

Hyperfine Characterization of Metastable Tetragonal Configurations in Pr-Doped Zirconias

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The Pr_xZr_{1-x}O₂ ceramic system obtained by coprecipitation has been investigated at zirconium sites as a function of Pr content (1, 10, and 15 mol %) and of annealing temperature by means of the perturbed angular correlations (PAC) technique. Praseodymium enters zirconia forming a tetragonal solid solution whose extent increases with Pr content. In 10 and 15 mol % Pr-doped samples, metastable tetragonal zirconia is present in its two known t- and t'-forms, the latter form being the one which involves a higher dopant concentration. While Rietveld refinement and thermal analyses indicate the uncompleted crystallization of the as-obtained powders, PAC allows the phase identification of the amorphous residues. Minor changes observed in the hyperfine interaction at high temperatures reveal the incipient ceramic degradation. Experiments indicate that, up to 15 mol % of dopant content, Pr behaves as an efficient zirconia stabilizer.

I. Introduction

Zirconia is a ceramic material of monoclinic structure from RT up to about 1150 °C, tetragonal up to 2370 °C, and cubic up to its melting point, at 2680 °C. With the knowledge of the enhanced structural and electric properties exhibited by the high-temperature phases,¹ much research has been devoted in the past decades to stabilize these polymorphs at temperatures down to RT. One of the most efficient means to achieve this goal is via the formation of a zirconia solid solution with given amounts of some aliovalent oxide. In the search of new stabilizing cations, Zr(Pr)O₂ solid solutions with a Pr content of 10 mol % synthesized by microwave hydrothermal² and of 1–15 mol % prepared by coprecipitation³ have been recently investigated. In both works it

was demonstrated that the mentioned concentrations of Pr dissolve in zirconia-forming tetragonal solid solutions.

Metastable tetragonal zirconia belongs to the $P4_2/nmc$ space group and exists in three forms: t, t', and t''. While the first of them is structurally similar to the equilibrium tetragonal phase with regular, eight oxygen coordinated zirconium sites, t' is constituted of defective zirconium surroundings and is reluctant to transform to the monoclinic phase. It exhibits an oxygen displacement from the positions in the ideal fluorite-type structure that leads to a lower tetragonality than that of the t-form ($c/a \approx 1.007$ versus 1.015) and this difference is reflected in its diffractogram by a smaller angular separation between the (400) and (004) reflections in the high angle region.⁴ In the case of stabilized zirconias obtained by substitutional doping with aliovalent oxides, structural oxygen vacancies appear for

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charge balance. If, in addition, the doping cation is oversized, the lattice cell enlarges. At nanoscopic scale, the smaller Zr finds it difficult to assume the 8-fold oxygen coordination and Zr-oxygen vacancy pairing becomes energetically favorable, resulting in a 7-fold Zr–O coordination that favors zirconia stabilization.⁵ Thus, the distorted t' -phase is the tetragonal metastable form which most directly manifests the inclusion of the stabilizing cations in the solid solution. The existence of the t'' form, in turn, has been reported more recently for many ZrO_2 – M_2O_3 systems ($M = Y, Er, Nd, Sm, Yb, Ce, \text{ and } Ca$), its occurrence depending on dopant concentration and calcination temperature.^{6–7} An oxygen displacement from fluorite positions smaller than that observed for the t' phase is also present in this structure. On account of its lack of tetragonality ($c/a = 1$), the t'' phase is hardly distinguishable from the fluorite-type cubic phase and is often referred to as pseudocubic. Yashima et al.,⁶ studying the yttria–zirconia system, have found that, for increasing concentration of yttria, a decrease in both the oxygen displacement and the c/a ratio was correlated with the progressive occurrence of the t' , t'' , and c metastable structures.

The perturbed angular correlations (PAC) method^{8,9} has proved to be an efficient tool in the investigation of zirconia-based ceramics at a nanoscopic level.^{9–13} It allows the determination of different nanoconfigurations around zirconium sites hardly resolvable by other techniques as well as their thermal evolution without temperature limitations. The PAC probes are the impurities of hafnium (1–5%) always existing in natural zirconium, randomly distributed at substitutional zirconium sites. The thermal neutron irradiation of the material activates some ^{180}Hf isotopes by converting them in the ^{181}Hf nuclear probes. The method briefly consists of an inspection of the angular correlation of two successive photons emitted by the daughter nucleus ^{181}Ta through the 133–482 keV disintegration γ – γ cascade. The comparison of the measured angular correlation against that of the isolated probe, known from the nuclear physics, allows gathering valuable information about the internal electric field gradients (EFGs) acting at Zr(Hf) lattice sites. This is achieved by fitting the experimental spin rotation curve $A_2G_2(t)$, commonly called PAC spectrum, to a theoretical function containing the EFG's quadrupole parameters: its intensity (through the quadrupole frequency ω_Q), its departure from axial symmetry (through the asymmetry

