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# Silver Insertion Mode in $\beta$-$Ag_xV_2O_5$ Tunnel Structure

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## Abstract

The $\beta$-$Ag_xV_2O_5$ phase of silver vanadate has a large homogeneity range, $0.29 \leq x \leq 0.41$; the $(V_2O_5)_n$ network of its crystal structure is typical of the $\beta$ phase of the vanadium oxide bronzes with its oxygenated tunnels running along [010]. Ag atoms are inserted in a novel manner, being distributed onto two distinct crystallographic sites, which explains the overstepping of the theoretical boundary limit of the $\beta$ phases, $x = 0.33$.

## Comment

The structure type of $\beta$ phases was depicted for the first time by Wadsley (1955) for the sodium vanadium oxide bronze $\beta$-$Na_xV_2O_5$. A wide family has followed, $\beta$-$M_xV_2O_5$, where $M$ represents alkaline, alkaline earth, Cu, Ag, Cd or Pb metals. Galy and co-workers (Galy & Hardy, 1964; Galy, Darriet & Hagenmuller, 1971) studied $Li_xV_2O_5$ and demonstrated the existence of two phases, $\beta$ and $\beta'$, the difference between them being the mode of lithium insertion. Various possibilities have been analysed and discussed by Galy, Darriet, Casalot & Goodenough (1970).

To understand the homogeneity range for these phases, related directly to the $M$-atom insertion mode, several investigations have been undertaken. The $\beta$ and $\beta'$ phases are characterized by closely related networks of $[V_2O_5]_n$ which result from the association by edges and corners of triple infinite chains built up by $V(1)O_6$ and $V(2)O_6$ octahedra and $V(3)O_5$ square pyramids (Fig. 1). In the $\beta$ phase of $Na_xV_2O_5$, the Na or $M$ atoms are distributed over a crystallographic site, $M(1)$ [here Ag(1)]; this site, repeated by a centre of symmetry of the $C2/m$ space group, produces a type of '$M$ doublet' inserted in the large bicapped rhombic prism O(6*b*)[O(8)O(4)O(8*c*)-O(4*c*)]$_2$O(6*d*). Due to the short distance which separates $M(1)$ and $M(1c)$, only 50% of the sites are occupied, giving a theoretical upper limit of $M_{0.33}V_2O_5$ for the $\beta$ phases.

Recently, in companion papers, Permer & Ferey (1993) and Savariault, Déramond & Galy (1993) reported investigations of the $\beta'$ phases of iron and copper; in these phases both iron and copper occupy the oxygenated tetrahedra built up by O(8), O(4) and two O(6*b*) [or O(8*c*), O(4) and two O(6*d*)]. Such an insertion mode allows these phases to reach the maximum formula $M_{0.66}V_2O_5$. The problem with $Ag_xV_2O_5$, studied by Casalot & Pouchard (1967), is knowing if it belongs to the $\beta$ or $\beta'$ type, or both, *via* its silver insertion within the tunnels.

The crystal structure clearly establishes that the Ag atoms are distributed in the bicapped rhombic prism but unusually over four sites, Ag(1), Ag(2), Ag(1*c*) and Ag(2*c*). Clearly, $Ag_xV_2O_5$ is not a $\beta'$ phase. Among the $\beta$ phases, $Ag_xV_2O_5$ is the first exhibiting these two insertion sites. The Ag(1) site in the monocapped trigonal prism O(6*b*)[O(8)O(8*c*)O(4*c*)]$_2$ is similar to that of Na in Wadsley's phase (Wadsley, 1955) (Fig. 2). Ag(1*c*) being situated 1.925 (3) Å from Ag(1) implies that these sites can only be half occupied, which is confirmed by Ha-Eierdanz & Müller (1993).

The coordination number (CN) 7 of Ag(1) indicates regular Ag—O distances [Ag(1)—O = 2.390 (1)–2.655 (2) Å] which correspond to classical $Ag^{I}$—O interatomic distances according to Wells (1975). Ag(2), close to Ag(1) at a distance of 0.415 (2) Å, still in the monocapped trigonal prism, is displaced towards O(6*b*) [Ag(2)···O(6*b*) = 2.160 (4) Å]. The Ag—O distances range from 2.160 (4) to 2.854 (3) Å. Of course, Ag(1) and Ag(2) cannot be occupied simultaneously as well as Ag(2) and Ag(1*c*) [or Ag(1) and Ag(2*c*)], but Ag(2) and Ag(2*c*), with an interatomic distance of 2.750 (4) Å, can.

The theoretical $x = 0.33$ value for the existence of the $\beta$ phase is not now the upper limit; the new limit is $x = 0.66$, as for the $\beta'$ phase.

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This structure determination shows how the family of silver vanadium oxide bronzes can exist for the homogeneity range $0.29 \leq x \leq 0.41$ and indicates its originality among $\beta$ and $\beta'$ phases, even if it constitutes a slightly different version of the $\beta$ phase.

