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The Structure of V_2GaO_5

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Abstract

Crystals of V_2GaO_5 ($V^{III}V^{IV}GaO_5$) are monoclinic, space group $C2/m$, with $Z = 6$, $a = 17{\cdot}758$ (5), $b = 2{\cdot}990$ (1), $c = 9{\cdot}323$ (3) Å, $\beta = 98{\cdot}44$ (2)°, $V = 489{\cdot}6$ Å^3 and $d_c = 5{\cdot}12$ Mg m^{-3}. Intensities for 605 reflexions, collected on a four-circle diffractometer, were used in the structure solution and the structure was refined to a final R value = 0·040 and R_w = 0·055. It is built up from β-gallia-like columns containing all the gallium atoms and from chains of VO_6 octahedra with the direction parallel to the c axis. Layers generated from these alternate chains, linked by corner-shared polyhedra, pile up along the b axis.

Introduction

Investigation of the ternary systems vanadium–metal–oxygen gave compounds containing vanadium in both oxidation states +3 and +4. These compounds were sintered at temperatures between 1273 and 1473 K under oxygen partial pressures ranging from 10^{-5} to 10^{-12} atm (1 to 10^{-7} Pa) using techniques already described (Cros, 1976). Phase equilibria in the V_2O_3–VO_2–Ga_2O_3 system at 1273 K showed formation of the compound $V_6Ga_2O_{13}$ ($V_4^{III}V_2^{IV}Ga_2O_{13}$) or $2V_3O_5$–Ga_2O_3 (Cros, Caramel & Kerner-Czeskleba, 1977).

In more recent investigations at temperatures above 1423 K a new compound containing vanadium(III) and (IV) and gallium could be prepared for the ratio V/Ga = 2 and with formula V_2GaO_5 ($V^{III}V^{IV}GaO_5$) or V_4O_7–Ga_2O_3 (Cros, in preparation).

These mixed oxides, although containing vanadium(III), are very stable in air at room temperature. Until now, single crystals have only been obtained for the V_2GaO_5 compound; its structure will be described in this paper.

Experimental

Single crystals of V_2GaO_5 used for the crystallographic study were obtained at 1423 K in the presence of iodine in a quartz tube sealed under primary vacuum, the oxygen partial pressure corresponding to the range of existence of the compound (Cros, in preparation). Under these conditions, spearhead-shaped crystals grow. They have to be broken along the twin axis in order to be suitable. Single crystals are also grown by transport reaction at 1573 K. In this case, needle-shaped crystals grow. Whatever the shape of the crystal, its longest edge is always along the b axis and the most developed face is parallel to the $(20\bar{1})$ plane. The crystal selected for this study was a plate of dimensions 0·24 × 0·16 × 0·06 mm. Crystallographic data were determined in a preliminary study using a precession camera.

Intensities were collected on a Nonius CAD-4 automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation and an ω–2θ scan. 605 of the measured reflections for $\theta \leq 30°$ having $\sigma(I)/I \leq 0·3$ (Susa & Steinfink, 1971) were used in the subsequent refinement. No absorption correction was made, $\mu = 14·4$ mm^{-1}.

Structure determination and refinement

The structure was solved by symbolic addition using *MULTAN* (Germain, Main & Woolfson, 1971) applied to 200 normalized structure factors with modulus greater than 1·08. A three-dimensional Fourier synthesis using the E values and the corresponding phases for the coefficients showed the presence of five independent peaks [four being in positions 4(i) and one in position 2(a)] having intensities of the same order of magnitude and corresponding to the cations. At this stage, since it was impossible to distinguish between the Ga and V atoms, the five metal-atom positions were refined using the scattering factors of V and taking into account isotropic temperature factors. After a first refinement one of the V atoms in position 4(i) had to be replaced by a Ga atom. Several cycles of least-squares refinement with the complete matrix yielded an R value of 0·19. Taking into account the heavy atoms, a difference Fourier map was calculated which located seven O atoms in position 4(i) and one in position 2(c). A further series of refinements gave R = 0·057. At this stage a study of the temperature factors of the metal atoms revealed that three of them had values lying between 0·36 and 0·52 Å^2, the two others being V atoms with very small (0·05 Å^2) or negative factors. When these two metal-atom sites were occupied statistically by Ga and V, the corresponding temperature factors were of the same order of magnitude as the other three and the ratio V/Ga = 2 was again found. A least-squares refinement with isotropic parameters converged to give R = 0·052. Taking into account the anisotropic vibrations of the atoms gave an R value of 0·040.