parameter η), and its degree of disorder due to the presence of impurities or defects in the lattice (through the spread or distribution width δ). Provided atomic or defect movements occur in the studied material, a model-dependent relaxation constant λ associated to dynamic processes can be as well-determined from the fit. This last magnitude is significant from the electrical point of view since it can be associated to the ionic conductivity of the ceramic. One of the most relevant features of the technique is that, due to its extremely localized character, up to five nonequivalent sites in the lattice, in amount (measured by the relative fraction or intensity) and nature (measured by the quadrupole parameters of the EFG), can be distinguished. A goal of the PAC method has been the neat characterization of the two metastable tetragonal forms, t and t' , in systems where both coexisted.^{9,11,12} In fact, the corresponding hyperfine pattern has been resolved in two perfectly distinguishable interactions ($\omega_Q = 165 \text{ Mrads}^{-1}$, $\eta \cong 0.55$, and $\delta \geq 25\%$ for metastable t' -form and $\omega_Q = 188 \text{ Mrads}^{-1}$, $\eta \cong 0.2$, and $\delta \leq 4\%$ for metastable t -form), different from that which describes the equilibrium tetragonal phase.¹⁴

Regarding the Pr– ZrO_2 system, in ref 2 where the Pr content was 10 mol %, information from XRD, thermal analyses, and PAC allowed the authors to conclude that the microwave hydrothermal method led to a homogeneous, tetragonal substitutional solid solution described at nanoscopic level by the defective and disordered t' -phase. Paper of ref 3 reports an initial study of praseodymium solubility in zirconia for samples with different Pr contents obtained by the coprecipitation method. Authors found that, in all cases, the Pr ions solubilized in the tetragonal zirconia structure. When Rietveld analysis was performed on samples doped with 10 and 15 mol % of Pr, the coexistence of the t' - and the t'' -forms was reported.

In the present work, an investigation on the Pr-doped zirconia (with 0, 1, 10, and 15 mol % of Pr content) system has been carried out using the PAC technique assisted by XRD and thermal analyses. The samples were prepared by coprecipitation and calcined for 2 h at 1000 °C. The aim of the study was to characterize at nanoscopic scale the tetragonal forms present in the as-obtained powders and to investigate any possible effect of subsequent thermal treatments on phase stability.

II. Experimental Section

A. Samples Preparation. Amorphous zirconia hydroxides containing amounts of praseodymium ion in the 0–15 mol % range were prepared by coprecipitation. These hydroxides gels were coprecipitated at pH = 9 with 1 M ammonia (NH_4OH , RPE, Carlo Erba, Milan, Italy) from zirconium chloride (1 M, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, RPE, Carlo Erba, Milan, Italy) and praseodymium nitrate ($\text{Pr}(\text{NO}_3)_3$, RPE, Carlo Erba, Milan, Italy) solutions. The amorphous coprecipitated hydroxides, carefully washed with distilled water, were dried in conventional furnaces at 120 °C and then ground in an agate mortar. The obtained powders (hereafter labeled according to the praseodymium content as ZrPr0, ZrPr1, ZrPr10, and ZrPr15) were calcined in air, in an electric furnace, for 2 h at 1000 °C.

B. Samples Characterization. XRD data were collected on a Philips PW3710 diffractometer using Cu K α radiation

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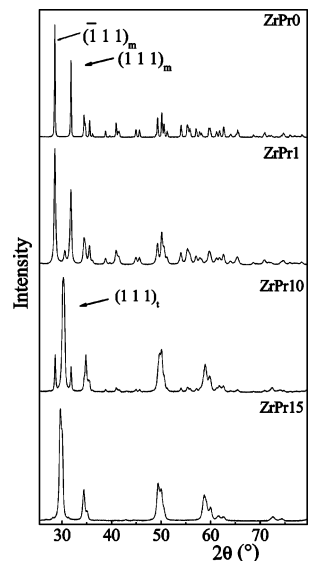


Figure 1. X-ray diffraction patterns of the as-prepared samples.

and a graphite monochromator, over the range $20^\circ \leq 2\theta \leq 80^\circ$ at a scanning rate of $0.004^\circ/\text{s}$ and step size of 0.02° . To perform combined Rietveld and reference intensity ratio (R.I.R.) analyses, GSAS software¹⁵ was used. Data were recorded between $5^\circ \leq 2\theta \leq 140^\circ$, adding 10 wt % of corundum (NIST SRM674a) to all samples as an internal standard.

