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Synthesis and characterization of vanadium-containing ZrO$_2$ solid solutions pigmenting system from gels

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A procedure is reported for the synthesis of vanadium-doped zirconia pigmenting system with different vanadium loadings which permitted their complete formation and further characterization. Monoclinic vanadium-zirconia solid solutions were prepared by gelling mixtures of zirconium *n*-propoxide and vanadyl acetylacetonate and studied over the range of temperature up to 1300 °C. Succesive steps of the reactions leading to the final monoclinic vanadium-zirconia solid solution phase were investigated by X-ray powder diffraction. It was found that the formation of the monoclinic solid solution took place by a phase transformation from a phase with the structure of tetragonal zirconia. The transformation temperature of metastable tetragonal to monoclinic phase was found to be governed by the nominal vanadium amount. Measurements of lattice parameters of monoclinic vanadium-zirconia solid solutions as a function of the nominal vanadium amount revealed that vanadium was dissolved in the zirconia lattice. Energy dispersive X-ray microanalysis and lattice parameters variation indicates that the maximum amount of vanadium into the monoclinic zirconia lattice was about 5 mol % of vanadium (3.7 wt % as V$_2$O$_5$). UV-Vis diffuse reflectance of monoclinic V-ZrO$_2$ solid solutions indicated that vanadium was dissolved as V^{+4} and that the color of vanadium-zirconia yellow pigments was produced by the dissolved vanadium.

1. Introduction

Vanadium containing single oxides ceramic pigments have been used for years in the ceramic industry. Two are the main host lattices from which yellow color is produced, i.e., monoclinic ZrO$_2$ (badeleyite) and SnO$_2$ (cassiterite), later with rutile crystalline structure. Both of them provide pigmenting systems widely utilised because of their color strength and chemical and thermal stability when dispersed in glazes.

Although many reports have been involved on technical aspects of the vanadium-containing zirconia pigmenting system, some chemical and structural points are not completely known yet. Some doubts concerning to the formation mechanism still remain, mainly those related with a sructural point of view. Thus, it is not fully established whether the pigment is a solid solution, an encapsulated pigment-that is, a composite in which a second phase, the chromophore, is protected by the more abundant- or, finally, even a mordient pigment, that is a monomolecular layer of pigment surrounding the second crystalline substrate. Thus, Booth and Peel [1] considered that the yellow color is due to a monomolecular thin film of V$_2$O$_5$ on the ZrO$_2$. Some previously reported results by Monros *et al.* [2] gave evidences of V$_2$O$_5$ encapsulation in ZrO$_2$, when specimens were prepared from either colloidal and polymeric gels. Recently Ren *et al.* [3] claimed that this ceramic pigmenting system was a solid solution of V^{+4} in ZrO$_2$. More recently, Tartaj *et al.* [4] stated that the origin of the color was mainly attributed to the presence of V$_2$O$_5$ in the outer layers of the zirconia grains and a small fraction ($\approx$15%) of the vanadium amount contained in the pigments was present as V (IV) substituting Zr (IV) in the monoclinic zirconia lattice.

Almost all results reported on this system have been obtained from specimens containing an excess of vanadium loadings and consequently after thermal treatments specimens must be submitted to either washing with a hot acidic solution or leaching by fusing with NH$_4$HSO$_4$ at 200 °C followed by washing with distilled water, to eliminate the excess of vanadium before further characterization.

Although the presence of V (IV) in the monoclinic zirconia lattice has been ascertained by UV-Vis spectrocopy [3] and electron spin resonance [3, 4], only a few indications are available as to the maximum amount of vanadium which can enter the badeleyite matrix and the role played by other factors, such as vanadia loads and temperature. For instance, no data have as yet been reported concerning variation of cell parameters as a function of vanadium dissolution. Thus, it is not possible to draw up a complete picture of the vanadium-zirconia pigmenting system on the basis of available data on distribution and chemical states of vanadium.

To contribute to the better understanding of the vanadium-ZrO_2 pigmenting system it would be needed to involve high reactive mixtures in which no excess of vanadium is required to obtain the final solid solution product and, therefore, no subsequent leaching to eliminate this excess is required. Moreover, we should take into account the important role played by the transformation of ZrO_2 from the monoclinic form to the tetragonal modification in the conventional preparation of the yellow vanadia-zirconia pigmenting system [5].

