

Hyperfine Study on Sol-Gel Derived-Hematite Doped Zirconia

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The nature and thermal evolution of nanoconfigurations around cations in a sol-gel derived solid solution of a ZrO₂ 15 mol % Fe₂O₃ nominal concentration have been investigated by means of the hyperfine techniques of the Mössbauer effect at the Fe sites and perturbed angular correlation spectroscopy (PAC) at the Zr sites, assisted by X-ray diffractometry and thermal analyses. The resulting substitutional solid solution is metastable tetragonal zirconia and exhibits a solubility of 12 mol % of Fe₂O₃ up to temperatures near 750 °C. The hyperfine experiments allowed the establishment of the existence of two nonequivalent sites for each of the probe cations. The most disordered one reflects the influence of the oxygen vacancy introduced after Fe³⁺ substitution for Zr⁴⁺, which is shared by host and dopant cations. The other tetragonal nanoconfiguration, characterized by PAC for the first time, has been thought to involve a direct interaction between the nearest Fe and Zr ions of the largely distorted cation network.

Introduction

At ordinary pressure, pure zirconia (ZrO₂) exhibits three crystallographic forms¹ that transform reversibly into one another according to the thermal sequence



To avoid the deleterious t → m transition² during a thermal cycling, thus promoting better structural ceramics, zirconia needs to be produced at room temperature (RT) in any of its high-temperature structures, cubic or tetragonal (i.e., in a metastable phase). One means to achieve this goal consists of the obtainment of a t/c zirconia solid solution (S-ZrO₂) as result of the addition of some stabilizing oxides such as CaO, MgO, Y₂O₃, Fe₂O₃, and RE₂O₃.³ In the case of dopant cations of a lower valence than zirconium, if assumed at Zr sites, oxygen vacancies appear for charge compensation, thus enhancing the anion diffusion and improving the performance of metastable zirconia as solid electrolyte.⁴ The hematite (α-Fe₂O₃)-zirconia solid solution, in turn, is known for its good catalytic properties.⁵

Various authors have investigated the latter system. The position of the undersized Fe³⁺ dopant cation in the S-ZrO₂ lattice is yet an unresolved question. Berry et al.,⁶ applying mainly Mössbauer spectroscopy (ME) to a solid solution obtained by the coprecipitation method, have reported that the observed quadrupole split absorption, of isomer shift $\delta_{\text{IS}} \approx 0.35$ mm/s and quadrupole splitting $\Delta \approx 0.97$ mm/s, describes Fe³⁺ incorporated at interstitial sites of a cubic or tetragonal zirconia solid solution. The dopant localization assignment was done considering the reluctance of the Fe³⁺ ions to adopt 8-fold oxygen coordination as would be required for the Fe³⁺ occupied substitutional sites in cubic zirconia. On the other hand, in an X-ray absorption spectroscopy (XAS) study concerning the effect of various trivalent dopants (Fe³⁺ included) on the stabilization of precipitation derived zirconias, Li et al.⁷ have reported that, irrespective of their relative size, all dopants substitute for Zr ions. Undersized dopants as Fe³⁺ compete with Zr ions for the oxygen vacancies, resulting in 6-fold oxygen coordination and a large distortion of the surrounding next nearest neighbor cation network. Confirming this cation localization, Wilhelm et al.⁴ and Narwankar and his group⁸ have interpreted the decrease in the lattice parameter of a S-ZrO₂ (cubic under XRD but tetragonal under electron diffraction) with an increasing amount of hematite, as indicative of the substitutional replacement of Zr⁴⁺ ions by the Fe³⁺ ions. Jiang et al.,⁹ by high-energy ball milling of monoclinic zirconia