For the PAC experiment, ^{181}Hf activities of around $200 \mu\text{Ci}$ were produced after 1 day of thermal neutron irradiation of the samples. Measurements were carried out at RT after annealings of 24 h at increasing temperatures of 400, 600, 800, and 1000 °C. The temperature of each annealing treatment was kept within $\pm 5^\circ\text{C}$.

Differential thermal analyses (DTA) between RT and 1000 °C in air at $10^\circ/\text{min}$ were performed using a Shimadzu Series-50 analyzer.

III. Results

Relevant data obtained from the experiments are shown in Figures 1–5. Figure 1 contains XRD information. Figure 2 displays the PAC spectra of the as-prepared powders and Figure 3 shows the fitted phase content in these samples vs Pr molar concentration. Since the quadrupole frequency and asymmetry parameter of the hyperfine interactions resulting from the fits of the PAC spectra do not exhibit any irregularity, only the thermal evolution of the relative fractions and the distribution width of the EFGs in the doped samples have been plotted in Figure 4. Figure 5 displays the DTA heating curves for these samples.

According to the XRD and PAC patterns of Figures 1 and 2, pure zirconia ZrPr0 is completely monoclinic.

As shown in Figure 1, XRD on ZrPr1 evidences a mixture of monoclinic (major component) and tetragonal phases. As can be seen from Figure 3 and Table 1, the starting PAC spectrum was fitted with 74% of the interaction corresponding to the monoclinic phase (Δ in Figure 3), 19% of an interaction describing a similar though somewhat distorted monoclinic phase (\blacktriangle), and 7% of a third interaction (\star). The last one is depicted by the quadrupole frequency of the t' -form and the

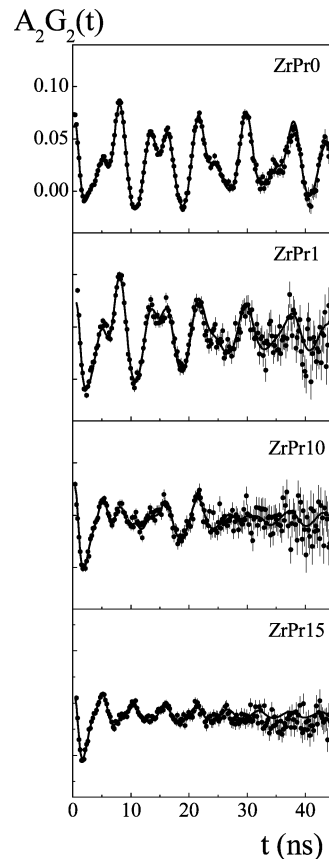


Figure 2. Spin rotation curves obtained for the as-prepared samples. Full lines represent the fitted interactions.

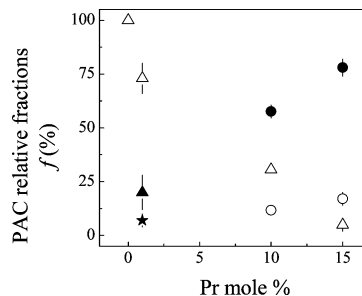


Figure 3. PAC relative fractions f as a function of Pr content. Symbols represent the interactions of monoclinic phase Δ ; distorted monoclinic phase \blacktriangle ; t -form \circ ; t' -form \bullet ; and t or t' -form \star .

asymmetry parameter of the t -form,¹² and an EFG spread intermediate between those corresponding to the two forms. As annealing temperature is raised (see Figure 4), the relative fraction of the monoclinic phase shows two minor increases: after calcining at 400 °C at the expense of the distorted monoclinic phase and after calcining at 800 °C also at the expense of the tetragonal phase.

