Incorporation of vanadium(V) into the rutile-type phase of GeO$_2$: the solid solution Ge$_{0.74}$V$_{0.21}$□$_{0.05}$O$_2$

I. Rosales,^{a}* E. A. Juarez-Arellano,^{b} C. R. Magaña,^{a} L. Bucio^a and E. Orozco^a

^{a}Instituto de Física, Universidad Nacional Autónoma de México, AP 20-364, 01000 México, DF, Mexico, and ^{b}Institut für Mineralogie – Abteilung Kristallographie, Universität Frankfurt Senckenberganlage 30, D-60054 Frankfurt am Main, Germany

Correspondence e-mail: bucio@fisica.unam.mx

The title compound, γ-vanadium germanium oxide, was prepared as polycrystalline material by conventional solid-state reactions starting from α-quartz-type GeO$_2$ and V$_2$O$_5$ in a K$_2$CO$_3$ flux at 1123 K. Some of the Ge^{4+} cations were replaced by V^{5+}, leading to a rutile-type phase where charge neutrality is accomplished by the presence of vacancies. X-ray photoelectron spectroscopy (XPS) confirms the presence of V^{5+} in this compound. Its crystal structure was refined from laboratory X-ray powder data using the Rietveld method and is composed of corner- and edge-sharing MO$_6$ octahedra where the metal positions M are statistically occupied by Ge and V. The four equatorial MO bonds lying in the (110) plane are 0.023Å shorter than the two axial bonds.

Comment

Compounds adopting the rutile structure have catalytic and electrochemical applications, such as GeO$_2$ (optical and insulating properties) and TiO$_2$ (semiconducting properties) (Mancini *et al.*, 1984). Examples of other rutile-type dioxides include VO$_2$ (McWhan *et al.*, 1974) and NbO$_2$ (Bolzan *et al.*, 1994), for which the preparation is accomplished under slightly reducing conditions at elevated temperatures. For dioxides of Ti, Ru, Ir, Sn and Ge, the rutile-type polymorph is the thermodynamically stable phase (West, 1998). Rutile-type GeO$_2$ has attracted attention because of its similarities with stishovite, the high-pressure polymorph of SiO$_2$, which is particularly interesting for understanding geochemical processes. The α-quartz-type GeO$_2$ polymorph is formed around 1310 K followed by fusion at 1389 K and is metastable at room temperature (Haines *et al.*, 2002). The investigation of the phase transition between rutile-type (r-) and α-quartz-type (α-) GeO$_2$ has been the subject of previous studies. Under normal conditions, a transition from α-GeO$_2$ to r-GeO$_2$ is not achieved by heating GeO$_2$ samples up to 1273 K. However, following the work by Sarver & Hummel (1961), the transition to a rutile-type phase is possible by introducing low quantities of vanadium into GeO$_2$, using K$_2$CO$_3$ as catalyst. We have prepared polycrystalline Ge$_{0.74}$V$_{0.21}$□$_{0.05}$O$_2$ by solid-state reactions starting from α-GeO$_2$ and V$_2$O$_5$, and have structurally characterized this compound by Rietveld analysis of conventional X-ray powder data, Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS).

The parameters to describe the rutile-type structure, *viz.* the axial ratio c/a and the oxygen positional parameter x, are 0.6516 and 0.3054, respectively, which are both close to the values of 0.6507 and 0.307 as obtained from the data given by Baur (1956) for the mineral argutite (r-GeO$_2$). The MO$_6$ octahedron (M = V, Ge) exhibits four equatorial bonds of

doi:10.1107/S1600536807010276

1.877 (1) Å lying in the (110) plane, and two axial bonds of 1.900 (1) Å located normal to the (110) plane (Fig. 1). The average $M-O$ distance of 1.885 Å is slightly larger than the average $M-O$ distance for argutite (1.881 Å), but plausible in view of the slightly greater ionic radius (Shannon, 1976) of V^{5+} (0.58 Å) in comparison with that of Ge^{4+} (0.53 Å).