The final positional and thermal isotropic parameters are given in Table 1. The atomic scattering factors used were those of Doyle & Turner (1968).*

Description of the structure

The structure of V_2GaO_5 is shown in projection down the b axis in Figs. 1 and 2. It is built up from two alternating types of chains, running along the c axis. The first type are chains of corner-linked octahedra, the octahedral sites containing only V atoms. These columns differ from those in rutile, where two adjacent octahedra are in perpendicular orientation (Fig. 3); in

Table 1. *Final atomic parameters for* V_2GaO_5 *and isotropic temperature factors*

	Wyckoff notation	x	y	z	$B_{\rm iso}$ (Å^2)
Ga	4(i)	0·15619 (5)	0	0·7240 (1)	0·23 (3)
M(1) (0·40 V + 0·10Ga)	4(i)	0·6778 (1)	0	0·0516 (2)	0·26 (4)
V(2)	4(i)	0·48604 (8)	0	0·6501 (2)	0·17 (3)
M(3) (0·35V + 0·15Ga)	4(i)	0·1899 (1)	0	0·3853 (2)	0·28 (5)
V(4)	2(a)	0	0	0	0·33 (5)
O(1)	4(i)	0·0106 (3)	0	0·2137 (7)	0·4 (1)
O(2)	4(i)	0·3991 (3)	0	0·3055 (7)	0·4 (1)
O(3)	4(i)	0·1992 (3)	0	0·9162 (7)	0·4 (1)
O(4)	4(i)	0·4239 (3)	0	0·9917 (7)	0·3 (1)
O(5)	4(i)	0·1879 (3)	0	0·1826 (7)	0·4 (1)
O(6)	4(i)	0·2288 (3)	0	0·6010 (6)	0·3 (1)
O(7)	4(i)	0·3810 (4)	0	0·6090 (7)	0·3 (1)
O(8)	2(c)	0	0	0·5	0·4 (2)

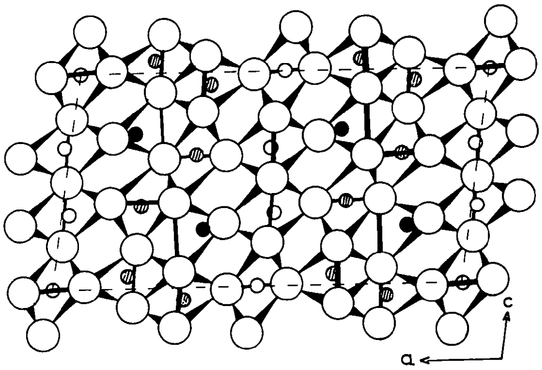

Fig. 1. A ball-and-spoke representation of the boundary in V_2GaO_5 viewed along **b**. Small black circles represent Ga atoms; shaded circles represent sites statistically occupied by Ga and V atoms. This figure shows that some of the cations are unusually displaced out of the centre of the octahedra. For greater clarity, this figure should be studied simultaneously with Fig. 2.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35382 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

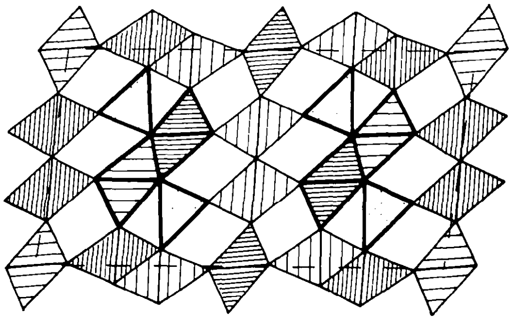

Fig. 2. 3 Å projection for V_2GaO_5. Shading of octahedra indicates two levels. β-Gallia elements are heavily outlined.

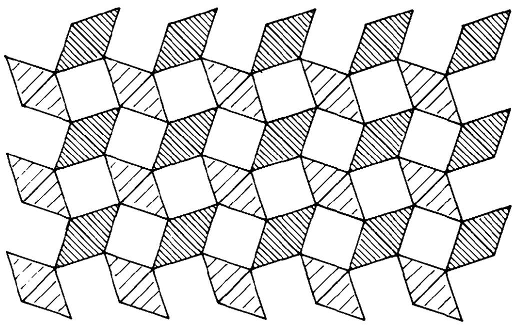

Fig. 3. [001] projection of the rutile structure.

