purpose of this paper.

2. EXPERIMENTAL

In order to attain the above aims two compositions shown in Table I were prepared. Samples were processed by several methods: (a) ceramic method (CE): oxides of industrial grade

(particle size by 3-8 mm) were dispersed in acetone medium in a planetary ball mill, acetone was evaporated in air to obtain raw mixture, (b) aqueous sol-gel process (CG): carried out from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Mg} \cdot 4\text{H}_2\text{O}$ and $(\text{CH}_3\text{COO})_3\text{Pr} \cdot 3\text{H}_2\text{O}$, all of analytical quality from Aldrich; the precursors were firstly solved in water and gelled with ammonia addition to pH 5-6, then the obtained gel was dried at 110°C , (c) citrates route (CI): developed with the same precursors than in the CG method, which are solved in water, complexed with citric acid and polyesterified with ethylenglycol (molar ratio citric acid:cation:ethylenglycol=2:1:1); the resine of the resulting polyester was obtained drying at 110°C and charring at 250°C , (d) polymeric gel from alkoxides (PG) obtained from $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Zr}$, $(\text{CH}_3\text{COO})_2\text{Mg} \cdot 4\text{H}_2\text{O}$ and $(\text{CH}_3\text{COO})_3\text{Pr} \cdot 3\text{H}_2\text{O}$ (from Aldrich) precursors, using the molar hydrolisis conditions $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Zr}:\text{H}^+:\text{H}_2\text{O}:\text{EtOH}:\text{acac}=1:0,18:3:26:1$, acetylacetone (acac) was added in order to control zirconium n-propoxide hydrolisis; the refluxed gel obtained was dried in air.

In order to compare directly the behaviour of obtained powders no washing and desagglomeration has been made. All dried powders were calcined at $500^\circ\text{C}/12\text{h}$ in order to eliminate organics and subsequently sieved at 40 mm, uniaxially pressed at 217 MPa. and reacted-fired at $1500^\circ\text{C}/2\text{h}$.

Raw powders, precalcined and sintered materials were characterized by XRD, SEM-EDX and electron microscopy. The zirconia cubic cell parameters calculations, the Vickers microhardness and density were all determined.

3. SYNTHESIS AND SINTERING DISCUSSION.

The main results obtained are shown in Table II, Table III, and in Figure 1 (XRD of sintered materials) and Figure 2 (SEM micrographs of samples).

XRD results show that all raw powders are amorphous, except for the ceramic sample, which presents peaks of oxide precursors, and the colloidal gel sample, which presents ammonium chloride crystallized from ammonia addition. In all $500^\circ\text{C}/12\text{h}$ precalcined samples, cubic zirconia has been found cristallized except in the ceramic sample which remain unreacted. All sintered samples at $1500^\circ\text{C}/2\text{h}$ doped with Pr_2O_3 show cubic zirconia as the only crystalline phase except for the ceramic sample which presents also periclase as residual phase. All undoped samples present monoclinic zirconia together with the cubic polymorph, except the colloidal sample, which present the best stabilization of cubic zirconia among undoped samples. These results indicate the stabilization effect of praseodymium in doped powders demonstrating the significance of chemical additions on the process (11) avoiding the partitioning process in Mg-ZrO₂ observed in the Pr-undoped samples and well known from the literature (12).

The chemical effect of praseodymium on stabilized zirconia could be described as a solid solution mechanism, indicated by cell parameters shown in Table III. In effect, lattice parameter of undoped samples are in accordance with ASTM values for cubic zirconia, but Pr-doped samples show higher values which can be associated to $\text{Pr}^{3+}/\text{Pr}^{4+}$ entrance in solid solution in the network.

Densification and Vickers hardness of sintered samples presented in Table III, show that CE and PG both doped and undoped samples, present worse results than CG and CI samples. Observations by scanning electron microscopy (Fig. 2) are in accordance with density and hardness results, in effect

TABLE I. COMPOSITION OF SAMPLES.

samples	% mol		
	ZrO ₂	MgO	Pr ₂ O ₃
CE/CG/CI/PG	88,00	12,00	--
CEPr/CGPr/CIPr/PGPr	82,10	12,63	5,26

TABLE II: XRD RESULTS

SAMPLE	RAW	500°C/12h	1.500°C/2h
CE	M(vs)Mg(w)	M(vs)Mg(s)	M(vs)C(w)Mg(vw)
GC	N(s)	C(w)	C(vs)
CI	A	C(w)	C(vs)M(w)
GP	A	C(w)	C(vs)M(vw)
CEPr	M(vs)Mg(w)Pr(vw)	M(vs)Mg(w)Pr(vw)	C(vs), Mg(vw)
GCPPr	N(s)	C(vw)	C(vs)
CIPr	A	C(vw)	C(vs)
GPPPr	A	C(vw)	C(vs)

CRYSTALLINE PHASES: A (Amorphous), M (monoclinic zirconia), C (cubic zirconia), Pr (Pr_2O_3), Mg (MgO), N (NH_4Cl). PEAK INTENSITY: vs (very strong), s (strong), m (medium), w (weak), vw (very weak).