Experimental

Polycrystalline material of the title compound was prepared by conventional solid-state reactions, starting from α-GeO_2 (CERAC 99.999%, 1.255 g) and V_2O_5 (J. T. Baker 99.7%, 0.546 g) with K_2CO_3 (J. T. Baker 99.9%, 0.415 g) as flux and as catalyst to set up the phase transition. The educts were mixed and ground in an agate mortar in order to obtain a fine powder, which was then heated in a furnace in air at 1123 K for two days. At the end of the treatment, the rutile-type phase was clearly identified by X-ray powder diffraction, although it was accompanied by amorphous phases which could eventually be removed by washing the sample with hot water. Because some of the employed V_2O_5 and GeO_2 could be lost after thermal treatment as vitrified products, it was necessary to determine the chemical composition for the resulting rutile-type phase. Chemical analysis was performed by means of Rutherford backscattering spectrometry (RBS), following the procedure reported by Bucio *et al.* (2001), and by X-ray photoelectron spectroscopy (XPS). The atomic concentrations obtained by RBS and XPS were, respectively, 0.71 (7) and 0.74 (7) for germanium, and 0.29 (3) and 0.26 (3) for vanadium. The XPS measurement was performed at ultra-high vacuum conditions in a Thermo-VG SCALAB 250 system equipped with a monochromatic Al $K\alpha$ source ($h\nu$ = 1486.6 eV) and a hemispherical analyzer.

Crystal data

$Ge_{0.74}V_{0.21}O_2$	$Z = 2$
$M_r = 96.43$	Cu $K\alpha$ radiation
Tetragonal, $P4_2/mnm$	$T = 295$ K
$a = 4.4001$ (1) Å	Specimen shape: flat sheet
$c = 2.8670$ (1) Å	$20 \times 20 \times 0.2$ mm
$V = 55.51$ (1) Å^3	

Data collection

Bruker Advance D8 diffractometer	Scan method: step
Specimen mounting: packed powder sample container	$2\theta_{min} = 5°$, $2\theta_{max} = 110°$
Specimen mounted in reflection mode	Increment in $2\theta = 0.02°$

Refinement

$R_p = 0.050$	Profile function: pseudo-Voigt
$R_{wp} = 0.07$	modified by Thompson *et al.*
$R_{exp} = 0.03$	(1987)
$R_B = 0.02$	18 parameters
$S = 2.0$	