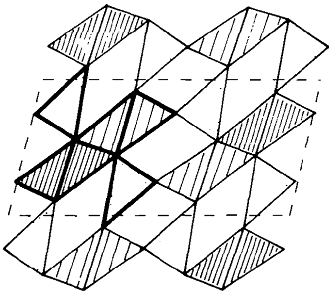

Fig. 4. 3 Å projection of β-Ga_2O_3 (Geller, 1960). One of the β-gallia elements is heavily outlined.

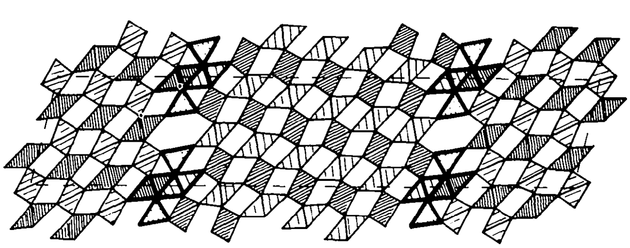

Fig. 5. 3 Å projection of $Ti_{21}Ga_4O_{48}$ (Lloyd, Grey & Bursill, 1976). β-Gallia elements are heavily outlined.

V_2GaO_5, the periodicity in the VO_6 octahedron columns is three, two neighbouring octahedra having the same orientation. The second type of chains, containing all the Ga atoms, are β-Ga_2O_3-like columns (Geller, 1960): the octahedra link pair-wise by edge-sharing, each corner of the common edge being linked to the corner of a tetrahedron (Fig. 4). This arrangement is significant in the V_2GaO_5 structure in the sense that two adjacent β-Ga_2O_3-like polyhedra are linked by

Table 2. *Bond distances* (Å) *and angles* (°)

Standard errors in parentheses apply to the last digits.

Ga tetrahedron			
2 × Ga–O(2^{iii})	1·787 (3)	2 × O(2^{iii})–O(3)	2·915 (7)
–O(6)	1·840 (6)	2 × –O(6)	2·952 (7)
–O(3)	1·842 (6)	–O(2^{iii})	2·990
Average	1·814	O(3) –O(6)	3·051 (8)
		Average	2·963
Bond angles O–Ga–O range 108·9 (2)–113·5 (3)			
M(1) octahedron			
M(1)–O(4^{i})	1·793 (6)	2 × O(3^{ii})–O(5^{ii})	2·521 (9)
2 × –O(5^{ii})	1·922 (4)	2 × –O(3^{i})	2·66 (1)
2 × –O(3^{ii})	2·028 (4)	2 × O(3^{i})–O(5^{ii})	2·764 (7)
–O(3^{i})	2·160 (6)	2 × O(4^{i})–O(5^{ii})	2·806 (7)
Average	1·976	2 × O(3^{ii})–O(4^{i})	2·882 (7)
		O(5^{ii})–O(5^{ii})	2·990
		O(3^{ii})–O(3^{ii})	2·990
		Average	2·771
Bond angles O–*M*(1)–O ranges	79·0 (2)–102·1 (3) 163·8 (3)–175·0 (3)		
V(2) octahedron			
V(2)–O(7)	1·848 (6)	2 × O(1^{iii})–O(8^{ii})	2·703 (6)
2 × –O(1^{iii})	1·956 (4)	2 × –O(2^{i})	2·718 (7)
–O(2^{i})	2·021 (6)	2 × –O(7)	2·781 (7)
2 × –O(8^{ii})	2·087 (1)	2 × O(2^{i}) –O(8^{ii})	2·790 (5)
Average	1·993	2 × O(7) –O(8^{ii})	2·892 (5)
		O(1^{iii})–O(1^{iii})	2·990
		O$(8)^{ii}$–O(8^{ii})	2·990
		Average	2·812
Bond angles O–V(2)–O ranges	83·8 (1)– 99·7 (3) 170·8 (2)–179·9 (3)		
M(3) octahedron			
M(3)–O(5)	1·885 (7)	2 × O(6) –O(6^{iii})	2·615 (9)
2 × –O(7^{iii})	1·960 (4)	2 × O(6^{iii})–O(7^{iii})	2·694 (9)
–O(6)	2·037 (6)	2 × O(5) –O(6^{iii})	2·754 (7)
2 × –O(6^{iii})	2·070 (4)	2 × O(5) –O(7^{iii})	2·865 (8)
Average	1·997	2 × O(6) –O(7^{iii})	2·963 (8)
		O(6^{iii})–O(6^{iii})	2·990
		O(7^{iii})–O(7^{iii})	2·990
		Average	2·814
Bond angles O–*M*(3)–O ranges	79·1 (2)–99·4 (3) 161·4 (3)–174·1 (2)		
V(4) octahedron			
2 × V(4)–O(1)	1·974 (6)	2 × O(4^{ii})–O(4^{iii})	2·68 (1)
2 × –O(4^{ii})	2·009 (4)	4 × O(1) –O(4^{iii})	2·812 (7)
2 × –O(4^{iii})	2·009 (4)	4 × O(1) –O(4^{ii})	2·821 (7)
Average	1·997	O(4^{ii})–O(4^{ii})	2·990
		O(4^{iii})–O(4^{iii})	2·990
		Average	2·823
Bond angles O–V(4)–O ranges	83·8 (2)–96·2 (2) 179·8 (1)–179·9 (1)		