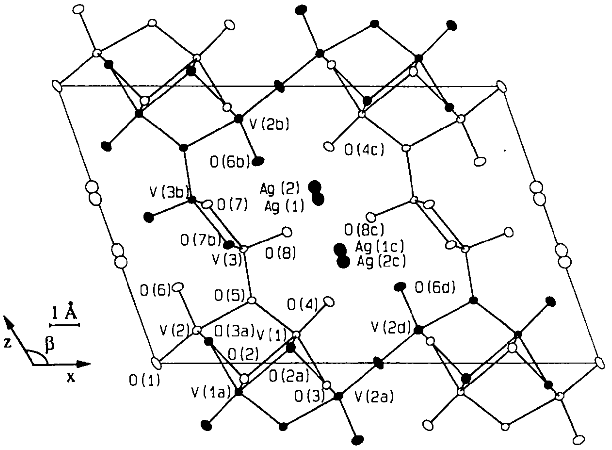

Fig. 1. Projection of the cell along the $b$ axis; symmetry codes are reported in Table 2. Open atoms are situated at elevation 0, filled atoms at elevation $\frac{1}{2}$.

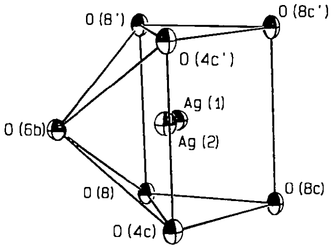

Fig. 2. View of the Ag-atom sites.

## Experimental

*Crystal data*

$Ag_{0.4}V_2O_5$
$M_r = 225.03$
Monoclinic
$C2/m$
$a = 15.388\ (8)$ Å
$b = 3.6139\ (3)$ Å
$c = 10.088\ (4)$ Å
$\beta = 109.94\ (2)°$
$V = 527.37\ (4)$ Å$^3$
$Z = 6$

$D_x = 4.25$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11\text{-}36°$
$\mu = 7.59$ mm$^{-1}$
$T = 293$ K
Elongated plates
0.4 × 0.1 × 0.025 mm
Black with metallic lustre

*Data collection*

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans [$\Delta\theta = (1.1 + 2.5\tan\theta)°$]

2055 observed reflections [$I > 3\sigma(I)$]
$R_{\text{int}} = 0.049$
$\theta_{\max} = 40°$

Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.62$, $T_{\max} = 0.99$
2353 measured reflections
2288 independent reflections

$h = -27 \rightarrow 27$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 18$
3 standard reflections (040, 006, $\bar{7}\bar{1}0$)
frequency: 60 min
intensity variation: none

*Refinement*

Refinement on $F$
$R = 0.0447$
$wR = 0.0498$
$S = 1.067$
2055 reflections
80 parameters
$w = 1.73/[\sigma^2(F) + 0.005F^2]$
$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 1.8$ e Å$^{-3}$
$\Delta\rho_{\min} = -3.3$ e Å$^{-3}$

Extinction correction: *SHELX76* (Sheldrick, 1976)
Extinction coefficient: $0.0025 \times 10^{-4}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$B_{\text{eq}} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | s.o.f.† | $x$ | $y$ | $z$ | $B_{\text{eq}}$ |
|---|---|---|---|---|---|
| Ag(1) | 0.36 | 0.4961 (6) | 1/2 | 0.5932 (1) | 1.53 (2) |
| Ag(2) | 0.24 | 0.4981 (1) | 1/2 | 0.6353 (2) | 1.95 (4) |
| V(1) | 1 | 0.33725 (3) | 0 | 0.10060 (4) | 0.65 (1) |
| V(2) | 1 | 0.11720 (3) | 0 | 0.11788 (4) | 0.76 (1) |
| V(3) | 1 | 0.28800 (3) | 0 | 0.41044 (4) | 0.746 (6) |
| O(1) | 1 | 0 | 0 | 0 | 1.30 (6) |
| O(2) | 1 | 0.1859 (1) | 0 | −0.0537 (2) | 0.83 (4) |
| O(3) | 1 | 0.3658 (1) | 0 | −0.0770 (2) | 0.94 (4) |
| O(4) | 1 | 0.4373 (2) | 0 | 0.2191 (2) | 1.22 (5) |
| O(5) | 1 | 0.2646 (1) | 0 | 0.2239 (2) | 0.83 (4) |
| O(6) | 1 | 0.1090 (2) | 0 | 0.2727 (2) | 1.63 (5) |
| O(7) | 1 | 0.2419 (2) | 0 | 0.5739 (2) | 0.89 (4) |
| O(8) | 1 | 0.3993 (2) | 0 | 0.4736 (2) | 1.31 (5) |

† Site occupancy factor.