For the refinement of the crystal structure the starting parameters were taken from r-GeO_2 (Bolzan *et al.*, 1997) with a statistical distribution of V^{5+} on the Ge^{4+} sites. The following parameters were refined: zero point, scale factor, cell parameters, peak shape, positional parameters, occupancy factors (for Ge^{4+} and V^{5+}) and isotropic displacement parameters. The occupancy factors for Ge^{4+} and V^{5+} were refined using a restraint in such a way that an increase of V^{5+} was coupled with a proportional decrease of Ge^{4+} taking into account the difference of their oxidation states and the results of the chemical analysis. The results of the final Rietveld refinement are shown in Fig. 2.
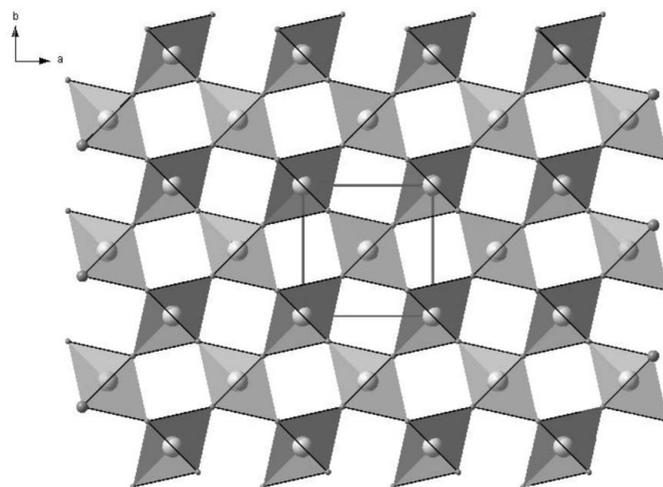
Figure 1
The rutile-type crystal structure of $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ in the polyhedral representation, viewed along the c axis. The statistically distributed V and Ge atoms are shown as large grey spheres and O atoms as small grey spheres of arbitrary radii.
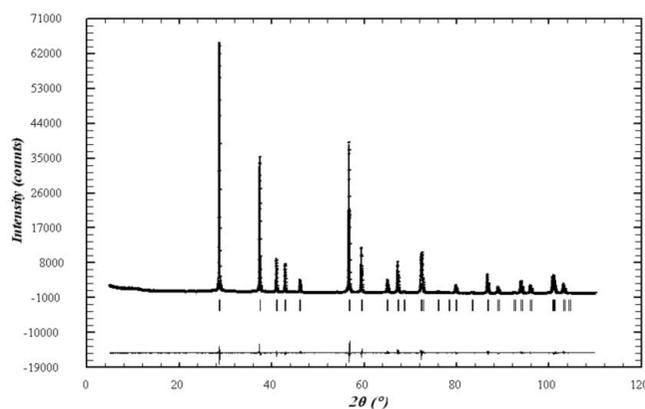
Figure 2
Final plots of the Rietveld refinement for $Ge_{0.74}V_{0.21}\square_{0.05}O_2$, showing the experimental (crosses) and calculated (line) intensities. The difference plot appears below. Vertical markers correspond to the calculated positions of the Bragg reflections.

Data collection: *DIFFRAC/AT* (Siemens, 1993); cell refinement: *FULLPROF* (Rodríguez-Carvajal, 2001; data reduction: *FULLPROF*; program(s) used to solve structure: coordinates taken from an isotypic compound; program(s) used to refine structure: *FULLPROF*; molecular graphics: *DIAMOND* (Crystal Impact, 2005); software used to prepare material for publication: *FULLPROF*.

References

Baur, W. H. (1956). *Acta Cryst.* **9**, 515–520.
Bolzan, A. A., Fong, C., Brendan, J., Kennedy, B. J. & Howard, C. J. (1994). *J. Solid State Chem.* **113**, 9–14.
Bolzan, A. A., Fong, C., Kennedy, B. J. & Howard, C. J. (1997). *Acta Cryst.* B**53**, 373–380.

Bucio, L., Ruvalcaba-Sil, J. L., Rosales, I., García-Robledo, J. & Orozco, E. (2001). *Z. Kristallogr.* **216**, 438–441.

Crystal Impact (2005). *DIAMOND.* Version 3.0e. Crystal Impact, Bonn, Germany.

Haines, J., Cambon, O., Philippot, E., Chapon, L. & Hull, S. (2002). *J. Solid State Chem.* **166**, 434–441.

Mancini, N., Pennisi, A. & Simone, F. (1984). *Sol. Energy Mater.* **11**, 209–221.

McWhan, D. B., Marezio, M., Remeika, J. P. & Dernier, P. D. (1974). *Phys. Rev. B,* **10**, 490–495.

Rodríguez-Carvajal, J. (2001). *FULLPROF.* Commission on Powder Diffraction (IUCr). Newsletter 26, pp. 12–19.

Sarver, J. F. & Hummel, F. A. (1961). *J. Electrochem. Soc.* **108**, 195–196.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Siemens (1993). *DIFFRAC/AT.* Version 3.2. Siemens Analytical Instruments, Madison, Wisconsin, USA.

Thompson, P., Cox, D. E. & Hastings, J. B. (1987). *J. Appl. Cryst.* **20**, 79–83.

West, A. R. (1998). *Solid State Chemistry and its Applications.* England: John Wiley and Sons.