Symmetry code

None $x, 0, z$	(ii) $\frac{1}{2}+x, \frac{1}{2}, z$
(i) $-x, 0, -z$	(iii) $\frac{1}{2}-x, \frac{1}{2}, -z$

sharing a tetrahedron. The tetrahedral sites are occupied by Ga, while the octahedral sites are statistically occupied by V and Ga atoms. The two types of chains are alternating, bound by corner-shared octahedra and tetrahedra. In Figs. 3, 4 and 5, this structure type is compared to those of rutile, β-Ga_2O_3 and $Ti_{21}Ga_4O_{48}$ (Lloyd, Grey & Bursill, 1976). The octahedral sites of the cations are very distorted with the exception of those in particular positions at the corners of the cell. However, these structure distortions are of the same order of magnitude as those observed for V_nO_{2n-1}, β-Ga_2O_3 or the mixed oxide $Ti_{21}Ga_4O_{48}$. The O—O distances lie between 2·52 and 2·99 Å. The metal–oxygen bonds and the oxygen–metal–oxygen angles show these deformations. However, some of the cations in the edge-sharing octahedra are particularly out of the centre and this displacement results in unusually short (1·793 Å) and long (2·160 Å) M—O bond lengths.

Characteristic bond lengths and angles are listed in Table 2.

Discussion

The structure of β-Ga_2O_3 is such that half of the Ga atoms occupy tetrahedral sites. V atoms are usually octahedrally coordinated in the oxides; pentahedral environments (square-based pyramid) are very seldom found (Cros, Tourné & Philippot, 1975). In V_2GaO_5, two of the nine cationic sites are tetrahedral, containing $\frac{4}{5}$ of the Ga atoms. One Ga atom out of five statistically occupies an octahedral site with a V atom. It has been shown that this distribution involves only the octahedra belonging to the β-Ga_2O_3-like blocks. Such a random distribution of Ga and Ti atoms over a small number of octahedral sites has also been found in $Ti_{21}Ga_4O_{48}$.

Like $Ti_{21}Ga_4O_{48}$, the compound $V^{III}V^{IV}GaO_5$ exhibits close analogies with β-Ga_2O_3: monoclinic symmetry, space group $C2/m$; the structure is generated from exactly superposed layers perpendicular to the b axis ($\simeq$ 3 Å). The β-Ga_2O_3 elements, linked by corner-shared polyhedra in the pure oxide, are separated by large tunnels within rutile-type blocks in $Ti_{21}Ga_4O_{48}$. In V_2GaO_5, two adjacent β-Ga_2O_3-like blocks share a tetrahedron in order to give chains parallel to the columns of VO_6 octahedra.

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The Structure of Sodium Pentacyanosulphitoferrate(II) 10½-Water

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Abstract

$Na_5[Fe(CN)_5(SO_3)].10\frac{1}{2}H_2O$ is monoclinic, space group $P2_1/n$, with a = 8·756 (1), b = 31·866 (6), c = 15·390 (3) Å, β = 90·67 (1)°, Z = 8. Final R = 0·036 for 550 parameters and 7142 reflections. The two complex ions in the asymmetric unit are essentially similar and have distorted octahedral configurations. The sulphite ions are coordinated to Fe through S with Fe—S = 2·255 (1) and 2·277 (1) Å. The mean Fe—C and C—N = 1·911 (1) and 1·163 (2) Å for ion (1) and 1·908 (1) and 1·160 (2) Å for ion (2). There is no evidence for a sulphite *trans* effect.

Introduction

In connection with structural studies of hexa- and pentacyano complexes of transition metals the mode of coordination of sulphite in the presence of cyanide and

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