XRD data for ZrPr10 sample (see Figure 1) indicate that the tetragonal polymorph is predominant at this concentration. Regarding the PAC experiment, the hyperfine pattern of the as-received sample is satisfactorily fitted, provided three interactions are included in the fitting procedure (see Figure 3 and Table 1). While 34% of Zr surroundings exhibit the monoclinic array and 15% the regular ordered t -configurations (\circ), the remaining 51% corresponds to the defective and disordered t' -form (\bullet). Upon the annealing at 400 °C (see

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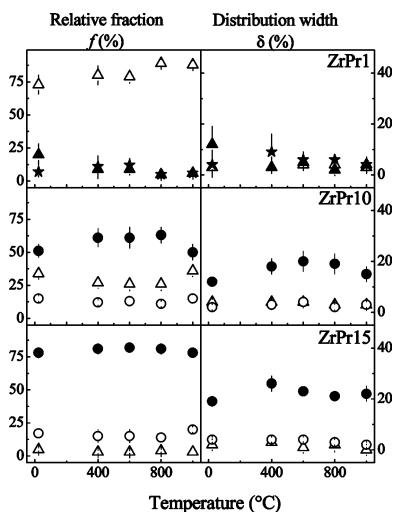


Figure 4. PAC relative fractions and distribution widths as a function of annealing temperature. Symbols correspond to the monoclinic phase Δ ; distorted monoclinic phase \blacktriangle ; t'-form \circ ; t'-form \bullet ; and t- or t'-form \star .

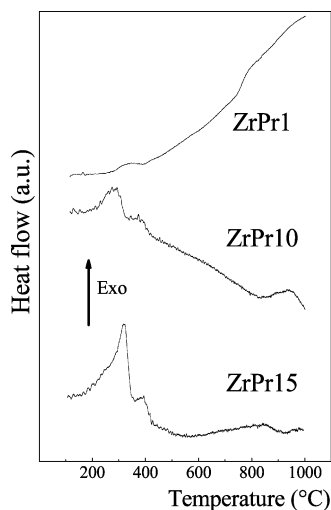


Figure 5. DTA heating curves obtained for the doped samples at 10 °C/min.

Figure 4), an already known improvement in the stabilization¹⁶ can be observed via the $m \rightarrow t'$ transformation. The increase in the t' -form abundance is accompanied by an increase in the EFG's distribution width toward the characteristic value for this configuration at nanoscopic level. In turn, the heating at 1000 °C provokes the inverse change and the different hyperfine contributions almost recover their starting intensities.

The diffractogram of ZrPr15, shown in Figure 1, is the characteristic one of the tetragonal structure, though monoclinic traces are still visible. The PAC spectrum is well-fitted with 3% of monoclinic phase, 19% of the ordered and regular tetragonal t' -form, and 78% of the t' -form (see Figure 3 and Table 1). As in ZrPr10, upon annealing at 400 °C (see Figure 4) the distribution width of the EFG of the t' -form reveals an apparent increase. After calcination at 1000 °C a subtle growth of the t' -form at the expense of the t' -form can be observed.

Table 1. Rietveld-R.I.R. and PAC Derived Relative Phase-Content, c/a Ratios, and Interplanar Spacings of the (111) Tetragonal Line in Doped Samples

		ZrPr1	ZrPr10	ZrPr15
	m-Phase			
PAC	$f(\%)$	74 ₆	34 ₃	3 ₁
Rietveld-R.I.R.	wt (%)	70.40 ₃	12.66 ₁	1.72 ₁
	Distorted m-Phase			
PAC	$f(\%)$	19 ₄		
	Amorphous			
Rietveld-R.I.R.	wt (%)	25.03 ₂	32.30 ₂	15.32 ₃
	t-Form			
PAC	$f(\%)$	7 ₃	15 ₂	19 ₃
Rietveld-R.I.R.	wt (%)	4.47 ₁	26.92 ₃	18.37 ₃
	c/a	1.018	1.016	1.017
	d	2.954	2.967	2.968
	t'-Form			
PAC	$f(\%)$		51 ₅	78 ₄
Rietveld-R.I.R.	wt (%)		28.02 ₃	64.49 ₁
	c/a		1.008	1.005
	d		2.986	3.004
Rietveld $R_w(\%)$		6.54	4.72	5.12

DTA heating curves on the doped samples plotted in Figure 5 exhibit two irreversible and exothermic changes: one over the 220–400 °C region and the other one, more pronounced in ZrPr10, above 750 °C. This last signal has been observed in previous works on stabilized zirconias and it has been related to the occurrence of the monoclinic phase due to either the increase of the crystallite size¹¹ or the dehydroxylation process.¹⁷

IV. Discussion

The undoped sample obtained by the precipitation method employed in this work resulted in 100% monoclinic zirconia. Concerning the doped samples, in agreement with a previous work³ the method led to partially stabilized zirconia in its tetragonal polymorph, the extension of the solid solution increasing with Pr content. In fact, both the t' - and t -forms grow at the expense of monoclinic zirconia, which decreases to 3% at the highest Pr concentration.