Amorphous and tetragonal zirconia, though not the thermodynamically stable form of pure zirconia under ambient conditions, can be readily obtained by various means [6–9]. The possibility of formation of a low-temperature tetragonal phase and its further tetragonal to monoclinic trasformation at also relatively low temperature would favour the achievement of the vanadium-zirconia pigmenting system at very low temperatures. It is to note that apart from the significant role played by the vanadium-zirconia system in the field of the ceramic pigmenting systems, it can also act as a good catalyst. Studies on the preparation and properties of vanadium in zirconia supports for catalytic applications have attracted much attention [10–11].

A new approach for the synthesis of this pigmenting system would be the preparation of precursors having higher reactivity at low temperature. On this basis, in this paper we intend to prepare the vanadium-containing zirconia solid solution pigmenting system from gel precursors obtained by mixing zirconium *n*-propoxide and vanadyl acetylacetonate. The high reactivity of the precursors allowed to moderate the thermal processing, favoring a lowering of the solid solution formation temperature. Consequently, the examination of some chemical and structural aspects of this pigmenting system would be facilitated.

2. Experimental procedure

2.1. Synthesis of gels

Gels of vanadium-containing zirconia with nominal stoichiometry $V_xZr_{1-x}O_2$, with $x = 0.0$, 0.005, 0.01, 0.015, 0.02, 0.025, 0.05, 0.075, 0.1, 0.15 and 0.175, were prepared. Zirconium *n*-propoxide ($Zr\ (OC_3H_7)_4$, (ZnP)) and vanadyl acetylacetonate ($C_{10}H_{14}O_5V$, $VO(acac)_2$) both provided by Merck & Co, were used as molecular precursors of zirconium and vanadium, respectively. Acetylacetone (acacH) and *n*-propanol (*n*-PrOH) both supplied by Panreac were used without further purification.

The procedure for the preparation of gels was the following. To a mixture of acacH and *n*-PrOH kept under an atmosphere of Ar in a glovebox a solution of ZnP was added. $VO(acac)_2$ was then dissolved in the solution kept in continuous stirring, in the amount required to obtain the desired V : Zr ratio in the final material. The molar ratios *n*-PrOH/ZnP and acacH/ZnP used were 8.1 and 1.1, respectively. After removing the solution from the glovebox the hydrolysis was performed by adding water. The molar ratio H_2O/ZnP used was 11.2. The resulting solution obtained which was orange was placed in a closed vessel and then left at 60 °C in a oven. Gels appeared after several times depending mainly on the amount of vanadium in the final solution. Further drying of gels was performed in a oven at 120 °C. Gels displayed more and more orangeness depending on the amount of vanadium. The precursors were ground into powders using an agate mortar and pestle. Each precursor was heated at 10 °C/min from room temperature up to 1300 °C. They were also annealed for several times at different temperatures. After each heating the sample was cooled in air in the furnace.

2.2. Techniques of characterization

Chemical and structural evolutions of dried gels and crystalline specimens were examined using several techniques.

X-ray powder diffraction analysis (Model D-500, Siemens, Karlsruhe, Germany) was performed using a graphite monochromatic Cu K_α radiation to assess the different phases present in the solids. Precise lattice parameters of monoclinic zirconia solid solutions was made using LSQC and POWCAL programs. The diffractometer had two 1° divergence slits, the scatter and receiving slits being 1° and 0.15°, respectively. The diffractograms were collected between 20° and 100° (2θ) at intervals of 0.02 (2θ) with an accumulation time for interval of 20 s. All experiments were measured using Al_2O_3 as internal standard.

Energy-dispersive X-ray analysis was performed using a scanning electron microscope (Model JSM-6300, Jeol, Oxford, England) operated at 20 kV. This instrument is equipped with an energy dispersive X-ray spectrometer (Pentafet, Oxford Instruments, Knoxwille, TN). Specimens were mounted in a polymer resin and polished with progressively finer SiC papers. Before acquiring the X-ray spectra samples were carbon coated. The type of analysis accomplished entailed obtaining the overall analysis of the whole sample before thermal treatment and after annealing at diferent temperatures. This kind of analysis was obtained from a large area of the specimen and it was an average of the area of the image on the scanning electron microscope screen. It was therefore performed at low magnification (lower than 1K). Quantitative analyses of specimens were made using the SEMQuant program with ZAF correction procedures and the default standards.

UV-Vis spectra of the specimens (Model Lambda 9, Perkin Elmer, Norwalk, Connecticut, U.S.A.) were obtained using the diffuse reflectance technique in the range of 200 to 1000 nm using a $BaSO_4$ plate as the reflectance standard. The absorbance was represented by the remision function, $F(R) = (1 - R)^2/2R$, were R is reflectance.

