On the Crystal Structure of $Cs_xV_2O_5$ (x ~ 0.3), a New Hexagonal Vanadium Bronze Structure Type

By Kjell Waltersson and Bertil Forslund

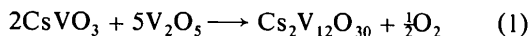*Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, Fack, S-104 05 Stockholm, Sweden*

A structural study of the hexagonal vanadium bronze $Cs_xV_2O_5$ (x ~ 0.3) has given the following results: unit-cell dimensions of a subcell: $a = 14.360$ (5), $c = 3.611$ (1) Å, $V = 644.9$ Å^3; $Z = 6$; space group $P6_3/m$. The final R_w value is 0.038 for 487 reflexions and 36 parameters (three-dimensional X-ray diffractometer data, Mo $K\alpha$ radiation). The two crystallographically independent V atoms are five-coordinated in VO_5 square pyramids, with V—O distances in the range 1.570–1.987 Å. The average value of 1.830 Å is close to the grand mean of 1.824 Å previously found for $V^{5+}O_5$ polyhedra. The VO_5 pyramids are linked by edges to form zigzag strings running in the c direction. Six strings are linked *via* corner-sharing to form tubes with the composition $\frac{1}{\infty}(V_2O_5)$. The structure contains two systems of tunnels, within and between such tubes. Cs ions are located in both types of tunnels. The presence of a superstructure, assumed to be due to an ordering of the Cs atoms within the tubes, has been observed, with the c axis length seven times that of the subcell. The compound shows semiconductor behaviour with an observed activation energy close to 0.07 eV.
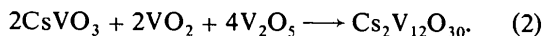
Introduction

Since the 1960's, considerable interest has been generated by solid state chemists in the field of vanadium bronzes (for a review, see Hagenmuller, 1973). Most work has been devoted to bronzes of the light alkali metals, Ag and Cu. Few investigations have been reported concerning reduced ternary Cs–V–O compounds.

Within a research programme at this Institute on the structural chemistry of V compounds (conducted by Dr K.-A. Wilhelmi), the system $Cs_2O–V_2O_5–VO_2$ has been investigated. Four compounds have been prepared and characterized by structure determinations, including preliminary investigations of the electrical and magnetic properties. The following compounds have been investigated: CsV_2O_5 – refinement of the structure proposed by Mumme & Watts (1971) (Waltersson & Forslund, 1977c); $Cs_2V_5O_{13}$ (Waltersson & Forslund, 1977b); and the bronze $Cs_{0.35}V_3O_7$ (Waltersson & Forslund, 1977a).

The preparation of a bronze with the stoichiometry $Cs_{0.33}V_2O_5$ was reported by Lucács, Strusievici & Liteanu (1971). The new compound was prepared at 500–520°C in a stream of nitrogen according to either of the reactions:

$$2CsVO_3 + 5V_2O_5 \longrightarrow Cs_2V_{12}O_{30} + \tfrac{1}{2}O_2 \quad (1)$$

or

$$2CsVO_3 + 2VO_2 + 4V_2O_5 \longrightarrow Cs_2V_{12}O_{30}. \quad (2)$$

The stoichiometry was derived from the loss of oxygen (TGA) and by chemical analysis for Cs, V^{4+} and V^{5+}. An unindexed powder pattern was also reported.

We have now been able to prepare good single crystals of this compound and investigate its crystal structure by X-ray methods. This paper is a first report, dealing with the structure determination. A forthcoming article will give details of the preparative studies and the physical properties.

Experimental

Pure samples, as judged from powder photographs, were obtained after heating finely ground mixtures of $CsVO_3$, V_2O_5 and V_2O_3 (mole ratio 4:9:1, corresponding to $Cs_{0.33}V_2O_5$) in evacuated silica tubes at 500°C for one month.

