

Rietveld refinement study of vanadium distribution in V^{+4} -ZrSiO₄ solid solutions obtained from gels

Francisco Jose Torres^a, Mari Angeles Tena^b, Javier Alarcón^{a,*}

^aDepartamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad de Valencia, 46100 Burjasot (Valencia), Spain

^bDepartamento de Química Inorgánica y Orgánica, Escuela Superior de Tecnología y Ciencias Experimentales, Universidad Jaime I, Castellón, Spain

Received 20 September 2001; received in revised form 15 November 2001; accepted 8 December 2001

Abstract

Vanadium-containing zircon gel precursors with nominal compositions V_x -ZrSiO₄ with $x=0.0, 0.004, 0.01, 0.04$ and 0.2 were prepared by a previously reported colloidal sol-gel technique and annealed for 30 h at 1400 °C. The Rietveld refinement of the structures by X-ray powder diffraction confirms previous results concerning the limit of solubility of V^{+4} in the zircon structure. The new finding regarding with the entry of V^{+4} in the Zr^{+4} site for zircon doped with high contents of vanadium is in accordance with reported results. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Crystal structure; Rietveld refinement; Sol-gel processes; Vanadium distribution; ZrSiO₄

1. Introduction

Turquoise vanadium-zircon ceramic pigmenting system is one of the most used ceramic pigments in the industry. That is the reason that a considerable effort has been made to improve the manufacture of this material from a technical view.^{1–3} However, some crystallochemical aspects regarding with the chemical state and location of vanadium in the zircon structure have been subjects of controversy until very recently.^{4–8} Many papers have been published on structural and chemical concerns of this pigmenting system. Thus, several authors have reported results based on the analysis of the electron spin resonance and the ultraviolet-visible (UV-vis) spectra of vanadium-doped zircon powders and single crystals.

Demiray et al.⁴ studying samples by X-ray diffraction and UV-vis spectroscopy claimed that basically the pigment consists of a V^{+4} -containing zircon solid solution, in which V^{+4} occupies dodecahedral positions. The authors reported that the lattice parameters of the vanadium-substituted zircon solid solutions did not change with respect to those of undoped zircon phase.

Di Gregorio et al.⁵ by comparing the energy level diagram calculated by the point-charge model and electronic spin resonance data in single crystals of vanadium doped ZrSiO₄ stated that V^{+4} would preferentially occupy tetrahedral environments, replacing Si^{+4} ions.

More recently, Xiayou et al.⁶ by using the experimental results of both Demiray and Di Gregorio and the energy level diagram calculated by a different model concluded that V^{+4} occupies both types of available sites in the zircon structure, i.e. tetrahedral and dodecahedral sites, replacing both Si^{+4} and Zr^{+4} .

Recently, Ocaña et al.⁷ concluded, from the study of X-ray absorption, infrared and spin resonance spectra of vanadium-doped zircon powders, that V^{+4} cations form a solid solution with the zircon lattice, substituting for both Si^{+4} and Zr^{+4} , although to a greater extent for the former.

These results are in agreement with previous ones reported by Chandley et al.⁸ obtained by the refinement of X-ray diffraction data from single crystals of ZrSiO₄ doped with vanadium, which concluded that V^{+4} substitute for Si^{+4} without excluding a partial substitution for Zr^{+4} .

It is to be noted that the application of non conventional synthetic techniques, such as sol-gel, for the preparation of this materials have allowed to increase the knowledge of this system.^{9–15} Recently a procedure was

* Corresponding author at: Department of Inorganic Chemistry, University of Valencia, Calle Doctor Moliner, 50, 46100-Burjasot (Valencia), Spain. Tel.: +34-9-6386-4584; fax: +34-9-6386-4322.

E-mail address: javier.alarcon@uv.es (J. Alarcón).

reported for the preparation of vanadium-doped zircon pigmenting system with different vanadium loadings which enabled their complete formation and further characterization.^{16–18} This method allowed the preparation and characterization of both the crystalline phases formed during the thermal processing and the final vanadium-zircon solid solution product. Energy dispersive X-ray microanalysis (SEM/EDX) data, measurements of lattice parameters and UV-vis diffuse reflectance of V–ZrSiO₄ solid solutions revealed that vanadium was dissolved as V⁺⁴ replacing Si⁺⁴ in tetrahedral sites in the crystal structure of zircon. The solubility limit of vanadium in ZrSiO₄ was about 0.01 mol of vanadium per mol of zircon (0.5 wt.% as V₂O₅).

