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Synthesis and Crystal Structure of β-SrV_2O_6

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The preparation and growth of single crystals together with a crystal structure determination of β-SrV_2O_6 are reported. This high temperature form of SrV_2O_6 crystallizes in the orthorhombic system, space group *Pnma*, with $a = 9.666$ (1) Å, $b = 3.6808$ (4) Å, $c = 12.529$ (3) Å, $Z = 4$. The structure, determined and refined down to $R = 3.1\%$, is described as isolated zigzag double strings with $[V_2O_6]_n$ composition extending along the [010] direction and built up by edge-sharing VO_6 octahedra. Strontium atoms occupy tricapped trigonal prisms of oxygen atoms pertaining to three different strings and assume the stability of the network. © 1991 Academic Press, Inc.

Introduction

Several phases pertaining to the *M*O–V_2O_5–VO_2 systems (M = Ca, Sr, Ba) had been investigated (*1–7*). In the perspective of an investigation of vanadates with lower vanadium oxidation number (III or IV) obtained by reduction of vanadates containing vanadium V, it was advisable to deepen some of their structural data. The polymorphism in $Sr_2V_2O_7$ had already been indicated (*3*); single crystals corresponding to a new polymorphic form have been obtained and their study is in progress. Presently, the polymorphism of SrV_2O_6 has also been established, and the aim of this paper is to report about the synthesis and the structure of the high temperature form, β-SrV_2O_6.

Experimental

Strontium carbonate and vanadium pentoxide with molar ratio 1 : 1 were intimately mixed, prefired at 670°C during 24 hr under an oxygen stream to remove carbon dioxide, reground, and heated again for 24 hr at the same temperature. The obtained yellow product exhibits the X-ray powder pattern already reported by Bouloux and Galy (*8*) and indexed in the orthorhombic system, space groups *C*222, *Cmm*2, or *Cmmm*, with the parameters $a = 8.245$ Å, $b = 12.293$ Å, and $c = 7.657$ Å. In order to obtain crystals, a melting of the powder was performed at 830°C, followed by a cooling down to 530°C at the rate of 5°C/hr, then down to room temperature at 60°C/hr. Pale yellow parallelepipedic single crystals were isolated from the material. The corresponding powder pattern was different from the previous one; a new polymorphic form of SrV_2O_6 was probably obtained. A selected crystal was studied using a precession camera with molybdenum $K\alpha$ radiation.

The compound crystallizes in the orthorhombic system; the possible space groups are *Pnma* or $Pn2_1a$. The full collection of

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TABLE I

PHYSICAL AND CRYSTALLOGRAPHIC DATA

Formula	SrV_2O_6
Molecular weight (g)	285.5
Color	pale yellow
Morphology	parallelepiped
Dimension (mm)	0.12 × 0.12 × 0.17
Crystal system	orthorhombic
Space group	*Pnma* (N° 62)
a (Å)	9.666(1)
b (Å)	3.6808(4)
c (Å)	12.529(3)
V (Å^3)	445.7(1)
Z	4
ρ calc (g cm^{-3})	4.26
$F(000)$	528
μ (Mo$K\alpha$) (cm^{-1})	156
Wavelength (Mo$K\alpha$) (Å)	0.71069
Monochromator	oriented graphite
Take off (°)	3.75
Detector width (mm^2)	4 × 4
Scan type	$\omega/2\theta$
Scan width (°)	$0.75 + 0.35 \tan \theta$
Prescan speed (° mn^{-1})	10
Maximum time (sec)	80
Reflections for cell refinement	25
Recorded reflections	1025, $2\theta \leq 70°$
hkl range	$0 \leq h \leq 15, 0 \leq k \leq 5, 0 \leq l \leq 20$
Intensity control reflections	0 0 8/0–4 0/8 0 0 every 3600 sec
Orientation control reflections	10–1 3/6 0 5 every 250 refl.
Transmission coefficient range	0.41–1.00
Number of unique data with $I \geq 3\sigma$	705
Number of refined parameters	56
R	0.031
R_w (w = 1)	0.037

data had been performed on a CAD4 Enraf–Nonius diffractometer; the refined cell parameters are a = 9.666(1) Å, b = 3.6808(4) Å, and c = 12.529(3) Å and allow one to index all the lines of the powder pattern. The studied compound is a new high temperature form of SrV_2O_6, called β-SrV_2O_6.