The single crystal used in this study was grown from a mixture of Cs_2CO_3 and V_2O_5 with a V/Cs ratio of 5:1, and a cooling rate ~10° h^{-1}. Higher cooling rates gave samples which looked beautiful but were, however, badly twinned. The melting and subsequent crystallization were performed in a stream of nitrogen in a microscope hot-stage device (Forslund, 1975) which allowed careful temperature control and continuous observation of the crystal growth. In order to isolate a well-developed crystal of the compound from the residual melt, we introduced a small piece of sintered alumina into the melt to absorb the liquid. Otherwise the crystals, which were easily cleaved along the

prism axis, were seriously damaged by the mother liquor on solidification.

The cell dimensions $[a = 14.360\,(2), c = 3.611\,(1)$ Å, $\gamma = 120°, V = 644.9$ Å$^3]$ of the hexagonal compound were obtained from a powder photograph, taken with a Guinier–Hägg camera and indexed with the aid of Weissenberg photographs. The powder pattern is listed in Table 1. The observed d values are in fair agreement with those reported by Lucács et al. (1971).

The density, determined by hydrostatic weighing (Niklewski, Kihlborg, Nygren & Sävborg, 1975), was found to be 3.45 g cm^{-3}. This value corresponds to the formula $Cs_{0.31}V_2O_5$ with six formula units in the unit cell.

A crystal $0.02 \times 0.02 \times 0.23(c)$ mm was mounted along the unique c axis. Oscillation and Weissenberg photographs proved it to be suitable for diffraction work.

A Siemens AED diffractometer with monochromatic Mo $K\alpha$ radiation, the θ–2θ scan technique, and the five-values measuring procedure were used. The scan range for individual lattice points was given by $\pm\Delta\theta = 0.81 + 0.158 \tan \theta$.

Three standard reflexions (300, 030 and 002) were automatically measured after every 47th lattice point throughout the data collection. No significant change in their net intensity was observed.

The intensities were collected for all the 721 independent reflexions with $\theta \leq 30°$. The reflexions $00l$: $l = 2n + 1$ were systematically absent and this reduced the number of observations to 718. The possible space groups were $P6_3$ (No. 173) and $P6_3/m$ (No. 176).

From the criterion $\sigma(I)/I \leq 0.40$, where $\sigma(I) = (I_t + I_b)^{1/2}$ and $I = I_t - I_b$, 487 intensity values were judged significant.

Lorentz–polarization, absorption and preparatory extinction corrections were applied to the data. The linear absorption coefficient $\mu(Mo\ K\alpha) = 70.2$ cm^{-1},

Table 1. Powder pattern of $Cs_xV_2O_5$

Cu $K\alpha_1$ radiation ($\lambda = 1.54050$ Å), and KCl ($a = 6.2930$ Å) as internal standard were used.

$h\,k\,l$	d_{obs}	$10^5 \sin^2 \theta_{obs}$	$10^5 \sin^2 \theta_{calc}$	I_{obs}
1 0 0	12.48	381	384	vw
1 1 0	7.186	1149	1151	vvw
2 1 0	4.703	2682	2685	m
3 0 0	4.148	3448	3452	s
3 1 0	3.446	4995	4987	m
2 0 1	3.123	6085	6084	m
1 2 1	2.864	7232	7235	s
4 1 0	2.713	8060	8055	m
5 0 0	2.490	9571	9590	w
3 3 0	2.3919	10370	10357	w
4 2 0	2.3482	10760	10740	vw
2 5 0	1.9921	14950	14960	m
1 6 0	1.8968	16490	16494	vw
0 0 2	1.8055	18200	18199	w

calculated for a supposed composition of $Cs_{0.3}V_2O_5$, was used in estimating a transmission factor for each reflexion (International Tables for X-ray Crystallography, 1962). This was done by the Gaussian integration method, with $4 \times 4 \times 12$ grid-points. The factor t in the formula $I = I_{obs}/t$ ranged from 0.837 to 0.869.

Structure determination

The structure was solved with three-dimensional Patterson and Fourier methods. Two crystallographically different V atoms and five different O atoms were derived, all in point sets (h) of the space group $P6_3/m$. The V and O positions were refined with a full-matrix least-squares program to an R value of 0.25.

A difference Fourier synthesis was then calculated with the refined V and O coordinates. The result showed a high density of electrons at $(\frac{1}{3},\frac{2}{3},\frac{1}{4})$. A high density of electrons extending around the line $x = y = 0$, and with a maximum at $z \sim 0.125$ was also observed. Therefore Cs atoms were located in point sets $2(c)$ and $4(e)$ with partial occupancy.