Also, by using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED), it was concluded that the method of preparation favoured the formation of a microcomposite precursor in which the nanoscale zirconia particles were coated by an amorphous silica layer and that high purity and non-agglomerated powders with controlled particle size of vanadium-containing zircon solid solution were formed by using the above synthetic procedure. The availability of a series of V–ZrSiO₄ solid solution specimens, in which the lattice parameter variation as a function of the vanadium content is shown, would allow further structural study from X-ray powder diffraction data.

It seems, therefore, interesting to attempt the refinement of the structure of several solid solutions with increased amount of vanadium, in order to elucidate the site at which V⁺⁴ cation prefers to be doped in ZrSiO₄ structure. To do it, after synthesizing, by a well controlled colloidal sol-gel via samples with increased vanadium loadings, and characterizing by different techniques, X-ray diffraction data from powders were refined by the Rietveld method.

2. Experimental procedure

Gel precursors with nominal compositions V_x–ZrSiO₄ with $x = 0.0, 0.004, 0.04$ and 0.2 were prepared by a previously reported procedure.^{16–18} Basically they have been

synthesized by gelling mixtures of previously prepared either zirconium and vanadium oxide colloidal solutions and tetraethylorthosilicate (TEOS). After drying at 120 °C the resulting gel precursor powders were ground into powders using an agate mortar and pestle and heated at 1400 °C in air during 30 h and then cooled in air in the furnace. For the preparation of X-ray powder diffraction specimens the heated 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 CuK_α 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 15 to 70° (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,¹⁹ by using the FULLPROF program.²⁰ The refinement was started using the *I4₁/amd* space group and structure parameters derived from Robinson et al.²¹ The pseudo-Voigt function was used for modelling diffraction profiles. Peaks below 35° (2θ) were corrected for asymmetry effects. In the final refinements the following parameters were refined: a scale factor; two-theta zero; three parameters from the background; unit cell parameters; peak profile parameters using a pseudo-Voigt function; peak asymmetry; FWHM; Lorentzian ratio (eta); asymmetry parameter; preferred orientation (001); positional x- and z-parameters of O and an overall isotropic temperature factor.

3. Results and discussion

Table 1 displays the unit cell parameters of the V–ZrSiO₄ solid solutions in the series on increasing the amount of vanadium. The final *R*-values for samples are also summarized in Table 1. As can be seen the *R_B*, *R_{wp}* (expected) and *R_{wp}* values indicate that the structural parameters obtained are correct. The general trend of lattice parameter variation is similar to the one previously

Table 1
Unit cell dimensions and structure refined parameters of tetragonal V_x–ZrSiO₄ solid solutions

	ZrSiO ₄	V _{0.004} –ZrSiO ₄	V _{0.04} –ZrSiO ₄	V _{0.2} –ZrSiO ₄
<i>a</i> (Å)	6.6004 (4)	6.6011 (4)	6.6040 (3)	6.6044 (3)
<i>c</i> (Å)	5.9786 (3)	5.9811 (3)	5.9822 (2)	5.9827 (3)
<i>V</i> (Å ³)	260.46 (5)	260.62 (5)	260.90 (3)	260.95 (4)
<i>R_p</i> (%)	8.70	7.47	6.74	8.50
<i>R_{wp}</i> (%)	8.35	7.52	6.95	8.70
<i>R_{wp}</i> (expected) (%)	4.59	3.52	3.18	5.40
<i>R_B</i> (%)	2.61	2.67	2.33	2.05

reported.¹⁶ The *a* and *b* dimensions increase with increasing vanadium content in the zircon structure. Also a smaller increase in the *c* axis length occurs for vanadium-rich zircon phases. The above changes in cell dimensions bring about an expansion of the unit cell, i.e. the unit cell volume is increased on increasing the vanadium amount. This behaviour is in agreement with the fact that the V⁺⁴ is occupying mainly the tetrahedral position, i.e. substituting the Si⁺⁴, in the zircon structure.

The change in the lattice parameters as the vanadium content increases in the solid solution is consistent with the idea of expansion of the unit cell as a small ion is replaced by a larger one. The zircon structure can be described as built of chains of alternating edge-sharing SiO₄ tetrahedra and ZrO₈ triangular dodecahedra extending parallel to the *c* axis, which are joined laterally by edge-sharing dodecahedra. The observed increase in lattice parameters can be understood assuming that V⁺⁴ is replacing Si⁺⁴ in tetrahedral sites. Obviously, the greater ionic radius of V⁺⁴ compared with Si⁺⁴ causes the progressive increase of the unit cell parameters with increasing substitution. Conversely, the mechanism of solid solution formation involving the replacement of Zr⁺⁴ by V⁺⁴ does not seem to be operative because the greater ionic radius of Zr⁺⁴ would produce a decrease in lattice parameters.