Structure Determination

All the experimental X-ray data and results are summarized in Table I. Corrections of X-ray flux fluctuations, Lorentz polarization, and absorption (*9*) had been applied to the *hkl* data. The structure was determined using the Patterson method and its refinement was carried out via full matrix least-squares calculations in the space group *Pnma*. This space group was chosen because, first, an inspection of *h*0*l and h*2*l* intensities revealed that their distributions are virtually identical, suggesting that all atoms were situated on, or very near, the levels $y = \pm 1/4\ b$ (classical case for these structures with a parameter near 3.6 Å); second, statistics tests are in favor of the centrosymmetric group, and a refinement carried out with the $Pn2_1a$ space group has given very strong correlations between parameters (35 coefficients higher than 0.999). Atomic scattering factors were corrected for anomalous dispersion (*10*). Secondary extinction had been applied (r^* = 5,43) (*11*). The calculations and drawings were performed with CRYSTALS (*12*) and ORTEP (*13*) using a superminicomputer VFX/80 ALLIANT. The structural details of β-SrV_2O_6 are summarized in Tables II and III.

TABLE II

FRACTIONAL COORDINATES AND THERMAL PARAMETERS

Atom	x	y	z	B_{eq} (Å^2)
Sr	0.63235(7)	1/4	0.38073(5)	0.52(4)
V1	0.0018(1)	1/4	0.6255(1)	0.30(6)
V2	0.2441(1)	1/4	0.41085(9)	0.28(6)
O1	0.1733(5)	1/4	0.6081(4)	0.4(2)
O2	−0.0294(6)	1/4	0.7545(4)	0.7(3)
O3	−0.1966(5)	1/4	0.5647(4)	0.5(2)
O4	0.0339(5)	1/4	0.4120(5)	0.5(2)
O5	0.2837(6)	1/4	0.2858(4)	0.7(2)
O6	0.3964(5)	1/4	0.4788(4)	0.6(2)
Atom	β_{11}	β_{22}	β_{33}	β_{13}
Sr	0.00173(7)	0.0087(4)	0.00075(4)	0.00016(3)
V1	0.00044(9)	0.0069(6)	0.00081(5)	−0.00020(7)
V2	0.00051(9)	0.0067(6)	0.00053(5)	0.00002(7)
O1	0.0006(4)	0.015(3)	0.0010(3)	−0.0002(3)
O2	0.0019(7)	0.015(3)	0.0010(3)	−0.0003(3)
O3	0.0011(4)	0.006(3)	0.0011(3)	0.0002(3)
O4	0.0006(4)	0.011(3)	0.0018(3)	−0.0003(3)
O5	0.0027(4)	0.016(3)	0.0006(3)	−0.0003(3)
O6	0.0008(4)	0.010(3)	0.0013(3)	0.0000(3)

Note. All atoms are situated in site 4*c* (Wyckoff notation). $B_{eq} = 4/3\ \Sigma_{ij}\ (a_i a_j)\ \beta_{ij}$. The form of anisotropic displacement parameter is $\exp[-(\beta_{11} h^2 + \beta_{22} k^2 + \beta_{33} l^2 + 2\beta_{12} hk + 2\beta_{13} hl + 2\beta_{23} kl)]$. β_{12} and β_{23} are fixed to 0.

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND O–V–O ANGLES (°)

Sr–O1$_{iii/iv}$	2.634(3)		
Sr–O2$_{v/vi}$	2.623(4)		
Sr–O3$_{viii}$	2.837(5)	V1–V2	3.566(2)
Sr–O5$_{vii}$	2.548(5)	V1–V2$_{ii}$	3.040(1)
Sr–O6	2.591(5)		
Sr–O6$_{iii/iv}$	2.561(4)		