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and hematite in different concentrations, have obtained nanostructured fully stabilized cubic substitutional solid solutions. The Mössbauer characterization of the solid solution consisted of a unique quadrupole doublet identified as due to high spin Fe^{3+} resulting from the average of two components of similar relative areas, quite broad line widths, and nearly equal isomer shifts (around 0.35 mm/s) but different quadrupole splittings (1.5 and 0.95 mm/s). In a more recent work on coprecipitated derived samples, Stefanic et al.¹⁰ found the same two quadrupole doublets that the authors interpreted as depicting two nonequivalent distributions of iron in the tetragonal (or cubic depending on the iron content and annealing temperature) substitutional solid solution. On the other hand, Ghigna and co-workers,¹¹ using ME and XAS techniques, studied a $\text{Zr}_{1-x}\text{Fe}_x\text{O}_{2-x/2}$ cubic solid solution prepared via combustion synthesis. They found that iron stabilizes cubic ZrO_2 entering mainly as $\text{Fe}(\text{II})$ and gives rise to roughly equal amounts of substitutional and interstitial Fe defects, the latter configuration involving a very short Fe–Zr distance that suggests the presence of a direct Fe–Zr metal-to-metal bond.

The perturbed angular correlations (PAC) nanoscopic method¹² measures the hyperfine interaction between the quadrupole moment Q of a probe nucleus (a radioactive nucleus inside the solid) and the electric field gradient (EFG) produced by the charge distribution at its nearest environment. If the nuclear quadrupole moment is known, the technique allows the determination of the EFGs existing at nonequivalent zirconium neighborhoods. Zirconia based ceramics are extremely suitable for the application of the PAC technique.^{13,14} In fact, natural zirconium contains 1–5% of hafnium impurities and upon neutron irradiation of the ceramic, ^{181}Hf activity is obtained. Finally, the ^{181}Ta nuclei resulting from ^{181}Hf β^- decay have proved to be a most efficient PAC probe. Being that Hf atoms are randomly distributed at Zr sites, the technique provides a thorough description of the lattice at a nanoscopic level. The EFG is conventionally described by the so-called hyperfine quadrupole parameters: the quadrupole frequency ω_Q that measures the EFG intensity and the asymmetry parameter η ($0 \leq \eta \leq 1$), which accounts for the degree of departure of the EFG from the axial symmetry ($\eta = 0$). A third parameter δ takes into account the spread or broadening of the EFG due to the eventual existence of impurities or defects affecting the Zr surroundings. Being that the method is extremely short-sighted ($\omega_Q \propto r^{-3}$), it does not average and allows us to distinguish among nonequivalent zirconium neighborhoods (i.e., chemical species, crystallographic phases within a same compound, and even different nanoconfigurations (distorted,

defective, disordered, dynamic) diffracting as a single phase to XRD) whose abundances or PAC relative fractions can as well be determined. The PAC experiment consists of the determination of the experimental function $A_2G_2(t)$, commonly called the PAC spectrum. By fitting this curve with an appropriate theoretical function, the mentioned quadrupole parameters of each of the lattice EFGs present in the zirconium containing material under study and also their relative abundance f_i are derived.

Two PAC hyperfine interactions have been previously found by the present authors to describe stabilized tetragonal zirconias at nanoscopic scales. They correspond to the already known forms of the metastable tetragonal phase—the t' -form and the t -form—determined in fine-grained pure zirconias¹⁵ as well as in doped tetragonal zirconias.^{16,17} The first of them is associated to a highly defective ($\omega_Q \approx 165$ Mrad/s and $\eta \approx 0.5$) and disordered ($\delta \geq 25\%$) tetragonal array caused, in the case of pure zirconias, by synthesis residues or defects derived from the preparation. In the case of zirconias doped with aliovalent oxides, it depicts, in addition, the Zr neighborhoods containing the oxygen vacancies generated for charge compensation provided that the dopant cations occupy Zr^{4+} lattice sites in the solid solution. The second interaction, in our earlier articles named the t_2 -form, is very similar to that known to describe the intense and quite symmetric EFG of the equilibrium tetragonal phase, although it is slightly asymmetric ($\eta \approx 0.2$). Typical PAC patterns and the quadrupole of the equilibrium t - ZrO_2 and metastable t' - and t -forms have been already reported.¹⁷