In the final cycles of the refinement, the two Cs occupancy factors were refined together with all the other parameters, leading to a composition of $Cs_{0.31}V_2O_5$. The final R_w and R values were 0.0382 and 0.0404 respectively, for 36 variables. The scattering factors used were for neutral atoms (McMaster, Kerr del Grande, Mallet & Hubbel, 1969) and the $\Delta f'$ and $\Delta f''$ values for Mo $K\alpha$ radiation were taken from International Tables for X-ray Crystallography (1962). Statistical weights were applied to the structure factors.*

The final positional and thermal parameters, together with their estimated standard deviations, are given in Table 2. The most important distances and angles are given in Table 3.

In a final three-dimensional $(F_o - F_c)$ Fourier synthesis, the maximum residual peak showed a height of 16% of the smallest O peak in the corresponding F_o Fourier synthesis.

The calculations were performed on IBM 1800 and IBM 360/75 computers.

Description and discussion of the structure

Fig. 1 is a projection on (001) of the $Cs_xV_2O_5$ structure. There are two crystallographically independent five-coordinated V atoms in VO_5 square pyramids linked by edges to form zigzag strings running in the c direction (see Fig. 2).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32111 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Six zigzag strings are linked together *via* corner-sharing by O(3) atoms to form hexagonal tubes with the composition $\frac{1}{\infty}$ (V_2O_5).

The mean values for V—O distances observed in the V(1)O_5 and V(2)O_5 square pyramids are 1·829 and 1·831 Å respectively, very close to the mean value, *viz.* 1·825 (5) Å, observed in different compounds containing pentavalent five-coordinated V polyhedra (Waltersson, Forslund, Wilhelmi, Andersson & Galy, 1974).

The different functions of the O atoms can be summarized in the following way. O(1) and O(2) are both bonded to three V atoms and are involved in the edge-sharing of the zigzag strings of VO_5 pyramids. The O(3) atom is connected to two V atoms and constitutes the common corner of two adjacent zigzag strings. The O(4) and O(5) atoms are each bonded to one V, but their functions are different. The O(4) atom is an apical O atom pointing into the tube, while the O(5) atom has a second V atom at a long distance of 2·87 Å and is involved in the bonding system between two neighbouring $\frac{1}{\infty}$ (V_2O_5) tubes.

There is a difference between the two VO_5 square pyramids. The V(1) atom has a sixth O [O(5)] at a distance of 2·87 Å. Thus, with regard to the O arrangement only, the O polyhedron can be seen as a very distorted octahedron. The apical bond length V(1)—O(4) is 1·57 Å, and the average basal bond length is 1·89 Å. On the other hand the V(2)O_5 polyhedron is regarded as a regular square pyramid. The sixth V(2)—O(4) distance is 3·17 Å. The apical bond length V(2)—O(5) is 1·59 Å, and the average basal bond length is 1·89 Å. As expected, the O(1)—O(2) edge, shared between the two VO_5 polyhedra, is very short (2·40 Å).

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *in* $Cs_xV_2O_5$

E.s.d.'s in the last decimal place are given within parentheses.

Vanadium—oxygen distances

V(1)—O(4)	1·570 (8)	V(2)—O(5)	1·593 (8)
—O(3)	1·797 (7)	—O(3)	1·803 (7)
—O(1) (2x)	1·895 (2)	—O(2) (2x)	1·894 (2)
—O(2)	1·987 (7)	—O(1)	1·969 (8)
—O(5)	2·867 (8)	—O(4)	3·165 (9)

Vanadium—vanadium distances

V(1)—V(2) (2x)	3·042 (2)	V(1)—V(2)	3·184 (3)