V1	O1	O2	O3	O4	O4$_i$	O4$_{ii}$
O1	1.672(5)	108.1(3)	150.8(3)	75.9(2)	98.4(2)	98.4(2)
O2	2.684(8)	1.644(6)	101.1(2)	176.1(2)	101.9(2)	101.9(2)
O3		2.876(8)	2.063(5)	75.0(2)	75.2(2)	75.2(2)
O4	2.802(8)		2.937(7)	2.693(6)	77.2(2)	77.2(2)
O4$_i$	2.732(5)	2.782(6)	2.438(5)	2.946(9)	1.930(2)	144.9(3)
O4$_{ii}$	2.732(5)	2.782(6)	2.438(5)	2.946(9)		1.930(2)

V2	O1	O3$_i$	O3$_{ii}$	O4	O5	O6
O1	2.564(5)	77.4(2)	77.4(2)	74.1(2)	178.3(2)	75.4(2)
O3$_i$	2.850(6)	1.921(1)	146.6(3)	76.1(2)	102.2(2)	97.3(2)
O3$_{ii}$	2.850(6)		1.921(1)	76.1(2)	102.2(2)	97.3(2)
O4	2.802(8)	2.438(5)	2.438(5)	2.032(5)	104.1(3)	149.5(3)
O5		2.758(6)	2.758(6)	2.886(8)	1.613(6)	106.3(3)
O6	2.697(7)	2.723(5)	2.723(5)		2.653(7)	1.701(5)

Note. (i) $-x, -y, 1 - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1 - x, -y, 1 - z$; (v) $1/2 - x, 1/2 + y, -1/2 + z$; (vi) $1/2 - x, -1/2 + y, -1/2 + z$; (vii) $1/2 + x, y, 1/2 - z$; (viii) $1 + x, y, z$.

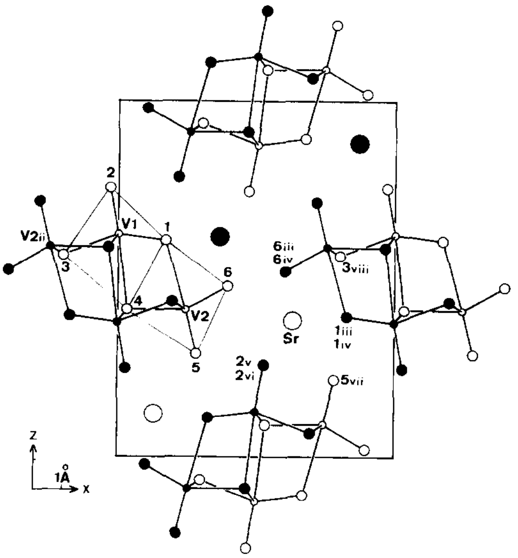

FIG. 1. Projection of β-SrV_2O_6 onto the plane (010), large circles are strontium atoms, intermediate ones are oxygen atoms, and the small ones are vanadium. Atoms in heavier outline are at $y = 3/4$, the lighter ones at $y = 1/4$.

The Structure of β-SrV_2O_6

The projection of the structure onto the (010) plane is given in Fig. 1. The two independent vanadium atoms (V1 and V2) are octahedrally surrounded by oxygen atoms. Two octahedra having an edge in common, by additional edge-sharing to similar pairs, above and below, lead to zigzag double strings extending along the *b*-axis (Fig. 2). All the atoms lie in the mirror planes of the space group *Pnma* (position 4*c*). These isolated strings with $[V_2O_6]_n$ composition are packed with the same orientation in layers parallel to the (001) plane, with orthogonal directions (nearly [101] and [10$\bar{1}$]) in every other layer, making an infinite puckered network. Strontium atoms occupy tricapped trigonal prisms of oxygen atoms pertaining to three different strings and cement the structure.