The sol-gel synthesis process offers the possibility of a better control of the composition in multicomponents systems. Besides, the use of metallic alkoxides as precursors allows the preparation of very fine ceramic powders of stabilized zirconia at lower temperatures than the ones required by solid-state methods. Crystallization occurs at a low temperature where long-range diffusion is still inhibited, thus favoring the formation of metastable phases that can accommodate larger amounts of stabilizing oxides than the equilibrium zirconia phases do.¹⁸

In this work, a sol-gel derived solid solution of nominal concentration 15 mol % Fe_2O_3 – ZrO_2 and its evolution with annealing treatments at increasing temperatures have been investigated at nanoscopic scales. The zirconia–hematite ceramic system presents the advantage that can be characterized alternatively by two highly localized nuclear hyperfine spectroscopies: the well-known ME technique that inspects the Fe nearest neighborhoods and the less commonly used PAC technique that probes the Zr nearest neighborhoods. It was expected that this dual nanometer scale investigation at the two cation sites could provide valuable information about the efficiency of the preparation method, the localization of

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dopant cations, and the effects of heat treatments on the obtained product.

Experimental Procedures

For the sol-gel sample preparation, zirconium *n*-propoxide 70% in propanol ($\text{Zr}(\text{O}(\text{CH}_2)_2\text{CH}_3)_4$) and (FeCl_3), both provided by Johnson Matthey, and 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$) obtained from Riedel-de Haën were used as starting materials. The Fe (III) chloride was initially treated by refluxing at 124 °C in 2-methoxyethanol for 6 h under nitrogen atmosphere to promote its partial alcoholysis. Total alcohol exchange of zirconium *n*-propoxide was performed by a similar refluxing treatment in 2-methoxyethanol. Finally, the (Zr, Fe) double alkoxide was obtained by mixing the zirconium and iron precursors by further refluxing and vacuum distillation. The 15 mol % Fe_2O_3 - ZrO_2 powders were obtained from the double metal alkoxide first gelificated at 120 °C under normal atmosphere (40% of relative humidity) and then milled and treated at 180 °C.

To select the temperatures for the annealing treatments, approximately 30 mg of the powder was first subjected to differential thermal and thermogravimetric analyses (DTA/TGA) using a Shimadzu Series-50 analyzer. The experiment was performed in air, at a flux of 50 mL/min and 10 °C/min, between RT and 900 °C. Pt crucibles and α - Al_2O_3 references were used. Subsequently, heating treatments of 2 h were carried out in air from 250 °C up to 850 °C. After each treatment, the powder was characterized by XRD and ME. The same thermal sequence was carried out on neutron-activated samples to perform the PAC experiments. XRD data were collected on a Phillips PW1710 diffractometer, using $\text{CuK}\alpha$ radiation and a graphite monochromator. Data were recorded in the range of $20^\circ \leq 2\theta \leq 80^\circ$ in steps of 0.02° with a counting time of 2 s per step. Powder diffraction spectra were exploited to calculate average crystallite sizes of the solid solution from the magnitude of the half-width of the main line for S- ZrO_2 ($2\theta \approx 30^\circ$, instrumental broadening of 0.1297°), using the Scherrer equation¹⁹ and having taken into account the microstrain contribution. The interplanar spacing was determined from the angular position of the main diffraction line, so allowing a comparative estimation of the cell size.

Mössbauer spectra were recorded in transmission geometry using a $^{57}\text{CoRh}$ source of approximately 5 mCi intensity by means of a standard 512 channels conventional constant acceleration spectrometer. Two ranges of velocities were employed to analyze in detail the different hyperfine interactions in the samples. One range covered velocities between -10 and $+10$ mm/s and the other one, -5 and $+5$ mm/s. Velocity calibration was performed against a 12 μm thick α -Fe foil. Isomer shifts reported are referred to this standard at 298 K. Lorentzian line shapes were fitted to the spectra with a nonlinear least-squares program.

For the PAC experiments, a ^{181}Hf activity of ≈ 200 μCi was obtained after 1 day of thermal neutron irradiation of approximately 100 mg of the material under study. The radioactive sample was placed in a fine quartz container, in air at normal pressure. For the annealing treatments, the quartz tube was placed inside a small tubular oven. The small dimensions of the sample guaranteed the temperature homogeneity throughout it, the temperature uncertainty being ± 1 °C. Each RT measurement lasted at least 2 days. The hyperfine interaction was determined using a two-CsF detector spectrometer of temporal resolution $\tau_R \leq 1$ ns.