	Bond angles	Oxygen–oxygen distances
O(1)—V(1)—O(1)	144·7 (5)	3·611 (1)
—O(2) (2x)	76·3 (2)	2·398 (7)
—O(3) (2x)	95·9 (3)	2·742 (8)
—O(4) (2x)	104·8 (2)	2·753 (8)
O(2)—V(1)—O(3)	148·2 (3)	3·640 (10)
—O(4)	109·0 (4)	2·905 (10)
O(3)—V(1)—O(4)	102·9 (4)	2·637 (11)
O(1)—V(2)—O(2) (2x)	76·7 (2)	2·398 (7)
—O(3)	143·3 (3)	3·580 (11)
—O(5)	113·0 (4)	2·977 (11)
O(2)—V(2)—O(2)'	144·9 (4)	3·611 (1)
—O(3) (2x)	93·9 (2)	2·701 (8)
—O(5) (2x)	105·6 (2)	2·784 (8)
O(3)—V(2)—O(5)	103·7 (4)	2·673 (10)

Caesium—oxygen distances

Cs(1)—O(3) (6x)	3·204 (6)	Cs(2)—O(4) (3x)	3·105 (8)
—O(5) (6x)	3·434 (6)	—O(4) (3x)	3·370 (8)
		Cs(1)—V(2) (6x)	3·937 (2)

Table 2. *The crystal structure of* $Cs_xV_2O_5$

Space group $P6_3/m$ (No. 176). Cell dimensions: $a = 14\cdot360$ (5), $c = 3\cdot611$ (1) Å, $\gamma = 120°$, $V = 644\cdot9$ Å³.
Cell content: 6 $Cs_xV_2O_5$.

Atom (n)	Occupancy	Point set	x	y	z	B (Å²)
Cs(1)	61·8 (5)%	2(c)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	—
Cs(2)	16·2 (2)	4(e)	0	0	0·13175 (225)	—
V(1)		6(h)	0·35248 (16)	0·26261 (15)	$\frac{1}{4}$	—
V(2)		6(h)	0·42593 (14)	0·08696 (15)	$\frac{1}{4}$	—
O(1)		6(h)	0·06385 (62)	0·37254 (60)	$\frac{1}{4}$	1·41 (16)
O(2)		6(h)	0·31732 (59)	0·38002 (54)	$\frac{1}{4}$	0·71 (13)
O(3)		6(h)	0·45382 (55)	0·22403 (58)	$\frac{1}{4}$	0·97 (13)
O(4)		6(h)	0·24499 (68)	0·15147 (63)	$\frac{1}{4}$	2·02 (17)
O(5)		6(h)	0·54223 (65)	0·09859 (59)	$\frac{1}{4}$	1·75 (16)

The anisotropic temperature factors for metal atoms are defined as
$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. β_{ij} values are given in Å² × 10⁵. E.s.d.'s are within parentheses.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs(1)	261 (17)	261 (17)	10414 (324)	130 (9)	0	0
Cs(2)	394 (37)	394 (37)	13661 (2222)	197 (19)	0	0
V(1)	244 (14)	153 (13)	1104 (140)	129 (11)	0	0
V(2)	139 (12)	123 (12)	671 (128)	63 (10)	0	0

The axes of the hexagonal tubes are on the line $x = y = 0$, and one V(1) atom in each of two adjacent tubes forms one very weak bond (2·87 Å) to its nearest O(5) oxygen. At the same time, another set of tunnels is formed, containing the M_1 sites (see below).

There is an interesting analogy between the structures of $Cs_xV_2O_5$ and $Cs_xV_3O_7$ (Waltersson & Forslund, 1977a). The same type of $\frac{1}{\infty}$ (V_2O_5) hexagonal tubes is present in both structures. Formally, the structure of $Cs_xV_3O_7$ can be derived from that of $Cs_xV_2O_5$ by 'fusing' the rings of six zigzag strings of VO_5 square pyramids, forming the hexagonal tubes, by a translation $(a/3,b/3,0)$ [or $(a/3,0,0)$ or $(0,b/3,0)$]. At the same time the overall V–O composition is changed to $\frac{1}{\infty}$ (V_3O_7) and the Cs^+ site M_1 (see below), present in $Cs_xV_2O_5$, is eliminated.

In $Cs_{0.35}V_3O_7$ the observed mean value of the V–O distances in the VO_5 polyhedra is significantly larger [viz. 1·845 Å (Waltersson & Forslund, 1977a)] than the mean values of 1·829 and 1·831 Å observed in $Cs_xV_2O_5$. This difference reflects the different degrees of reduction. The formal oxidation numbers of the V atoms in the structures of $Cs_{0.35}V_3O_7$ and $Cs_{0.30}V_2O_5$ are 4·55 and 4·85 respectively.