Further study of the vanadium coordination polyhedra (Fig. 2 and Table III) shows, as in previously described structures, V atoms are moved toward one of the apexes of the octahedron, i.e., O2 for V1 and O5 for V2, giving the shortest distances (double bond character V=O), respectively V1–O2 and V2–O5, symmetrically opposed to the longest ones, V1–O4 and V2–O1. The found distances are in agreement with the ones already encountered and discussed, for example, in the recently refined V_2O_5 structure (*14*) and metavanadates CaV_2O_6 (*15, 16*) α- and β-CdV_2O_6 (*16, 17*), α- and β-CuV_2O_6 (*18–20*). This tendency of vanadium V for square pyramidal coordination (SP) (V1 and V2 being respectively at 0.44 and 0.45 Å from the basal plane of the SP (O1O3O4$_i$ O4$_{ii}$ and O3$_i$O3$_{ii}$O4O6)) induces a rather large V1–V2 distance across the shared edge in the plane (010), (i.e. 3.566(2) Å) while the V1–V2$_{ii}$ distance shrinks to 3.040(1) Å. The second short V–O distances

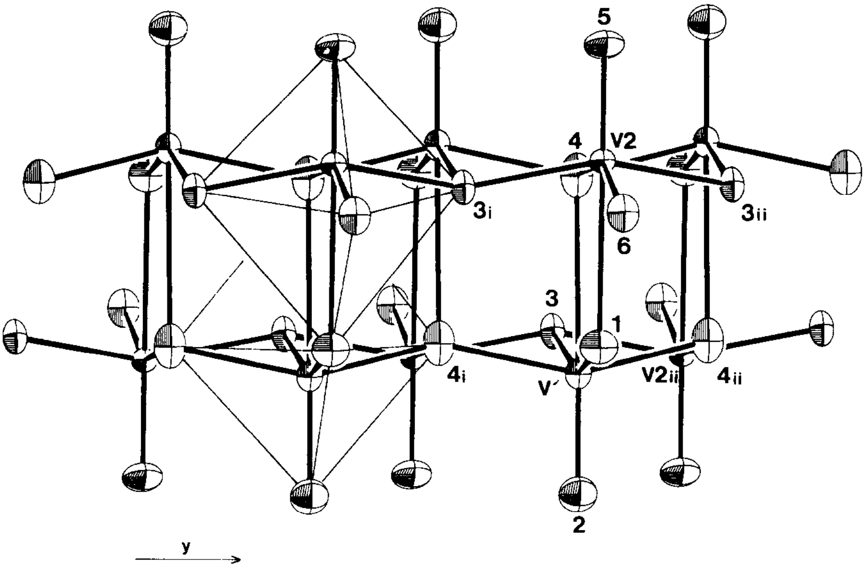

FIG. 2. Perspective view of a $[V_2O_6]_n$ string extending along the *b*-axis.

are V1–O1 and V2–O6; they correspond to unshared oxygen atoms which are on the border of the strings and interact mainly with strontium atoms. The strings exhibit in their internal association a weakness in the bonding, V–O distances being respectively at 2.693(6) Å and 2.564(5) Å.

The environment of strontium (CN = 9) is a tricapped trigonal prism (Fig. 3). Eight Sr–O distances range from 2.548(5) to 2.634(3) Å; the last one, Sr–$O3_{viii}$, through a rectangular face of the trigonal prism, slightly longer (2.837(5) Å), corresponds to an oxygen firmly linked to two vanadium atoms. Dihedral angles between the faces of the trigonal prism are 47.0, 65.2, and 67.8°.

Discussion

The structure of β-SrV_2O_6 appears to be isostructural with PbV_2O_6 studied by Jordan and Calvo (*21*) and hence rather different from the one found for CaV_2O_6, α- and β-CdV_2O_6, α- and β-CuV_2O_6 (*15–20*), and the brannerite $ThTi_2O_6$ (*22*). Nevertheless double strings $[M_2O_6]$ have already been reported by Wadsley in the alkalinotitaniobates $KTiNbO_5$, KTi_3NbO_9 (*23*), and by Lavaud and Galy in $Cu_xV_4O_{11}$ (*24*), but in these cases they are linked to each other by

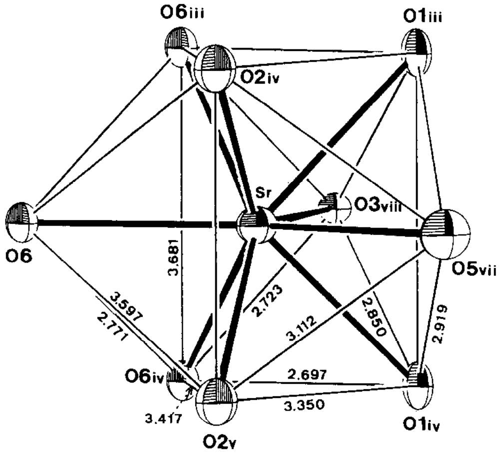

FIG. 3. Coordination polyhedron of the strontium atom.