3. Results and discussion

3.1. Formation of monoclinic V-ZrO_2 solid solutions

A study of the effect of heat treatment on pure zirconia gels was performed in order to know the crystallization path from the gel precursor to the monoclinic zirconia

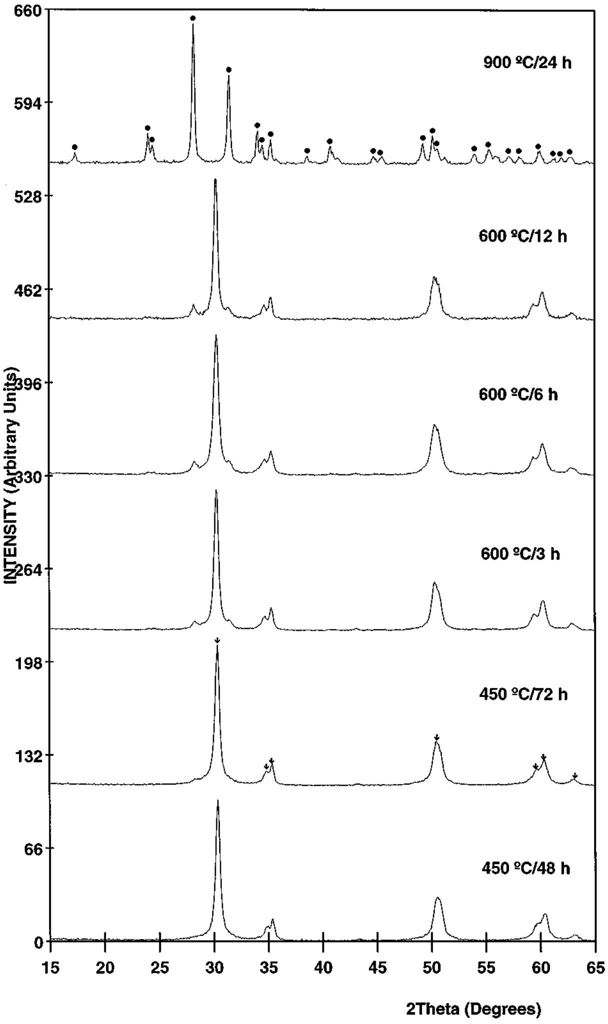


Figure 1 X-ray diffraction patterns of sample with $x = 0$, i.e. undoped zirconia, at increasing temperatures and/or heating times (● is monoclinic zirconia and ↑ tetragonal zirconia).

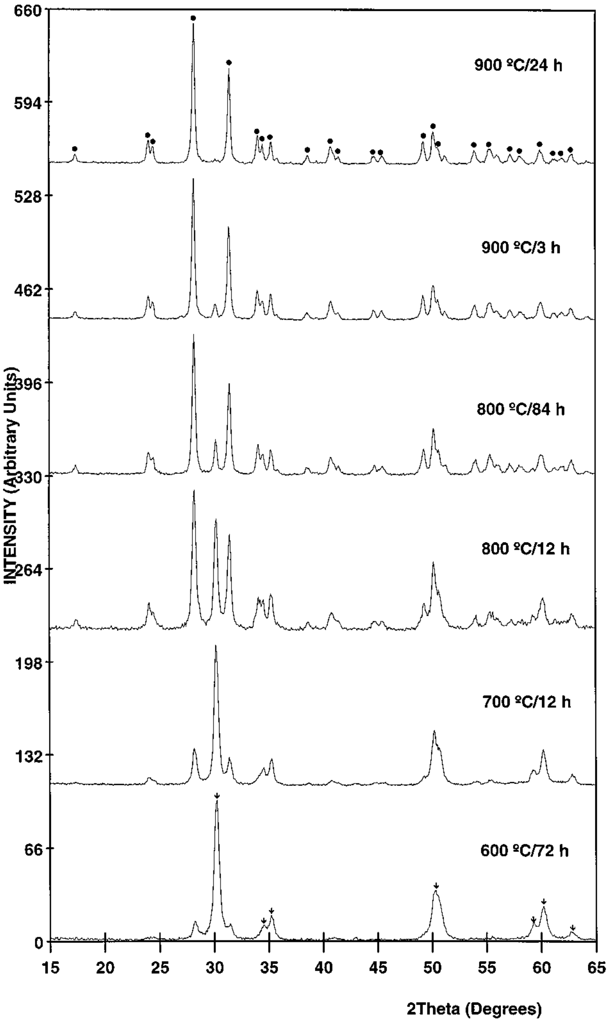


Figure 2 X-ray diffraction patterns of sample with $x = 0.005$, i.e. zirconia doped with the lower amount of vanadium, at increasing temperatures and/or heating times (● is monoclinic zirconia and ↑ tetragonal zirconia).

crystalline phase. Dried gel of pure ZrO_2 was amorphous to X-ray diffraction.