The valences of the two crystallographically different V atoms in γ-LiV$_2$O$_5$ are +4 and +5 (Galy, Darriet & Hagenmuller, 1971). The V–O distances and their change as a function of the formal oxidation number of the V atom are summarized in Table 4.

In this context it must be emphasized that the V–O bond distances for $Cs_{0.35}V_3O_7$ and $Cs_{0.3}V_2O_5$ refer to the subcell structure determinations (see below).

According to the refinement, approximately $\frac{2}{3}$ of the total Cs content is distributed inside the tunnels at the M_1 site ($x = \frac{1}{3}$, $y = \frac{2}{3}$, $z = \frac{1}{4}$). The remaining Cs atoms are dispersed along the line $x = y = 0$ (M_2 site). The observed density of electrons along the line $x = y = 0$, calculated in a Fourier (F_o) synthesis, indicates a 'disorder' of the same kind as was noticed in the determination of the subcell of $Cs_{0.35}V_3O_7$ (Waltersson & Forslund, 1977a). This is also reflected in the thermal parameters β_{33}. In a rotation photograph of a crystal, annealed at 470°C for one month, a very weak extra layer, hardly visible, was detected, corresponding to an interplanar distance of ~5·1 Å. The actual c axis length is seven times that of the subcell. Therefore the presence of a superstructure is assumed to be due to an ordering of the Cs atoms in the M_2 site, with a Cs–Cs separation of ~5·1 Å.

The O environment of the Cs atom in the M_1 position (CN = 12) is reasonable: the mean Cs–O distance of 3·37 Å is in excellent agreement with the value of 3·37 Å given for twelve-coordinated Cs atoms (International Tables for X-ray Crystallography, 1962).
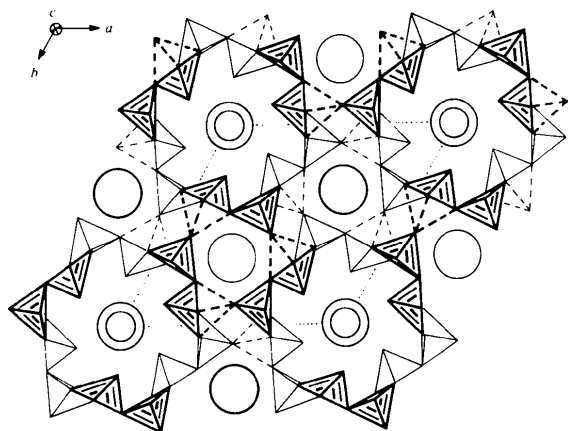

Fig. 1. The structure of $Cs_{0.3}V_2O_5$ projected on (001). The c axis is directed into the plane of the paper. The VO_5 square pyramids are drawn at the levels $z = -\frac{1}{4}$ and $z = \frac{1}{4}$. The large circles indicate the Cs positions.
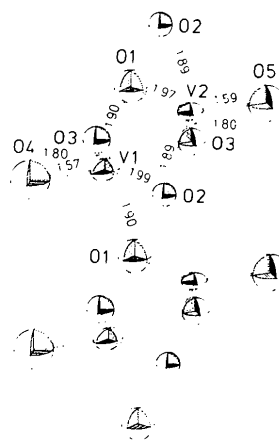

Fig. 2. The V(1)O$_5$ and V(2)O$_5$ polyhedra forming the zigzag string of square pyramids. The thermal ellipsoids are drawn at 90% probability.

Table 4. V–O bond distances (Å) in γ-LiV$_2$O$_5$, $Cs_{0.3}V_2O_5$ and $Cs_{0.35}V_3O_7$

	γ-LiV$_2$O$_5$		$Cs_{0.3}V_2O_5$		
	V(1)	V(2)	V(1)	V(2)	$Cs_{0.35}V_3O_7$
Apical V–O	1·59	1·61	1·570	1·593	1·572
V–O bond range in pyramid base	1·91–2·00	1·77–1·97	1·80–1·99	1·80–1·97	1·90–1·95
Average of V–O bonds in pyramid base	1·95	1·88	1·894	1·890	1·914
Formal valence	+4	+5	+4·85	+4·85	+4·55

References

FORSLUND, B. (1975). Fourth Scandinavian Symposium on Thermal Analysis.

