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Rietveld Refinement of Tetragonal V^{4+}–ZrO_2 Solid Solutions Obtained from Gels by X-ray Powder Diffraction

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The crystal structure of three tetragonal $V_xZr_{1-x}O_2$ solid solutions, with $x = 0.025$, 0.05, and 0.075, prepared by heating dried gel precursors at 450°C in air atmosphere, have been determined by Rietveld refinement on the basis of powder X-ray powder diffractometer data. They contain V^{4+} cations surrounded by eight oxygens, four at a distance between 2.079 and 2.093 Å and another four at longer distances between 2.369 and 2.348 Å. The estimation of the crystal average oxygen position from the X-ray lattice parameter of $V_xZr_{1-x}O_2$ conform with the relationship proposed by Howard *et al.* (*J. Am. Ceram. Soc.* 81, 241 (1998)). © 2002 Elsevier Science

Key Words: **sol–gel chemistry; solid solution; X-ray powder diffraction; crystal structure, Rietveld refinement.**

1. INTRODUCTION

ZrO_2-based materials have received increasing attention for a wide range of applications. The three polymorphs of zirconia, viz., monoclinic, tetragonal, and cubic, have been well characterized. The polymorphic forms and other chemical/physical properties of a ZrO_2 material can be designed and then engineered by using processing materials techniques such as the sol–gel methods. More specifically, the crystallographic structure, microstructural features, and chemical and thermal stabilities can all be controlled to meet the desired applications. The various polymorphs of zirconia can be made stable or metastable even at room temperature by the addition of some metal oxides. Solid solutions of zirconia and various metal ions have been widely investigated (1–4).

Monoclinic vanadium-containing ZrO_2 ceramic pigments have been used for years in the ceramic industry because of their color strength and chemical and thermal stability when dispersed in glazes (5, 6). Apart from this, the vanadium oxide dispersed on zirconia can also act as an effective catalyst for selective catalytic reduction of NO_x with ammonia, partial oxidation of alkanes, and oxidative dehydrogenation of alkanes (7, 8).

Efforts aimed at elucidating the structure of the vanadium-containing zirconium ceramic pigments from specimens prepared from gels indicate the incorporation of V^{4+} into both the tetragonal and monoclinic zirconia matrix (9–14). Tetragonal V^{4+}–ZrO_2 solid solutions have been prepared for compositions in the V_2O_5–ZrO_2–SiO_2 ternay and V_2O_5–ZrO_2 binary systems on heating gel precursors obtained from different starting reagents (9–12). For the case of ternary compositions the temperature of the formation of these V^{4+}–ZrO_2 solid solutions was strongly dependent on the amount of vanadium in the starting composition. As vanadium oxide loading increased, the temperature required to transform gel precursor into the tetragonal solid solution decreased (9, 10). In contrast, in the binary compositions the temperature of formation of these tetragonal solid solutions occurred after annealing at 450°C for all specimens independently of the vanadium content (11, 12). Results on the characterization of tetragonal solid solutions by several techniques such as X-ray powder diffraction, diffuse reflectance spectroscopy, and electron spin resonance indicated that the chemical state of vanadium in the tetragonal zirconia was $+4$.

The aim of this paper is, therefore, to report the structure refinement for tetragonal V^{4+}–ZrO_2 solid solutions by the Rietveld technique and to confirm the cation distribution in a solid solution series of those solid solutions synthesized from gels.

2. EXPERIMENTAL

2.1. Preparation and Characterization of Samples

The preparation methods have been described earlier (11, 12). Three tetragonal $V_xZr_{1-x}O_2$ solid solutions, with $x = 0.025$, 0.05, and 0.075, were prepared by heating dried gel precursors up to 450°C at a rate of 10°C/min in an air atmosphere. Further isothermal treatments at 450°C were given as required to produce a crystalline phase displaying the structure of tetragonal zirconia. After each heating, the sample was cooled in air in the furnace.

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High-resolution electron microscopy (Hitachi, H-800) revealed that this sample is formed by tetragonal nanocrystals around 10 nm in size.

2.2. *Rietveld Refinement*

For the preparation of X-ray powder diffraction specimens the crystallized zirconia gels were ground with an agate mortar and pestle. The X-ray diffraction patterns of the powder samples were recorded using Bragg-Brentano geometry at room temperature by means of a Siemens D-500 X-ray powder diffractometer. The experimental conditions used were Cu$K\alpha$ radiation (40 kV, 20 mA, 1° divergence slit, 0.05° detector slit), scintillation detector, and a secondary graphite monochromator.

The peak positions and the integral intensities of the observed reflections were collected by step scanning from 20° to 120° (2θ) with a step size of 0.02° (2θ) and a counting time of 10 s for each step.