Table 2. *Selected geometric parameters* (Å)

| | | | |
|---|---|---|---|
| V(1)—O(4) | 1.595 (2) | V(3)—O(7$^{\text{ii}}$) | 1.8847 (7) × 2 |
| V(1)—O(2$^{\text{i}}$) | 1.8771 (5) × 2 | V(3)—O(6) | 2.627 (2) |
| V(1)—O(5) | 1.935 (2) | Ag(1)—O(6$^{\text{ii}}$) | 2.437 (3) |
| V(1)—O(3) | 1.985 (2) | Ag(1)—O(4$^{\text{iii}}$) | 2.565 (2) × 2 |
| V(1)—O(2) | 2.318 (2) | Ag(1)—O(8) | 2.390 (1) × 2 |
| V(2)—O(6) | 1.609 (2) | Ag(1)—O(8$^{\text{iii}}$) | 2.655 (2) × 2 |
| V(2)—O(1) | 1.7899 (4) | Ag(2)—O(6$^{\text{ii}}$) | 2.160 (4) |
| V(2)—O(3$^{\text{i}}$) | 1.8913 (7) × 2 | Ag(2)—O(4$^{\text{iii}}$) | 2.327 (2) × 2 |
| V(2)—O(5) | 2.153 (2) | Ag(2)—O(8) | 2.558 (2) × 2 |
| V(2)—O(2) | 2.316 (2) | Ag(2)—O(8$^{\text{iii}}$) | 2.854 (3) × 2 |
| V(3)—O(8) | 1.611 (2) | Ag(1)—Ag(2) | 0.415 (2) |
| V(3)—O(5) | 1.791 (2) | Ag(1)—Ag(1$^{\text{iii}}$) | 1.925 (3) |
| V(3)—O(7) | 2.004 (2) | Ag(2)—Ag(2$^{\text{iii}}$) | 2.750 (4) |

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (iii) $1 - x, y, 1 - z$.

$\beta$-$Ag_{0.4}V_2O_5$ powder was prepared in two steps. First, $AgVO_3$ was obtained by heating at 873 K a mixture of $V_2O_5$ and $Ag_2CO_3$ in the ratio 1:1. Second, $\beta$-$Ag_{0.4}V_2O_5$ was obtained from $AgVO_3$, $V_2O_3$ and $V_2O_5$ mixed in the ratio 4:7:1 and heated at 873 K in a sealed quartz tube. Crystallogenesis was conducted by melting the bronze powder at 973 K, followed by slow cooling (283 K h$^{-1}$) to 873 K and finally quenching in air.

Lorentz and polarization corrections were applied to intensity data. Patterson methods were used to solve the structure. Calculations were performed using *SHELX* software (Sheldrick, 1976, 1985) on an Alliant VFX/80. Distances were calculated using *ORFFE* (Busing, Martin & Levy, 1964); molecular graphics were obtained using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71519 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1054]

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# Structure du Sulfure d'Ytterbium, $Yb_2S_3$

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## Abstract

The Yb atoms occupy independent, slightly distorted octahedral sites. All the metal sites are fully occupied. The structure consists of pairs of $[YbS_6]$ octahedra forming chains parallel to the $\langle 111 \rangle$ axis. In this direction, between two pairs of octahedra, there is an empty octahedral site. The compound may also be described as a layered structure; each layer is alternately composed of Yb and S atoms.

## Commentaire

Le présent travail fait partie d'une étude systématique des sulfures de terres rares effectuée au laboratoire. Rappelons que l'ytterbium présente la particularité de pouvoir prendre deux états de valence ($2^+$ et $3^+$).

L'étude du binaire Yb–S révèle en particulier, l'existence du sulfure d'ytterbium trivalent $Yb_2S_3$, rhomboédrique dont la structure de type $Al_2O_3$ est à rapprocher de celle de $Lu_2S_3$ (Range & Leeb, 1975). La structure cristalline de ce composé a été entreprise à partir de clichés de poudre (Flahaut, Domange & Pardo, 1964; Sleight & Prewitt, 1968). Il nous a semblé donc indispensable de reprendre cette étude sur monocristal.

Le sulfure d'ytterbium utilisé, de couleur jaune, est préparé par action de sulfure d'hydrogène sur l'oxyde $Yb_2O_3$ dans une nacelle en graphite, chauffée dans un four à induction à 1373 K. Les monocristaux sont obtenus par chauffage à 1273 K pendant huit jours du mélange 10KBr + $Yb_2S_3$ en ampoule de silice scellée sous vide. Le refroidissement est lent. KBr est éliminé par lavage à l'eau froide.

La Fig. 1 présente la structure en volume ainsi que l'enchaînement des octaèdres. Les coordonnées atomiques relatives et les facteurs d'agitation thermique isotrope équivalents sont donnés dans le Tableau 1, les principales distances interatomiques et les angles entre les liaisons Yb—S dans le Tableau 2.

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