GALY, J., DARRIET, J. & HAGENMULLER, P. (1971). Rev. Chim. Minér. 8, 509–522.

HAGENMULLER, P. (1973). Comprehensive Inorganic Chemistry, edited by A. F. TROTMAN-DICKENSON. New York: Pergamon.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

LUCÁCS, I., STRUSIEVICI, C. & LITEANU, C. (1971). Rev. Roumaine Chim. 16, 245–254.

McMASTER, W. H., KERR DEL GRANDE, N., MALLET, J. H. & HUBBEL, J. H. (1969). Compilation of X-ray Cross Sections, UCRL-50174, Sec. II, Rev. 1.

MUMME, W. G. & WATTS, J. A. (1971). J. Solid State Chem. 1, 310–318.

NIKLEWSKI, T., KIHLBORG, L., NYGREN, M. & SÄVBORG, Ö. (1975). Chem. Commun. Univ. Stockholm, 12, 1–13.

WALTERSSON, K. & FORSLUND, B. (1977a). Acta Cryst. B33, 775–779.

WALTERSSON, K. & FORSLUND, B. (1977b). Acta Cryst. B33, 784–789.

WALTERSSON, K. & FORSLUND, B. (1977c). Acta Cryst. B33, 789–793.

WALTERSSON, K., FORSLUND, B., WILHELMI, K.-A., ANDERSSON, S. & GALY, J. (1974). Acta Cryst. B30, 2644–2652.

The Crystal Structure of $Cs_2V_5O_{13}$

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The crystal structure of $Cs_2V_5O_{13}$ has been determined and refined to a final R_w value of 0·019 from 267 independent reflexions and 35 variables. Three-dimensional X-ray diffractometer data (Mo $K\alpha$ radiation) were used. The space group is $I4mm$ (No. 107), and the unit-cell dimensions are $a = 7.762(1)$, $c = 11.746(2)$ Å, $V = 707.7$ Å, $Z = 2$. The new structure type can be visualized in different, complementary ways: it can be regarded as composed of VO_4 tetrahedra and VO_5 square pyramids in the ratio 4:1 (joined exclusively by corner-sharing) forming $^2_\infty(V_5O_{13}^{2-})$ layers, held together by Cs^+ ions; or composed of isolated isocyclic rings of $V_4O_{12}^{4-}$ tetramers and VO^{2+} (vanadyl) and Cs^+ ions. The observed, averaged V–O distances for the four- and five-coordinated V atoms are 1·71 and 1·96 Å respectively; the V–O distance in the vanadyl ion is 1·587(16) Å. The Cs^+ ions have twelve nearest O neighbours in the range 3·24–3·54 Å. The structure is compared with those of $K_2V_3O_8$ and $K_3V_5O_{14}$.

Introduction

During recent years, the formation conditions, crystal structures and physical properties (electrical and magnetic) of binary vanadium(IV,V) oxides and ternary, heavy alkali–metal vanadium(IV, V) oxides have been investigated at this Institute. The structures of the following compounds have been studied: $Cs_{0.35}V_3O_7$ (Waltersson & Forslund, 1977a), $Cs_{0.3}V_2O_5$ (Waltersson & Forslund, 1977b), and CsV_2O_5 (Waltersson & Forslund, 1977c).

Reid & Watts (1970) reported the synthesis of a new, reduced, ternary caesium vanadium oxide with tetragonal symmetry. Unit-cell dimensions were $a = 7.72$ and $c = 11.73$ Å. The compound was tentatively given the formula $Cs_{0.94}V_2O_{5.3}$. The preparative technique used was electrolysis at 540°C of a melt containing 37 mol% Cs_2O and 63 mol% V_2O_5. Fotief & Golofkin (1972) also reported the preparation (by heating mixtures of Cs_2CO_3 and V_2O_5 at 500°C in vacuum) of a tetragonal phase with a suggested composition of $CsV_3O_{7.5}$. The powder pattern was consis-