The crystal structure was refined with the Rietveld method (15) by using the FULLPROF software (16) based on the code of the DBW program (17). The refinement was started using the $P4_2/nmc$ space group and structure parameters derived from Taufer (18). The pseudo-Voigt function was used for modeling diffraction profiles. Peaks below 35° (2θ) were corrected for asymmetry effects. In the final refinements the following parameters were refined: a scale factor; 2θ zero; three parameters from the background; unit cell parameters; peak profile parameters using a pseudo-Voigt function; peak asymmetry; FWHW; Lorentzian ratio (η); asymmetry parameter; preferred orientation (001); positional z parameter of O, an overall isotropic temperature factor, and occupancy parameter.

3. RESULTS AND DISCUSSION

The formation of phases with the structure of tetragonal ZrO_2 from gel precursors took place after heating at 450°C (11, 12). Further thermal treatment was required to obtain well-defined, sharp peaks. Since the tetragonal to monoclinic phase transformation occurred on increasing temperature, the specimens were submitted to subsequent prolonged treatment at 450°C. The powder pattern of these latter specimens showed reflections characteristics of a tetragonal zirconia. The three tetragonal zirconia powder patterns were very similar but with small differences in d spacings and hence unit cell dimensions. It is noteworthy that after prolonged annealing at 450°C weak peaks associated with the monoclinic phases were detected. Therefore, to obtain improved R factors, the refinement was performed by assuming the presence of two components: tetragonal $V–ZrO_2$ and monoclinic $V–ZrO_2$. An estimation of the relative content of both phases has been obtained.

TABLE 1
Crystallographic Data and Details of the Rietveld Refinement for Tetragonal $V_xZr_{1-x}O_2$ Solid Solutions

	$V_{0.025}Zr_{0.975}O_2$	$V_{0.05}Zr_{0.95}O_2$	$V_{0.075}Zr_{0.925}O_2$
a (Å)	3.5957(2)	3.5932(2)	3.5897(2)
c (Å)	5.1826(3)	5.1820(4)	5.1822(4)
V (Å^3)	67.01(1)	66.90(1)	66.78(1)
R_p (%)	7.53	7.16	5.86
R_{wp} (%)	9.61	9.02	7.56
R_{wp} (expected) (%)	4.31	4.13	4.16
R_B (%)	7.34	7.75	4.06
Tetragonal phase (wt%)	94.7	93.8	94.4
Monoclinic phase (wt%)	5.3	6.2	5.6

Table 1 displays the unit cell parameters derived from the refinement using all the observed reflections, the structure-refined parameters, and the amount (in wt%) of tetragonal and monoclinic doped zirconias. The final Rietveld plot for the solid solution $V_{0.05}Zr_{0.95}O_2$, shown as representative, is given in Fig. 1. A comparison of the observed and the calculated pattern for the sample displayed in the lower trace of Fig. 1 shows very good agreement in the range of diffraction angles between 20° and 120° (2θ). The R_p and R_{wp} values from the Rietveld refinement converged between 7.53 and 9.61 for all the tetragonal $V_xZr_{1-x}O_2$ specimens. The amount of monoclinic form of the former solid solutions is, as can be seen in Table 1, very similar in the three samples.

The present Rietveld analysis confirmed the tetragonal structure of $V_xZr_{1-x}O_2$ solid solutions obtained by low-temperature treatment of vanadium-containing amorphous zirconia gels.

The structure parameters of metastable tetragonal $V^{4+}–ZrO_2$ solid solutions, i.e., final atomic positions of O and overall thermal parameters, are given in Table 2.

Table 3 shows the interatomic distances in the three tetragonal $V_xZr_{1-x}O_2$ solid solutions.

A simple, approximate relationship between the departure of the oxygen from the position it would have in the ideal fluorite structure and the tetragonality (c/a) of the zirconia-derived phase were reported by Howard *et al.* (19). The relationship provides a means to estimate the oxygen position with a considerable degree of confidence. Since that relationship is rather empirical, it is of interest to check the results of measurements in tetragonal $V_xZr_{1-x}O_2$ solid solutions. The relationship between the oxygen shift parameter δ and the tetragonality (c/a) was $\delta = 0.24\,[1-(a^2/c^2)]^{1/2}$. The estimation of the crystal average oxygen position from the X-ray lattice parameter of $V_xZr_{1-x}O_2$, is 0.454, 0.453, and 0.451 for $V_{0.025}Zr_{0.975}O_2$,