It is to be noted, however, that some reports claimed on the possibility that V⁺⁴ enters both the Si⁺⁴ and Zr⁺⁴ sites.^{6,8} In this sense, in our prepared series of solid solutions with increasing nominal vanadium loadings and, consequently, as previously shown, increased vanadium contents into the ZrSiO₄ lattice,¹⁶ it would be possible to determine the trend of the occupancy with the increased amount of vanadium in the zircon lattice by the Rietveld refinement of X-ray powder data.

Table 2 displays the *x* and *z* final atomic co-ordinates of O and the occupancy of vanadium in each of the two available sites. It is to note the trend in the occupancy of the V⁺⁴ cations through the solid solution when increasing the amount of vanadium. From Table 2 it is observed that the V⁺⁴ is uniquely located in the tetrahedral sites up to amounts of nominal vanadium of *x*=0.04. For samples with higher vanadium loadings, i.e. with *x*=0.2, the Zr⁺⁴ occupying the dodecahedral

Table 2
Atomic coordinates of O (site 16h) and occupancy of tetragonal V_{*x*}-ZrSiO₄ solid solutions from Rietveld refinement

	<i>x</i>	<i>z</i>	Occupancy			
			Si	V (Si)	Zr	V (Zr)
ZrSiO ₄	0.0640 (5)	0.1965 (4)	1.00	–	1.00	–
V _{0.004} -ZrSiO ₄	0.0633 (5)	0.1957 (4)	0.993	0.007	1.00	0.0
V _{0.04} -ZrSiO ₄	0.0644 (4)	0.1963 (4)	0.987	0.013	1.00	0.0
V _{0.2} -ZrSiO ₄	0.0562 (6)	0.1972 (5)	0.982	0.018	0.974	0.026

Table 3
Interatomic distances (Å) in the ZrSiO₄ and the three tetragonal V_{*x*}-ZrSiO₄ solid solutions

	ZrSiO ₄	V _{0.004} -ZrSiO ₄	V _{0.04} -ZrSiO ₄	V _{0.2} -ZrSiO ₄
Si (V)–O	1.627 (3)	1.634 (3)	1.626 (3)	1.664 (4)
Zr (V)–O	2.116 (4)×4 2.281 (2)×4	2.111 (3)×4 2.280 (2)×4	2.120 (3)×4 2.280 (2)×4	2.068 (4)×4 2.314 (3)×4

site is substituted for V⁺⁴. Thus, the mechanism of the solid solution formation changes when the vanadium content entering in the zircon structure increases. A striking fact is that the V⁺⁴ substituting for Si⁺⁴ in ZrSiO₄ is not dependent on the chemical environment present during the synthesis of ZrSiO₄, since by our synthetic method the synthesis of zircon takes place by reaction of monoclinic vanadium-doped ZrO₂ and SiO₂.^{16–18} So, in the incorporation of V⁺⁴ in zircon the V changes from an heptacoordinated oxygen surrounding in monoclinic V–ZrO₂ solid solutions to a tetrahedral one in the zircon structure.

The above fact is clearly evidenced in Table 3, in which interatomic distances in the undoped ZrSiO₄ and the three tetragonal V_{*x*}-ZrSiO₄ solid solutions are displayed. The effect of doping vanadium into the silicon site is that the four oxygens bonded to the Si(V) ions move away from their original positions, altering the Si(V)–O bond length from 1.627 to 1.664. As can be seen in Table 3, for small amounts of V⁺⁴ the Zr(V)–O interatomic distances almost do not experienced changes. The effect of locating V⁺⁴ into the zirconium site is to shorten four Zr(V)–O bonds and lengthen the other four Zr(V)–O ones. It is to note, however, that the greatest distortion of polyhedron in the lattice on doping occurs in tetrahedral sites.

4. Conclusion

The above results obtained from a series of vanadium-containing zircon solid solutions with increased vanadium amounts are in accordance with the partial substitution of V⁺⁴ for both Si⁺⁴ and Zr⁺⁴. The location of V⁺⁴ into the zircon lattice is dependent on the amount of vanadium doped into ZrSiO₄. For low amount of vanadium the V⁺⁴ occupies preferentially the tetrahedral site, i.e. substituting V⁺⁴ for Si⁺⁴, whereas for high vanadium contents it occupies both dodecahedral and tetrahedral, i.e. substituting V⁺⁴ for both Zr⁺⁴ and Si⁺⁴.