Several X-ray diffraction patterns obtained at increasing temperature and/or time periods during succesive heatings in air of a dried gel are shown in Fig. 1. The tetragonal phase appears first upon heating to about 450 °C. Further heating to 600 °C causes that the phase transformation begins to occur and very small peaks of monoclinic zirconia at about 28.0° and 31.5° (2θ) are seen. The transformation continues by subsequent thermal treatments at temperatures above 600 °C to produce a material that is essentially the monoclinic phase after heating to 900 °C for 24 h.

The crystallization of tetragonal ZrO_2 as the first crystalline phase from zirconia gel precursors obtained by different techniques of preparation is well known. Many explanations has been advanced to understand the low temperature stabilization of the tetragonal phase [12–15]. However, which of the mechanisms is responsible for stabilization of the tetragonal phase is still a matter of debate.

It is to be noted that the further transformation to the monoclinic zirconia takes place over a wide range of temperatures, i.e. between 600 °C and 900 °C. This behaviour is similar to other reported on the structural transformation of zirconia gels [9, 16]. *In situ* X-ray diffraction experiments performed on similar zirconia gels, in which the tetragonal crystalline form first crystallized when heated at several temperatures up to 1100 °C for 2 h and allowed to cool to room temperature, shown that the phase transformation occurred when the sample was cooled. As it has been claimed [9] it seems reasonable to believe that the tetragonal to monoclinic phase transformation can be controlled by embryo formation and growth phenomenon.

On heating vanadium-containing gel precursors with increasing vanadium content the steps over the temperature range up to the monoclinic V-containing ZrO_2 solid solution are similar to the observed in pure zirconia. Figs 2–4, corresponding to samples with $x = 0.005$, 0.05 and 0.125, respectively, show the set of crystalline phases at several temperatures and/or time periods. As it can be seen, the first crystalline phase in all thermal treated specimens is detected at around 450 °C. This phase displays the structure of tetragonal zirconia and we have recently shown that is a V^{+4}-ZrO_2 solid solution [17, 18].

It is to note that regarding the tetragonal to monoclinic phase transformation in the V^{+4}-ZrO_2 solid solution, the temperature required to complete the

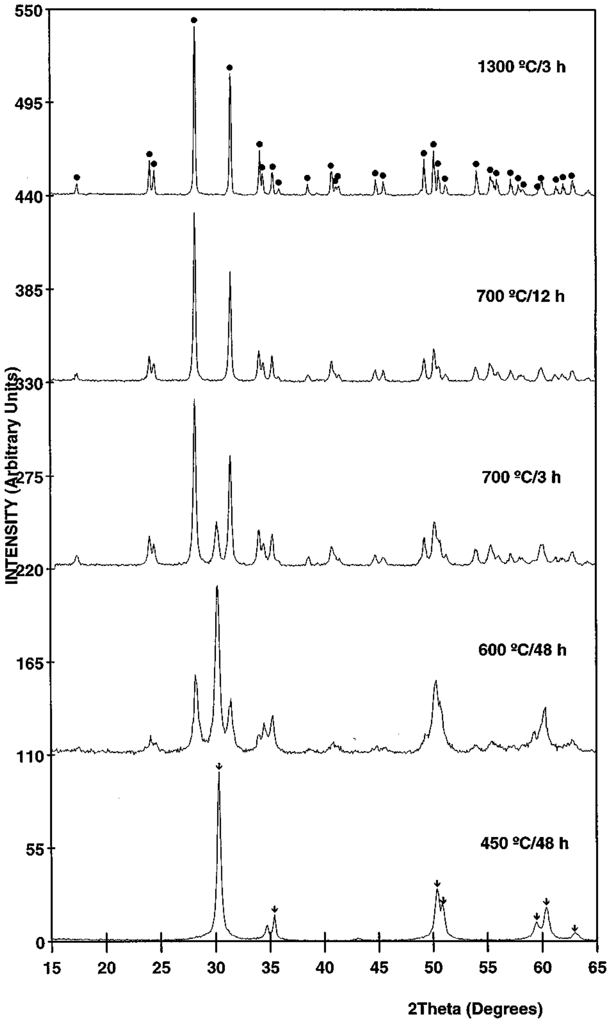


Figure 3 X-ray diffraction patterns of sample with $x = 0.05$ at increasing temperatures and/or heating times (● is monoclinic zirconia and ↑ tetragonal zirconia).