Results

Figure 1 shows the TGA/DTA curves of the as-prepared powder. TGA indicates a minor mass loss near 120 °C; relevant mass losses at about 250, 350, and 480 °C; and an

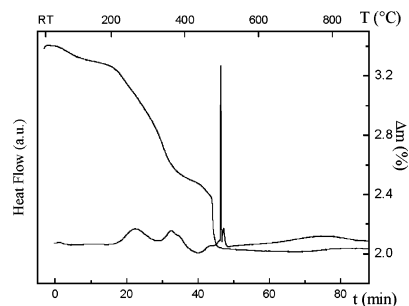


Figure 1. Thermal analyses of the investigated powder.

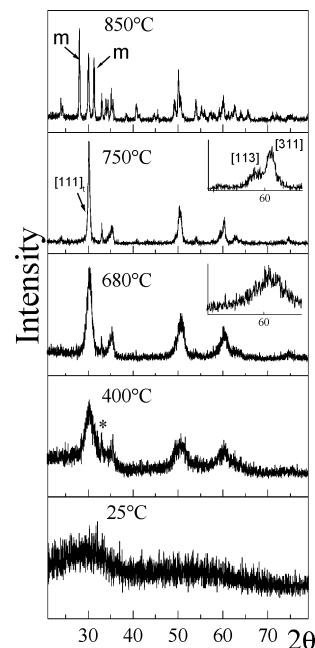


Figure 2. Selected X-ray diffractograms after annealing at the indicated temperatures. Asterisk denotes the main diffraction line of hematite.

incipient mass gain above 750 °C. Taking into account previous literature on sol-gel derived zirconia ceramics,¹⁶ the signals have been assigned, respectively, to the elimination of water, solvent, organic residues, and OH^- groups, and the mass gain is attributed to the absorption of atmospheric oxygen. Except for the first, all the changes mentioned can be clearly observed in the DTA as exothermic peaks, the last one being very broad and centered at about 800 °C. A double DTA peak at 500 °C, not correlated with any mass change, can also be observed. All thermal signals were irreversible.

In Figure 2, selected XRD patterns are presented. The as-obtained powder is amorphous, showing a broad and smeared peak at the position of the main diffraction lines of zirconia polymorphs. Each subsequent heat treatment results in a better definition of the lines, the material becoming crystalline upon annealing at 520 °C. Despite the broad peaks impeding a clear phase identification and intensity estimation, at 400 °C it can be observed that the $(\text{OH})^-$ containing lattice consists of at least two phases: traces of not yet crystalline hematite (evidenced by the diffraction line at $2\theta \approx 33^\circ$) and a major contribution of a zirconium compound that diffracts as a very fine grained stabilized S- ZrO_2 . Diffractograms upon annealing at higher temperatures show the persistence of the segregated hematite amount. At 680 °C, the improved

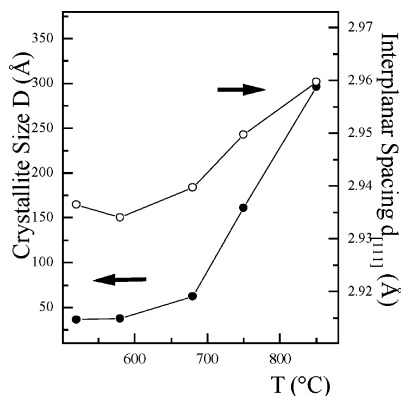


Figure 3. XRD derived crystallite size and interplanar spacing for the [111] diffraction line of t-zirconia.