References

1. Seabright, C. A., US Pat. No. 2441407, 1948.
2. Matkovich, V. I. and Corbett, P. M., Formation of zircon from

- zirconium dioxide and silicon dioxide in the presence of vanadium dioxide. *J. Am. Ceram. Soc.*, 1961, **44**, 128–130.
- Eppler, R. A., Mechanism of formation of zircon stains. *J. Am. Ceram. Soc.*, 1970, **53**, 457–462.
 - Demiray, T., Nath, D. K. and Hummel, F. A., Zircon-vanadium blue pigments. *J. Am. Ceram. Soc.*, 1970, **53**, 1–4.
 - Di Gregorio, S., Greenblatt, M., Pifer, J. H. and Sturge, M. D., An ESR and optical study of V^{+4} in zircon-type crystals. *J. Chem. Phys.*, 1982, **76**, 2931–2937.
 - Xiayou, H., Gui-Ku, B. and Ming-Guang, Z., The study of the optical and the EPR spectra of V^{+4} in zircon-type crystals. *J. Chem. Phys Solids*, 1985, **46**, 719–720.
 - Ocaña, M., Gonzalez-Elipe, A. R., Orera, V. M., Tartaj, P. and Serna, C. J., Spectroscopic studies on the localization of vanadium (IV) in vanadium-doped zircon pigments. *J. Am. Ceram. Soc.*, 1998, **81**, 395–400.
 - Chandley, P., Clark, R. J. H., Angel, R. J. and Price, G. D., Site preference of vanadium doped into $ZrSiO_4$ and $ZrGeO_4$ and of terbium doped into $ZrGeO_4$. *J. Chem. Soc. Dalton Trans.*, 1992, **9**, 1579–1584.
 - Monrós, G., Carda, J., Escribano, P. and Alarcón, J., $V-ZrSiO_4$ solid solutions. *J. Mater. Sci. Lett.*, 1990, **9**, 184–186.
 - Monrós, G., Carda, J., Escribano, P., Tena, M. A. and Alarcón, J., Effects of ZrO_2 precursors on the synthesis of $V-ZrSiO_4$ solid solutions by sol-gel methods. *J. Mater. Sci.*, 1992, **27**, 351–357.
 - Monrós, G., Carda, J., Tena, M. A., Escribano, P., Cantavella, V. and Alarcón, J., The stoichiometry of blue vanadium doped zircon obtained by sol-gel methods. *Mater. Res. Bull.*, 1992, **27**, 753–760.
 - Monrós, G., Martí, M. C., Carda, J., Tena, M. A., Cantavella, V. and Alarcón, J., The encapsulating efficiency for vanadium of ZrO_2-SiO_2 gels prepared from alkoxides to give $V-ZrSiO_4$ blue coloured stains. *Br. Ceram. Trans.*, 1993, **92**, 120–127.
 - Monrós, G., Carda, J., Tena, M. A., Escribano, P., Sales, M. and Alarcón, J., Different kind of solid solutions in the $V_2O_5-ZrSiO_4-NaF$ system by sol-gel processes and their characterization. *J. Eur. Ceram. Soc.*, 1993, **11**, 77–86.
 - Valentín, C., Sales, M. and Alarcón, J., Síntesis y caracterización de soluciones sólidas de $V-ZrSiO_4$ preparadas a partir de geles coloidales. *Bol. Soc. Esp. Cerám. Vidrio.*, 1998, **37**, 39–46.
 - Tartaj, P., Serna, C. J. and Ocaña, M., Preparation of blue vanadium-zircon pigments by aerosols hydrolysis. *J. Am. Ceram. Soc.*, 1995, **78**, 1147–1152.
 - Valentín, C., Muñoz, M. C. and Alarcón, J., Synthesis and characterization of vanadium-containing $ZrSiO_4$ solid solutions from gels. *J. Sol-Gel Sci. Tech.*, 1999, **15**, 221–230.
 - Alarcón, J., Crystallization behaviour and microstructural development in $ZrSiO_4$ and $V-ZrSiO_4$ solid solutions from colloidal gels. *J. Eur. Ceram. Soc.*, 2000, **20**, 1749–1758.
 - Torres, F. J., Folgado, J. V. and Alarcón, J., Structural evolution and vanadium distribution in the preparation of $V^{+4}-ZrSiO_4$ solid solutions from gels. *J. Am. Ceram. Soc.*, in press.
 - Rietveld, H. M., A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.*, 1969, **2**, 65–71.
 - Rodríguez-Carvajal, J., Computer Program FullProf, Version 3.51. Laboratoire Leon Brillouin, CEA-CNRS, Grenoble, France, 1998.
 - Robinson, K., Gibbs, G. V. and Ribbe, P. H., The structure of zircon: a comparison with garnet. *Am. Mineral.*, 1971, **56**, 782–790.