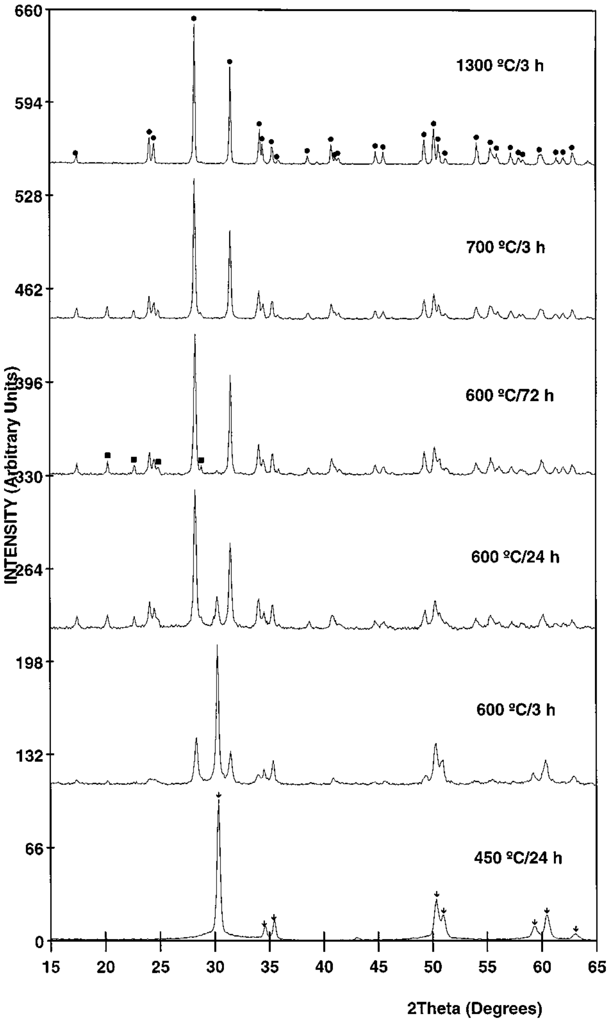


Figure 4 X-ray diffraction patterns of sample with $x = 0.125$ at increasing temperatures and/or heating times (● is monoclinic zirconia, ■ is ZrV_2O_7 and ↑ tetragonal zirconia).

phase trasformation to the monoclinic form during the cooling step is dependent on the nominal vanadium amount in the sample. As it can be seen in Figs 2–4, the higher vanadium loading the lower transformation temperature. Thus, for specimen with the lower amount of vanadium, i.e. $x = 0.005$, the transformation temperature is similar to the pure zirconia, whereas for specimens with $x = 0.05$ and $x = 0.125$ are 700 and 600 °C, respectively. This fact can be understood assuming that the transformation temperature is dependent on the composition of the tetragonal V^{+4}-ZrO_2 solid solution. Thus, the lower transformation temperature expected will correspond to the tetragonal V-richer zirconia, i.e. to the specimen in which the limit of solubility of vanadium in the tetragonal zirconia lattice was reached.

3.2. Characterization of monoclinic V-ZrO_2 solid solutions

Monoclinic V-ZrO_2 solid solution specimens obtained after heating gel precursors at two different temperatures, i.e. at the lower temperature required to obtain the monoclinic crystalline form (between 700 and 900 °C depending on the vanadium amount in the starting composition) and at 1300 °C, were studied by spectroscopic and diffraction techniques to obtain information on the chemical state of vanadium and the limit of solubility of vanadium into the monoclinic zirconia lattice.