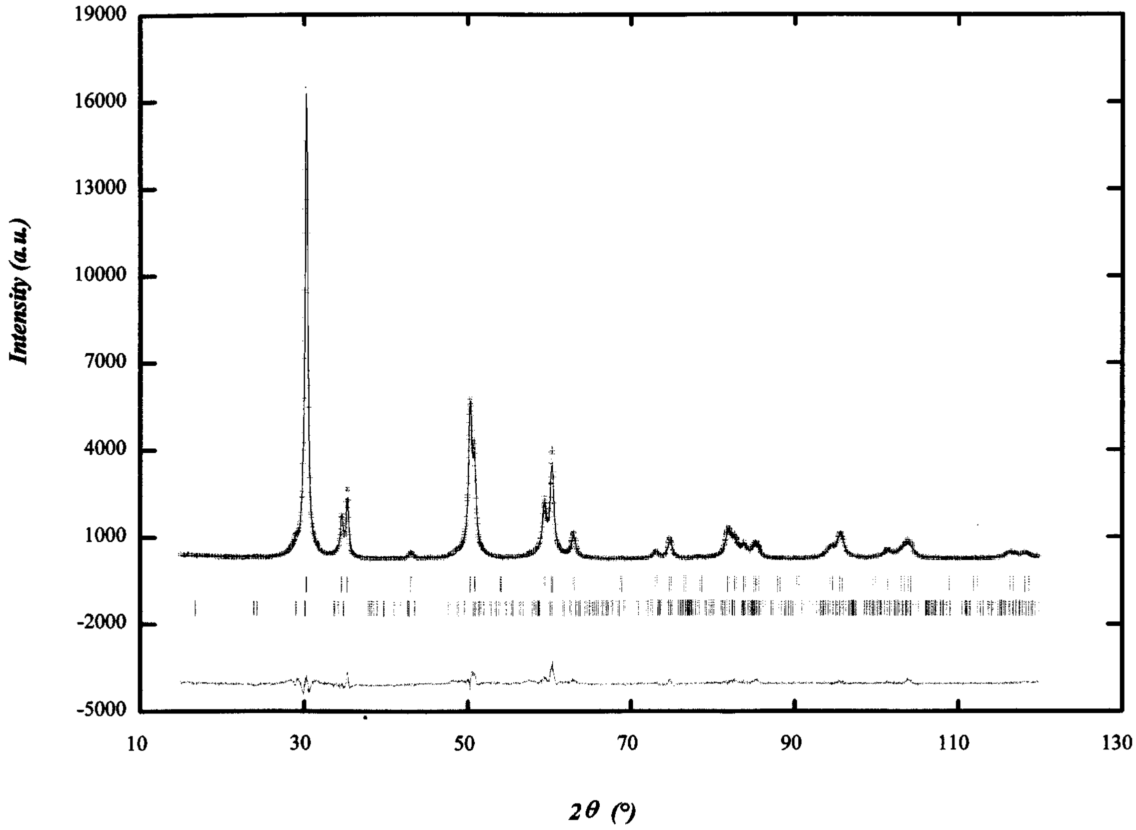

FIG. 1. X-ray powder diffraction data for $V_{0.05}Zr_{0.95}O_2$. The points are the observed intensities and the line is the Rietveld fit. The small vertical bars indicate the positions of allowed *hkl* reflections. The difference between the observed and the calculated profiles is plotted below the diffraction pattern.

$V_{0.05}Zr_{0.95}O_2$, and $V_{0.075}Zr_{0.925}O_2$, respectively. Thus, the results obtained by X-ray diffraction conform with the relationship proposed by Howard *et al.* (19).

4. CONCLUSIONS

The crystal structure of three tetragonal $V_xZr_{1-x}O_2$ solid solutions, with $x = 0.025, 0.05$, and 0.075, prepared by low-temperature treatment of vanadium-containing amorphous zirconia gels, have been determined by Rietveld refinement on the basis of powder X-ray powder diffractometer data. The results confirmed the tetragonal structure of V^{4+}-ZrO_2 solid solutions. The final oxygen positions obtained using the Rietveld method conform with the estimated oxygen positions from the X-ray lattice parameter alone according to the relationship proposed by Howard *et al.* These results from X-ray powder diffraction on V^{4+}-ZrO_2 solid solutions confirm a simple approximate relationship between the oxygen position parameter and the tetragonality.

TABLE 2
Atomic Coordinates of O (Site 4d), Occupancy, and Isotropic Structure Parameters of Metastable Tetragonal $V_xZr_{1-x}O_2$ Solid Solutions from Rietveld Refinement

		Occupancy		
	z	V	Zr	*B* (Å^2)
$V_{0.025}Zr_{0.975}O_2$	0.455(1)	0.10	0.90	0.10 (fixed)
$V_{0.05}Zr_{0.95}O_2$	0.452(1)	0.09	0.91	0.10 (fixed)
$V_{0.075}Zr_{0.925}O_2$	0.450(1)	0.13	0.87	0.33(2)

TABLE 3
Interatomic Distances (Å) in the Three Tetragonal $V_xZr_{1-x}O_2$ Solid Solutions

	$V_{0.025}Zr_{0.975}O_2$	$V_{0.05}Zr_{0.95}O_2$	$V_{0.075}Zr_{0.925}O_2$
O–O	2.591 (×2)	2.589 (×2)	2.591 (×2)
	2.589 (×4)	2.577 (×4)	2.586 (×4)
O–Zr (V)	2.093 (×2)	2.093 (×2)	2.088 (×2)
	2.348 (×2)	2.348 (×2)	2.361 (×2)
Zr(V)–O	2.079 (×4)	2.093 (×4)	2.088 (×4)
	2.369 (×4)	2.348 (×4)	2.361 (×4)

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