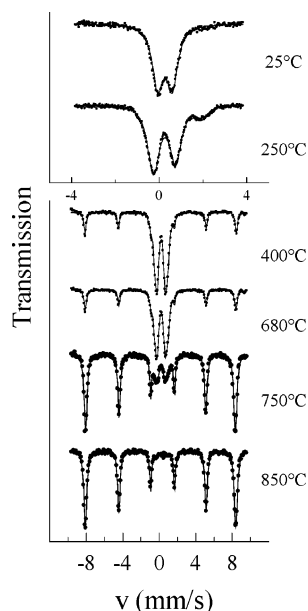


Figure 4. Selected Mössbauer spectra obtained after annealing the powder at the indicated temperatures.

definition of the peaks suggests the existence of a double peak at $2\theta \approx 60^\circ$. In fact, the distinction of the [113] and [311] reflections after being heated at 750°C led to the identification of the structure of S-ZrO₂ as tetragonal. Finally, upon cooling from 850°C , it can be seen that the metastable $t \rightarrow m$ transformation has taken place to a great extent. Figure 3 shows the average size of the crystallites and the interplanar spacing corresponding to the [111] main diffraction line of the tetragonal zirconia solid solution, both of them estimated from the diffractograms obtained after annealing at temperatures above 500°C . A relevant change of the two parameters can be observed at an annealing temperature of 750°C . At lower temperatures, the crystallite size, initially lower than 50 \AA , shows a smooth tendency to increase with temperature, while the interplanar spacing remains well-undervalued relative to that of pure tetragonal zirconia. At 850°C , the characteristic value for undoped zirconia, ca. 2.96 \AA , is achieved, and the particle size is increased to over 300 \AA .

Mössbauer spectra are displayed in Figure 4. In agreement with previous results,²⁰ the broad and unique fitted quadrupole doublet of quadrupole splitting $\Delta = 0.66 \text{ mm/s}$ and isomer shift $\delta_{\text{IS}} = 0.38 \text{ mm/s}$ is in correspondence with the XRD amorphous appearance of the as-obtained powder. After

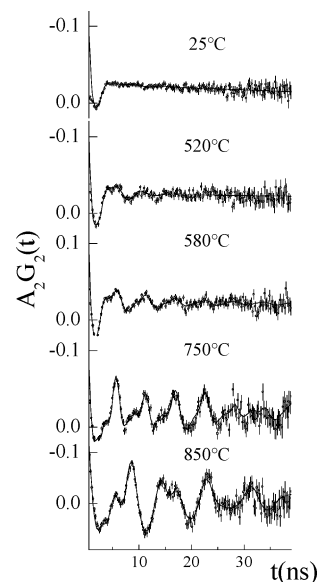


Figure 5. Selected postannealing PAC spectra. Annealing temperatures are indicated. Solid lines are the fitting curves.

the 250°C annealing, the spectrum can be well-fitted with about 20% of an interaction of $\delta_{\text{IS}} = 0.85 \text{ mm/s}$ and $\Delta = 2.4 \text{ mm/s}$ and of an extremely broad line-width ($\Gamma = 0.73 \text{ mm/s}$) that, according to the isomeric shift and line-width, can be assigned to some amorphous Fe²⁺ compound.²¹ This interaction is accompanied by two nearly equally abundant quadrupole contributions, hereinafter I_1 and I_2 , depicting the still rather amorphous Fe and sol-gel residues containing the zirconium compound. Both of them exhibit large line-widths ($\Gamma_1 = 0.53 \text{ mm/s}$ and $\Gamma_2 = 0.46 \text{ mm/s}$), similar isomer shifts identifying Fe³⁺ ($\delta_{\text{IS}} \approx 0.36 \text{ mm/s}$), and different quadrupole splittings: $\Delta_1 = 1.40 \text{ mm/s}$ and $\Delta_2 = 0.86 \text{ mm/s}$. Because of the large line widths determined for the two latter interactions, spectra fitting was also performed using quadrupole splitting distributions. This procedure led to very similar results. While the annealing at 400°C evidences the transformation of the Fe²⁺ doublet into a magnetic sextet of characteristics resembling that of $\alpha\text{-Fe}_2\text{O}_3$, the ME spectrum after annealing at 480°C is unambiguously fitted with 21% of hematite ($B = 52 \text{ T}$, $\delta_{\text{IS}} = 0.37 \text{ mm/s}$, $2\epsilon = -0.20 \text{ mm/s}$, and $\Gamma = 0.23 \text{ mm/s}$). As for the I_1 and I_2 quadrupole components, except for a subtle decrease in the line-widths up to the 520°C annealing temperature, their other hyperfine parameters (and also relative areas up to 680°C) remain nearly the same up to 750°C , the average parameters values being $\Delta_1 = 1.42 \text{ mm/s}$ and $\Gamma_1 = 0.48 \text{ mm/s}$ for I_1 and $\Delta_2 = 0.86 \text{ mm/s}$ and $\Gamma_2 = 0.40 \text{ mm/s}$ for I_2 . After the thermal treatment at 750°C , the amount of hematite increased from 20 up to about 80% at the expense of I_1 and I_2 and after calcining at 850°C , 95% of the iron ions appear nucleated as hematite.