3.2.1. Lattice parameters variation and limit of solubility of vanadium

Table I displays the lattice parameters as a function of the vanadium concentration in the starting mixture for specimens heated at 1300 °C for 3 h. As it can be seen the decreasing trend of the a and c lattice parameters with the amount of nominal vanadium is evident, reaching the smallest values for about $x = 0.05$. On the other hand, the trend of the b lattice parameter is opposite, i.e. increases with the amount of vanadium, but for the specimen $x = 0.05$ this increasing is not so pronounced. This behaviour by which one axis expand while the other two contract (or *vice versa*) is characteristic of non-cubic crystals. As a consequence of the lattice parameter variation the cell volume decreases with enhancing the vanadium loading. The minimum value of it is attained for the specimen with x about 0.05. The change in the lattice volume as the vanadium content increases in the solid solution is consistent with the idea of contraction of the unit cell as a large ion is replaced by a smaller one. The monoclinic zirconia structure can be described as a distortion of the cubic

TABLE I Lattice parameters as a function of the vanadium concentration in the starting mixture for specimens heated at 1300 °C for 3 hours

Sample	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
$x = 0.0$	5.1515 ± 0.0005	5.2022 ± 0.0005	5.3162 ± 0.0004	99.24 ± 0.01	140.61 ± 0.01
$x = 0.005$	5.1431 ± 0.0004	5.2056 ± 0.0004	5.3128 ± 0.0004	99.21 ± 0.01	140.40 ± 0.01
$x = 0.01$	5.1428 ± 0.0004	5.2067 ± 0.0004	5.3128 ± 0.0004	99.20 ± 0.01	140.43 ± 0.01
$x = 0.02$	5.1430 ± 0.0004	5.2068 ± 0.0004	5.3140 ± 0.0004	99.20 ± 0.01	140.47 ± 0.01
$x = 0.05$	5.1410 ± 0.0004	5.2032 ± 0.0004	5.3124 ± 0.0004	99.20 ± 0.01	140.27 ± 0.01
$x = 0.075$	5.1446 ± 0.0004	5.2068 ± 0.0004	5.3152 ± 0.0004	99.20 ± 0.01	140.55 ± 0.01

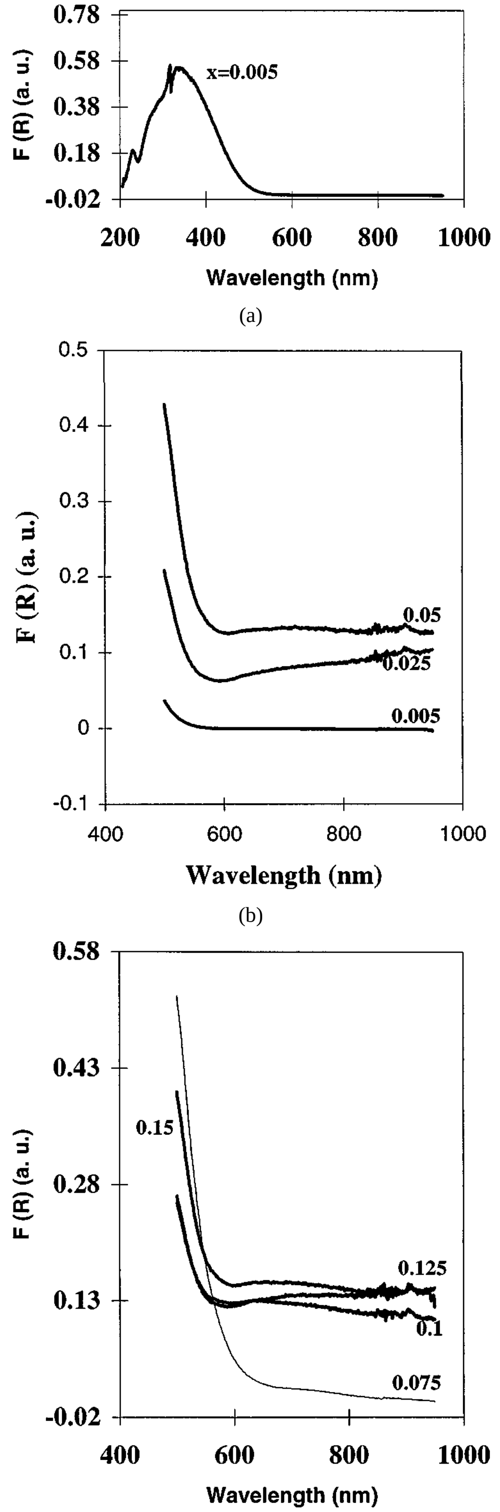
fluorite (CaF_2) structure [19]. The observed decrease in lattice volume can be understood assuming that the mechanism of the solid solution formation is sustitutional, i.e. that the Zr^{+4} is replaced by V^{+4} in the seven coordinated sites of the monoclinic zirconia structure. Obviously, the smaller ionic radius of V^{+4} compared with Zr^{+4} for 7-fold symmetry (78 and 65 pm, respectively) [20] causes the progressive decrease of unit cell volume with increasing substitution. The ionic radius of V^{+4} in 7-fold symmetry (65 pm) was calculated by averaging those of 6- and 8-fold symmetries. Thus, it seems reasonable conclude that experimental results are consistent with the whole process of solid solution formation assumed above.