In ZrPr1, the stabilized tetragonal zirconia achieves 7%, having the PAC distinction between the t' - and t -forms not being possible. For higher Pr concentrations, the resulting solid solution, revealed by XRD as tetragonal zirconia, is rendered by PAC through two hyperfine contributions, corresponding to the regular t' -form (minor) and the defective t' -form (major).

PAC results evidence some modifications after annealings at the temperatures at which DTA curves reveal irreversible processes. According to previous literature,^{3,18} the signal below 400 °C is probably reflecting the crystallization of some portion of the ceramic powder that had not been accomplished during synthesis. In light of these results, Rietveld-R.I.R. analyses on the as-prepared samples were performed,

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confirming not only the presence of relevant amounts of noncrystalline material but also the separate contributions of the t' - and the t -components to the tetragonal structure. The c/a values, the relative intensities, and also the interplanar spacings corresponding to the (111) reflections of both structures are listed Table 1.

Surveying Table 1, it can be seen that for 1 mol % Pr content, the Rietveld-R.I.R. refinement helped to assign the PAC interaction showing mixed characteristics to the t -form. On the other hand, PAC assisted in the phase identification of the amorphous amount determined by Rietveld-R.I.R. In fact, the latter must be correlated with the PAC fraction of distorted monoclinic phase, as far as upon heating at 400 °C it partially rearranges into the ordinary monoclinic phase. For 15 mol % of Pr content the amorphous amount must be included in the PAC relative fraction of the disordered t' -form since the corresponding EFG's distribution width displays its typical thermal evolution¹² after annealing from 400 °C on. For the sample of intermediate Pr content, in turn, the PAC relative fractions of both the monoclinic phase and the t' -form are probably involving amounts of amorphous material. Once again an improvement of the EFG's distribution width of t' toward its typical values is interpreted as if the starting structure would have been not well-crystallized. On the other side, the high amount of disordered t' -form makes it difficult to distinguish an amorphous distorted monoclinic fraction within the fitted fraction of the monoclinic phase.

From the information in Table 1 and concerning the interplanar spacing d , it can be observed that it remains constant for the t -form over 10% of Pr content. On the contrary, for the t' -form, it is still increasing at 15% of Pr content. This evidence suggests that the solubility limit for the t -form has been achieved at or below 10% of Pr content but not for the t' -form even at the highest Pr content.

In correspondence with the DTA change above 750 °C, after the annealings at 1000 °C, ZrPr1 becomes almost fully monoclinic and, in ZrPr10 and ZrPr15, partial $t' \rightarrow m$ and $t' \rightarrow t$ transformations respectively occur. In ZrPr10 it seems that the Pr content is not enough to compensate the destabilization due to the ordinary crystallite growth with temperature. In ZrPr15, in turn, the subtle transition from the non-

transformable t' -form to the transformable t -form of tetragonal zirconia is probably indicating an incipient degradation.

The present results suggested that the phase assignment in ref 3 be revised. In fact, the c/a values reported there must actually correspond to the t -form and t' -form, being no t'' -form is present.

Conclusions

An investigation on the 1, 10, and 15 mol % Pr-doped zirconias prepared by coprecipitation has been carried out using the PAC technique assisted by XRD and thermal analyses. Results allowed the characterization of the nanostructures present and the determination of the effects of thermal treatments on phase stability.

The preparation procedure does not yield fully crystallized powders. For all Pr concentrations, a tetragonal solid solution has formed at different degrees. The stabilization extent ranges from 7% (at 1 mol % Pr) to 97% (at 15 mol % Pr). For Pr content of 1 mol % the solid solution is described by the t -form. For 10 mol % and 15 mol % of Pr, a mixture of the t -form and the distorted, oxygen vacancies containing t' -form describes the stabilized zirconia. The higher the Pr content, the higher both the relative fraction and the cell size of t' -form. Knowing that this form is the nontransformable metastable structure of tetragonal zirconia, it can be stated that, up to 15 mol % dopant content, Pr behaves as an efficient substitutional solid solution stabilizer.

Related to the thermal evolution of the studied system, two changes are observed. The first one, at temperatures lower than 400 °C, is associated to crystallization. At nanoscopic scale, the detected modifications in the hyperfine interactions allowed the amorphous material in each sample to be characterized. The second change, above 750 °C, precludes the degradation of the ceramic. In fact, small increments in the monoclinic fraction for 1 and 10 mol % Pr content and in the transformable t -form fraction for 15 mol % Pr content reveal the tendency of the solid solution to destabilize after annealing at the highest temperature.

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