The best fits of the PAC spectra (see Figure 5) were obtained with the contribution of four hyperfine interactions

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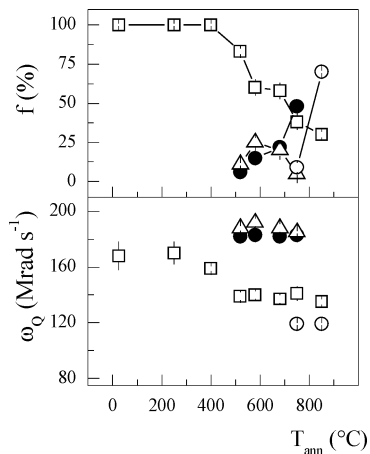


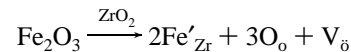
Figure 6. PAC relative fractions and quadrupole frequencies of the different nanoconfigurations around Zr^{4+} as a function of annealing temperature: □: t' ; △: X; ●: t ; and ○: m . Lines are just to guide the eye.

(not all of them coexisting at a same temperature) (i.e., the two corresponding to the t' - and t - forms of metastable tetragonal phase of zirconia)¹⁷ that of monoclinic zirconia and an unknown interaction, hereinafter denoted as X, corresponding to such an intense and ordered EFG as that of t -phase but nearly quite asymmetric ($\eta \approx 1$). Figure 6 exhibits the evolution of the fitted relative fractions and quadrupole frequencies over the whole thermal range investigated. Up to annealing temperatures of 400 °C, the inclusion of only the defective t' -form (□) is enough to achieve satisfactory fits of the experimental data. The unique change observed in this thermal region is the gradual reduction of the quadrupole frequency (and also its spread, not shown) as preparation residues are being eliminated from the amorphous powder. Upon cooling from 520 °C, small amounts of the X interaction (△) and that describing the more regular tetragonal t -form (●) must be added. Regarding the parent t' -form, the intensity of its EFG (proportional to ω_Q) acquires a stationary value up to the highest annealing temperatures. While the relative fraction of the X interaction exhibits its maximum abundance at 580 °C, the t -form increases up to half the sample after its annealing at 750 °C. At this temperature, a minor amount of monoclinic phase (○), somewhat distorted ($\eta \geq 0.45$) and disordered ($\delta \approx 10\%$), can be detected. After the final annealing at 850 °C, the powder becomes predominantly monoclinic through the $t \rightarrow m$ metastable phase transition.

Discussion

Despite the different heat treatments that the powders are subjected to during thermal analyses (see Figure 1) and postannealing diffraction experiments at RT (see Figure 2), combined results from the two techniques indicate that: (a) the double DTA peak at about 500 °C with no mass change associated must correspond to the crystallization of the zirconia tetragonal solid solution and of a minor amount of precipitated hematite and (b) the extended DTA exothermic signal centered at 800 °C associated to oxygen absorption¹⁶ must be linked to the appearance of the monoclinic zirconia phase accompanied with further partition of hematite. The much undervalued interplanar spacing determined for the [111] tetragonal diffraction line (plotted in Figure 3) for

temperatures lower than 750 °C suggests the relevant effect of the substitutional localization of the undersized Fe dopant cations in the solid solution according to the following reaction:



Moreover, the drastic increase in the cell dimension observed at higher temperatures, to values irreconcilable with a substitutional $Zr(Fe)O_2$ solid solution, matches the occurrence of the metastable $t \rightarrow m$ phase transition. On the other side, the simultaneous growth of the crystallite size seems indicative of the relevance of this property as it concerns the stability of the solid solution.