It is to note that as far as we know results on lattice parameter as a function of the increasing vanadium content of monoclinic vanadium-zirconia solid solution have still not been reported. However, the variation of the lattice parameters of one vanadium-containing sample with respect to those corresponding to pure zirconia have been observed by some authors [3, 4]. The fact that we were able to prepare and measure the evolution of the lattice parameters in specimens with very low amounts of vanadium loading can be understood because the synthetic procedure employed, which was different from those reported in the literature, led to a precursor gel with high homogeneity and as consequence high reactivity at low temperatures.

According with the above results and assuming that the limit of solubility of vanadium in monoclinic zirconia is closed to the one corresponding to the sample with a nominal value of $x = 0.05$, SEM/EDX of that sample thermal treated at temperatures to which the monoclinic zirconia solid solution is already formed, was performed at low magnification in order to evaluate the real amount of vanadium inside the monoclinic zirconia. The V_2O_5 amount (in wt %) of that sample heated at 700 °/42 h and 1300 °C/3 h were 4.3 ± 0.2 and 3.7 ± 0.1, respectively. The value of the vanadium content obtained for that sample indicates that all the starting vanadium has been incorporated into the monoclinic zirconia and practically no vanadium has been lost by volatilization. It is to note that this solubility limit of vanadium was higher than the one reported previously by Ren *et al.* [3].

3.2.2. Reflectance spectra of solid solutions

In order to evidence the chemical state of the vanadium cation inside the monoclinic zirconia lattice diffuse reflectance spectroscopy of specimens displaying the monoclinic zirconia structure was performed. Figs 5 and 6 shows the reflectance spectra of specimens

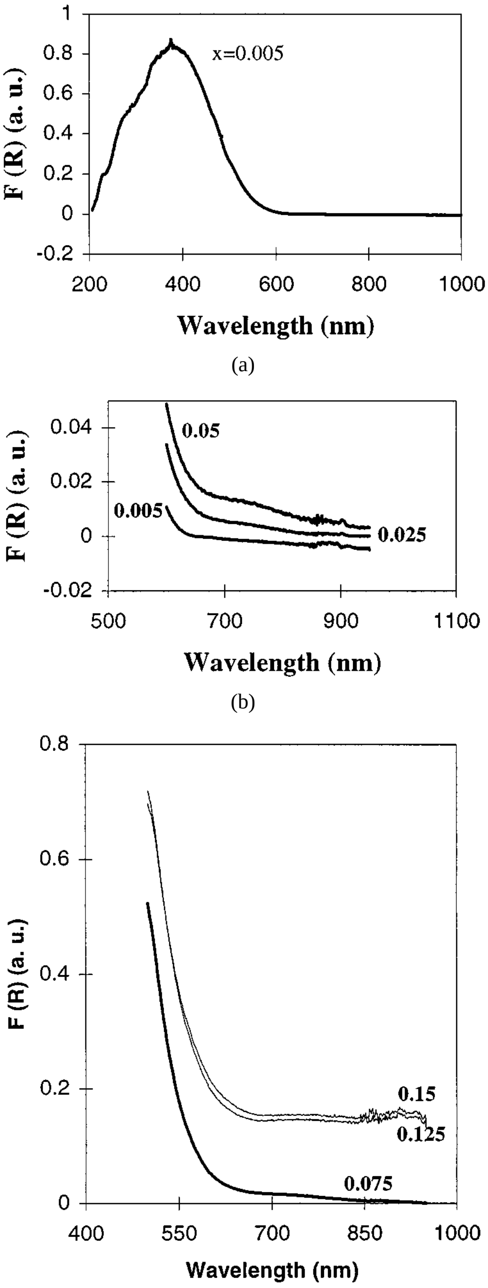


(a)

(b)

(c)

Figure 5 Reflectance spectra of monoclinic $V_xZr_{1-x}O_2$ solid solutions: (a) $x = 0.005$ heated at 900 °C for 24 h; (b) $x = 0.005$, 0.025 and 0.05 heated at 900 °C/24 h, 800 °C/24 h and 700 °C/12 h, respectively; (c) $x = 0.075$, 0.1, 0.125 and 0.15 heated at 700 °C/3 h.