Figure 1. XRD diffractograms of sintered samples.

Figure 2. Scanning micrographs of samples: (a) CEPr, (b) CIPr.

TABLE III: CELL PARAMETERS, DENSITY AND VICKERS HARDNESS.

Sample	a=b=c(Å)	d (%)	VH (GPa)
ASTM 27-997 cubic ZrO ₂	5.09	-	-
CE	5.08(1)	92	8.0(6)
CG	5.08(1)	93	11.4(2)
CI	5.08(1)	94	12.0(5)
PG	5.08(1)	92	9.5(7)
CEPr	5.13(1)	91	2.9(2)
CGPr	5.14(1)	92	10.9(6)
CIPr	5.13(1)	95	11.1(6)
PGPr	5.13(1)	91	8.7(5)

TABLE IV: GRAIN ACTIVATION ENERGY (eV).

SAMPLE	E _a (eV)
CEPr	0.80
GC	1.36
GP	1.17
GPPr	1.16

CE and CEPr samples present high open porosity with grain size of about 5 mm. There are also two sizes of pores, large pores of 15-40 mm and abundant micropores of 3-5 mm, forming the classical porosity channels resulting in the intermediate step of densification (Fig. 2.a). In all PG, CG and particularly in CI samples, the porosity becomes closed and 2-3 mm sized (Figure 2.b), with grain size of about 3 mm in CI, PG and CG samples.

4. ELECTRICAL RESULTS AND DISCUSSION.

Electrical behaviour of sintered materials has been studied by complex impedance spectroscopy.

Among the undoped samples, CE presents a different feature: the grain boundary contribution is not shown but their bulk resistance is higher (in the order of 10^5 W versus 10^3 in GP and CI samples at 600°C) in accordance with the high amount of monoclinic phase present on these samples. Monoclinic zirconia absence in CG sample decreases dramatically their bulk resistance (about 10^2 W at 600°C).

Praseodymium additions decrease systematically the resistance of the tablets but the effect depends largely on the method of synthesis. In CI-CIPr and CE-CEPr samples both bulk and grain boundary are 10 times higher in undoped samples. In PG-PGPr the resistance decreases 5 times in the doped sample. On the other hand, in GC-GCPr samples the effect is only 2 times. This behaviour is in accordance with XRD results: CEPr sample presents now cubic zirconia as the most important crystalline phase, PGPr and CIPr are free of monoclinic zirconia, and the GCPr sample is the only with no change in crystalline phase is observed by XRD analysis. The impedance spectra of significant samples, in order to illustrate the above

Figure 3. impedance spectra of samples at 600°C.

mentioned features (CEPr, CIPr, GPPr spectra at 600°C), are shown in Figure 3.

The presence of a foreign cation would have a negative impact on the bulk conductivity of the cubic zirconia due to the microstructural mismatch that a different structure can produce, and also due to the possibility of the segregation of the dopant at intragrain region, which could produce a blocking effect at the grain boundary. However, if dopant enters in the host lattice, it could introduce a local charge and lattice distortion due to mismatch of both valence and ion size respect to the Zr^{4+} ion. This is the case of praseodymium: no evidence for praseodymium phases evidence is detected by XRD analysis and praseodymium enters in the zirconia lattice by substitutional solid solution increasing its unit cell size. In the literature (12,13) is shown that for dopants larger than the host cation, oxygen vacancies would occupy positions near the host cation, as the Zr^{4+} ion-oxygen vacancy pair is energetically more favorable than the one formed by oversized dopants, the vacancies introduced by Pr^{3+} on the lattice are probably trapped near Zr^{4+} ions increasing the overall conductivity of the material.

The bulk contribution of the samples to the impedance spectra show an Arrhenius behaviour with temperature. The activation energy calculated for the different samples is shown in Table IV. Results are in accordance with the literature (2) and praseodymium addition shows a slight positive effect on the activation energy. Most studies must be carried out in order to explain the low activation energy and relative high conductivity of CEPr sample and the differences observed in cubic zirconia obtained by the used routes of synthesis: probably the resulting Pr^{3+}/Pr^{4+} ratio and clustering of the oxygen vacancies have a significant role.

5. CONCLUSIONS.

In summary it is shown that powders obtained by chemical processes like the citrate route, colloidal gel or hydrolisis of zirconium alkoxides, stabilize easily the Mg-FSZ at only 500°C. On the other hand the introduction of Pr in solid solution avoids the Mg-PSZ partitioning with temperature, and increases significantly the conductivity introducing additional oxygen vacancies which most probably are trapped close to Zr^{4+} ions.

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