Regarding Mössbauer results, the amount of Fe^{2+} containing material not forming part of the amorphous solid solution, after suffering an oxidation process at low temperatures, becomes α - Fe_2O_3 at 480 °C and maintains unaltered up to 680 °C. While the existence of an Fe^{2+} compound in the starting powder could be explained as coming from some impurity present in the $FeCl_3$ starting reactive, the observed oxidation to Fe^{3+} could be attributed to the atmosphere under which the heating treatments are performed. From the amount of precipitated hematite, the solubility of α - Fe_2O_3 in zirconia can be calculated. It exhibits a maximum value of 12 mol % over the mentioned thermal region and decreases to 3 mol % at 750 °C. Concerning the I_1 and I_2 interactions depicting the amorphous Fe plus sol-gel residues containing the Zr compound, the decreasing line-width of both components seems to reflect the increasing crystallinity of the solid solution as preparation residues are being lost with temperature. From the near-to-crystallization annealing temperature on, the solid solution of tetragonal stabilized zirconia involves two nearly equally populated nanoscopic configurations around the Fe^{3+} cation sites, depicted by the now better defined I_1 and I_2 interactions. Very similar quadrupole splits were determined by other authors as mentioned in the Introduction^{9,10} and also by Burggraaf and co-workers.²² This latter group ascribed the Mössbauer doublet of lower quadrupole splitting (I_2) to very small precipitates of superparamagnetic Fe_2O_3 . With the aim of elucidating this point, a ME experiment on a sample first annealed at 500 °C was conducted at 22 K. No increased ferromagnetic content was detected, as would correspond if superparamagnetic hematite was present at RT. Also, the possibility of a variation in the nanoconfiguration content with the reduction in the Fe_2O_3 concentration was investigated. Two samples with 6 and 3 mol % of hematite, corresponding to minimum Fe concentrations compatible with the detection of the solid solution, were prepared by the same synthesis method as the present one and then analyzed. Within experimental errors, the ME spectra of these diluted samples were fitted with similar amounts of the same two hyperfine interactions. Finally, the authors were inclined to agree with Stefanic et al.'s¹⁰ point of view and associate the two doublets to the presence of two nonequivalent positions of substitutional iron in the zirconia lattice. In the case of a substitutional solid solution,

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two Zr^{4+} cations are replaced by two Fe^{3+} cations with the concomitant appearance of an oxygen vacancy for charge balance. Li et al.⁷ have reported that substitutional undersized dopant ions compete with Zr ions for the charge compensating oxygen vacancies inherent to this localization. They inferred a 6-fold coordination and a nearest neighbor oxygen vacancy association for Fe^{3+} ions in the solid solution. But they also found an unusually broad length dispersion of next nearest neighbors denoting a very large distortion of the cation network. In light of the present results, it seems reasonable to consider that one of the Fe ions could identify the configuration reported by Li, substitutionally positioned and suffering the off-centered displacement toward the oxygen vacancy it shares with Zr^{4+} host cations. The other Fe^{3+} , in turn, might be probably additionally influenced by the presence of some nearest Zr ions of the largely disturbed cation network.