(a)

(b)

(c)

Figure 6 Reflectance spectra of monoclinic $V_xZr_{1-x}O_2$ solid solutions heated at 1300 °C for 3 h: (a) $x = 0.005$; (b) $x = 0.005$, 0.025 and 0.05; (c) $x = 0.075$, 0.125 and 0.15.

heated at the lower temperature required to obtain the monoclinic crystalline form of the solid solution (between 900 and 700 °C for several time periods) and at 1300 °C for 3 h, respectively. The reflectance spectra of all specimens containing increasing amounts of vanadium and thermal treated at lower temperature is similar to that of sample with the lower amount of vanadium, i.e. $x = 0.005$, heated at 900 °C for 24 h, shown in the Fig. 5a and chosen as a representative sample. From this spectrum a broad and intense band in the range between 200 and 500 nm is observed that can be caused by a charge transfer mechanism. In view of the structure of the monoclinic zirconia this transfer band is considered to be a convolution of at least three absorption peaks [3]. A closer look to the spectra in the range between 400 and 1000 nm in an enlarged scale for these specimens with increasing amount of vanadium is shown in Fig. 5b and c. The spectra reveals the presence of a weak band peaked around 750 nm which can be caused by a d-d transition. Fig. 6 show the reflectance spectra of samples heated at high temperature, i.e. 1300 °C for 3 h. Comparison between spectra in Figs 5 and 6 reveals that further heating results in a more defined and intense spectra.

The chemical state of vanadium in these samples after being thermal treated at so high temperatures may be V^{+4} and/or V^{+5}. Since as evidenced by the XRD powder study for specimens with amounts of vanadium lower than $x = 0.1$ the only crystalline phase detected was the monoclinic zirconia, the vanadium may be placed either as a solid solution of V^{+4} and/or V^{+5} in monoclinic zirconia or an amorphous V^{+5} oxide. Obviously the V^{+4} chemical state only will be stable, and therefore detected, when it can be placed inside some crystalline matrix. In addition, it is well known that the electronic configuration of the V^{+5} cation is d^0 and consequently no allowed *d*-*d* transitions are shown. From the above statements it can be inferred that the weak band at around 700 nm may be attributed to V^{+4} in monoclinic zirconia. Furthermore, it has been reported that some V(IV) compounds, i.e. ($V(OBut)_4$), give rise to a intense charge transfer band at 350 nm [21]. It seems reasonable, therefore, to conclude that the whole reflectance spectra of the specimens consist of spectra from V^{+4} cations in monoclinic zirconia crystalline phases. It is to note that a similar charge transfer band, displaying a yellow color instead of a brown color, has been observed by minute particles of V_2O_5, i.e. containing V^{+5}, thinly coating ZrO_2 grains [1]. This fact along with the difficulty to evidence the presence of very small amounts of V^{+4} cations have delayed the correct explanation for the origin of its lemon yellow color.

EPR mesurements of these samples thermal treated at low temperatures for several times, i.e. between 900 °C and 700 °C, and 1300 °C for 3 h have been reported elsewhere [18] and confirm the presence of V^{+4} cations in the monoclinic zirconia lattice.

4. Conclusions

Monoclinic vanadium-zirconia solid solutions were prepared by gelling mixtures of zirconium *n*-propoxide and vanadyl acetylacetonate and studied over the temperature range up to 1300 °C. Characterization of V-ZrO_2 solid solutions was carried out mainly by X-ray powder diffraction, measurements of lattice parameters, energy dispersive X-ray microanalysis and diffuse reflectance spectroscopy. The results can be summarized as follows:

(a) A phase with the structure of tetragonal ZrO_2 was the first crystalline phase formed from the amorphous gel precursors containing increasing vanadia loadings. The temperature of formation of these zirconias is not dependent on the amount of vanadium in the starting composition.

(b) The formation of monoclinic vanadium-ZrO_2 solid solution took place by the phase transformation from the phase with the structure of tetragonal zirconia.

(c) Changes of lattice parameters as a function of the nominal amount of vanadium revealed that the dissolved vanadium ions replace Zr^{+4} in seven coordinated sites in the monoclinic zirconia structure.

(d) Lattice parameters variation and energy dispersive X-ray microanalysis indicated that the maximum amount of vanadium into the monoclinic ZrO_2 lattice was about 5 mol % of vanadium (3.7 wt % V_2O_5).

(e) Diffuse reflectance spectroscopy revealed that the chemical state of vanadium in V-doped monoclinic ZrO_2 was V^{+4}.

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