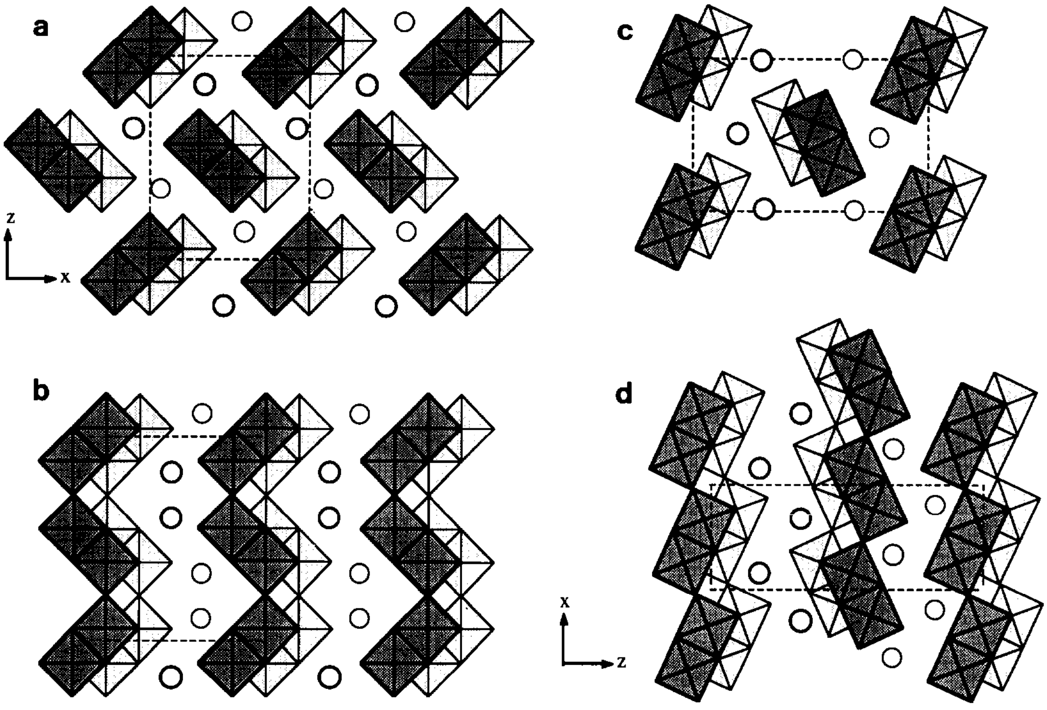

FIG. 4. Projection of the idealized structure of β-SrV_2O_6 (a), "SrV_2O_5" (b), "AB_2O_6" (c), and $KTiNbO_5$ (d).

corner-sharing in order to accommodate the various stoichiometries.

Looking at the idealized structure of β-SrV_2O_6 and $KTiNbO_5$ (Fig. 4a and 4d), their similarities prompt one to imagine that the former can give by reduction a possible "SrV_2O_5" layer structure (Fig. 4b). This structural transformation is achieved via a crystallographic shear operation with a 1/2 [100] slip of every other layer parallel to the (001) plane. Finally, it leads to the assembly of $[V_2O_6]_n$ strings by corner-sharing, giving puckered $[V_2O_5]_n$ layers parallel to the (100) plane. During this operation strontium atoms are moved in order to hold together the layers. The latter, $KTiNbO_5$, could lead, by an inverse process to an AB_2O_6 network (Fig. 4*c*) very similar to β-SrV_2O_6.

The phase transition $\alpha \rightarrow \beta$, which occurs in SrV_2O_6 around 675°C, is accompanied by a drastic decrease of the packing efficiency, $V_\alpha = 129.3$ Å^3 against $V_\beta = 111.5$ Å^3 per unit. The study of this transition and the crystal structure of α-SrV_2O_6 will be discussed in a forthcoming paper.

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