Let us now discuss the PAC results (see Figure 6) in the light of the interpretation just formulated. Over the temperature range at which preparation residues are being eliminated from the amorphous material, the PAC technique is incompetent for distinguishing nonequivalent configurations around the probes' sites within the greatly disordered t' -form. It just recognizes a defective zirconia lattice described by an EFG of decreasing intensity and spread as residues are being lost with temperature. Once the crystallization temperature (≈ 500 °C) is achieved, (i) a somewhat less intense EFG (of constant quadrupole parameters up to its disappearance) depicts the distorted t' -form and (ii) two ordered interactions (i.e., that associated to the regular tetragonal structure (the t -form) and the novel X interaction) of very intense and highly asymmetric EFG give account of two different Zr^{4+} crystalline neighborhoods. Assuming that the interaction describing the t -form is exclusively felt by the Zr probes (the first coordination shell contains eight oxygen nearest neighbors but no Fe cations), the remaining X interactions depicting the defective t' -phase could be probably related to the two ME interactions described previously probed by the Fe cations. It seems reasonable that the $t'-I_1$ pair of more disordered interactions could be reflecting the presence of the shared structural charge compensating oxygen vacancy, observed by Zr probes through a fraction of the defective t' -form and by Fe probes through I_1 . The more ordered pair of the X and I_2 interactions, in turn, might be describing some additional influence between very close Zr and Fe ions, each probe inspecting its own neighborhood. To check the hypothesis of this alternative dopant localization, an extended X-ray absorption fine structure spectroscopy (EXAFS) experiment as that published for some other fluorite-structured oxides²³ would be of great help.

After heating at higher temperatures, the solid solution loses stability. In agreement with ME results after annealing at 750 °C revealing that near 80% of Fe ions have become outside the host lattice as hematite, PAC informs us that both X and t' -hyperfine interactions describing the tetragonal solid solution decrease to give rise to the growth of the free of Fe structures, t - ZrO_2 and m - ZrO_2 . An explanation of the absence of the latter polymorph in the corresponding diffractogram may be the distortion and disorder exhibited by this structure

at the nanoscopic level. The last annealing treatment results in a relevant partition of the solid solution into monoclinic zirconia and hematite.

Conclusions

A ZrO_2 15 mol % Fe_2O_3 system has been prepared by the sol-gel method. The resulting powder has been subjected to annealing treatments at increasing temperatures up to 850 °C. The nanoconfigurations around the Fe and Zr cations have been investigated, respectively, by means of the hyperfine techniques of Mössbauer spectroscopy and perturbed angular correlations, assisted by XRD and thermal analyses. The study led to the following conclusions:

(i) the sol-gel method employed in this work produces a $Zr^{4+}_{1-x}Fe^{3+}_xO_{2-x/2}$ solid solution of nanosized particles that crystallizes around 500 °C and remains stable up to 750 °C.

(ii) Before crystallization, the hyperfine techniques have made it possible to correlate the gradual loss of preparation residues as the temperature increases with the decreasing spread in the EFGs at cation sites in the precursor compound of the $Zr(Fe)O_2$ tetragonal solid solution. ME measurements, in turn, have informed us about an oxidation process occurring in the starting fraction of the Fe^{2+} amorphous compound. The technique was also sensitive to the two Fe^{3+} surrounding precursors of the crystalline ones.

(iii) Once preparation residues are lost, zirconia crystallizes in its tetragonal polymorph. The total of 12 mol % seems to be the upper concentration of hematite incorporated in zirconia to produce a tetragonal solid solution under the present synthesis conditions.

(iv) The low values of the interplanar spacing determined the evidence of the relevant effect of the substitutional localization of the undersized Fe cations in the host lattice.

(v) From the crystallization temperature on, two nonequivalent nanoconfigurations for each one of the probe cations are found. The most disordered one is due to the influence of the oxygen vacancy that appears whenever aliovalent dopant ions are located at host sites, which are shared by host and dopant cations. The corresponding PAC interaction is the one assigned to the t' -form already found in other substitutional zirconia solid solutions. The second nanoconfiguration has been supposed to reflect some additional influence on cation probes, as could be the mutual interaction between nearest Fe and Zr ions of the largely distorted neighboring cation network. The PAC characterization of this site is novel and corresponds to a largely asymmetric and very intense EFG.

(vi) After annealing at 850 °C, most of the solid solution separates into hematite and monoclinic zirconia. The correlation between the decomposition of the solid solution and the growth of the crystallite size reflects the dependence of the solid solution stability on particle size. This fact corroborates the goodness of the sol-gel synthesis, leading to nanoparticles, for the preparation of stabilized zirconias.

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