

## The Crystal Structure of a New Silver Vanadium Oxide Bronze, $\text{Ag}_{1-x}\text{V}_2\text{O}_5$ ( $x$ approximately 0.32)

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A new silver vanadium oxide bronze,  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$  has been synthesized with supercritical water at temperatures between 300–700°C and pressures of 2000 atm. It is monoclinic with the following unit cell dimensions:

$$a = 11.742 \text{ \AA}; \quad b = 3.667 \text{ \AA}; \quad c = 8.738 \text{ \AA}; \quad \beta = 90.48^\circ$$

The space group is  $C2/m$ . The crystal structure was determined by Fourier methods and was refined by least squares techniques with the occupancy  $1-x$  for Ag included as a variable.

The structure consists of layers of the composition  $\text{V}_2\text{O}_5$  which are built up of strongly distorted  $\text{VO}_6$ -octahedra having edges and corners in common. The layers are held together by the Ag ions which have an approximately fivefold coordination.

The ordinary methods of preparing lower transition metal oxides usually involve dry conditions. The crystal structure of a new silver vanadium oxide bronze which was synthesized under hydrothermal conditions will be reported here.<sup>1</sup> The same compound was also independently prepared in dry experiments by Hardy, Galy, Casalot and Pouchard.<sup>2</sup>

### EXPERIMENTAL

50–100 mg of  $\text{V}_2\text{O}_5$  was mixed with 5–30 mg water and heated in sealed silver capsules at temperatures between 300 and 700°C and pressures of 2000 atm. Blue-black crystals up to one mm in size, sometimes rod-formed, sometimes plate-like, were formed after usually three days heating. A single phase was always found to be present after opening the capsules. An X-ray spectrographic investigation revealed the presence of considerable amounts of silver besides vanadium in the crystals. The unit-cell dimensions were found to be

$$a = 11.742 \text{ \AA}; \quad b = 3.667 \text{ \AA}; \quad c = 8.738 \text{ \AA}; \quad \beta = 90.48^\circ$$

The indexed Guinier powder pattern is given in Table 1. The  $h0l$ ,  $h1l$  and  $h2l$  reflections were recorded with  $\text{CuK}\alpha$  radiation on an integrating Nonius Weissenberg goniometer using the multiple film technique, and estimations of intensity were made visually by

means of a standard scale. The  $V^{5+}$  scattering curve used was derived from tables given by Freeman.<sup>3</sup> For  $O^{2-}$  the scattering curve given by Suzuki<sup>4</sup> and for  $Ag^+$  the curve given by Worsley<sup>5</sup> were used.

Table 1. Guinier powder pattern of  $Ag_{1-x}V_xO_5$ . Dimensions of the monoclinic unit cell  $a = 11.742 \text{ \AA}$ ;  $b = 3.667 \text{ \AA}$ ;  $c = 8.738 \text{ \AA}$ ;  $\beta = 90.48^\circ$ .

	$\sin^2 \theta_{\text{obs}}$	$hkl$	$\sin^2 \theta_{\text{calc}}$
w	0.02518	201	0.02518
w	0.04790	20 $\bar{2}$	0.04790
vwv	0.04860	202	0.04868
vst	0.05629	111	0.05629
w	0.06997	003	0.06997
st	0.07620	40 $\bar{1}$	0.07623
m	0.07925	112	0.07930
vw	0.07969	11 $\bar{2}$	0.07969
w	0.08280	310	0.08284
vst	0.09094	311	0.09091
m	0.10078	402	0.10071
vwv	0.11463	312	0.11450
m	0.15163	510	0.15169
st	0.15483	600	0.15491
w	0.15998	511	0.15995
st	0.17646	020	0.17646

#### STRUCTURE DETERMINATION

Assuming the composition of the compound to be  $AgV_2O_5$ , approximate coordinates for silver, vanadium and oxygen atoms could be obtained from the Patterson projection on to (010). The systematic absences,  $hkl$  with  $h + k \neq 2n$  gave the space group alternatives  $C2$ ,  $Cm$ , or  $C2/m$ . The  $h0l$  and  $h2l$ , with due regard for observational errors and for the effects of thermal motion, were found to be identical. All the atoms were therefore assumed to be situated in two planes normal to the  $y$ -axis and  $b/2$  apart, making  $C2/m$  a probable space group.

The first electron density projection on to (010) showed all the atoms in the expected positions. However, the height of the silver peak indicated fractional occupancy of its site. After a difference synthesis the fraction  $x$  in  $Ag_{1-x}V_2O_5$  was approximately determined to be 0.5.

The  $h0l$  and  $h1l$  data were next processed by a full matrix least squares refinement using the Busing-Levy program written for the IBM 7090 computer. The  $x$  and  $z$  coordinates for each atom, the scale factors, the individual isotropic temperature factors and the occupancy of the Ag site were all varied in the refinement cycles. Rollet's weighting procedure was used<sup>6</sup> for the intensity data, the weight  $w$  of an individual observation being

$$w = \frac{|F_0|}{|F^*|} \text{ if } |F_0| < |F^*|$$

$$w = \frac{|F_0|}{|F^*|} \text{ if } |F_0| > |F^*|$$

where  $|F^*|$  is the average of the observed structure factors.

Assuming the crystal to have the space group  $C2/m$ , six cycles gave a reliability figure of 10.1 %. The input occupancy of Ag was 0.5 for the least-squares treatment and it refined rapidly to  $0.68 \pm 0.03$ . The results are summarized in Table 2.

Table 2. Atomic coordinates and temperature factors with standard deviations for  $Ag_{1-x}V_xO_5$ .

Space group $C2/m$ $(0,0,0; \frac{1}{2}, \frac{1}{2}, 0) +$					
Atom	Point position	$x$	$y$	$z$	$B$
$V_1$	$4(i)$	$0.2309 \pm 0.0009$	0	$0.3391 \pm 0.0011$	$1.5 \pm 0.3$
$V_2$	»	$0.9334 \pm 0.0008$	0	$0.3362 \pm 0.0011$	$1.0 \pm 0.3$
Ag	»	$0.6167 \pm 0.0007$	0	$0.0247 \pm 0.0009$	$2.8 \pm 0.3$
$O_1$	»	$0.079 \pm 0.003$	0	$0.395 \pm 0.004$	$0.7 \pm 0.7$
$O_2$	»	$0.759 \pm 0.003$	0	$0.383 \pm 0.004$	$1.6 \pm 0.9$
$O_3$	»	$0.397 \pm 0.003$	0	$0.356 \pm 0.004$	$0.3 \pm 0.7$
$O_4$	»	$0.942 \pm 0.003$	0	$0.161 \pm 0.004$	$2.8 \pm 1.2$
$O_5$	»	$0.209 \pm 0.004$	0	$0.171 \pm 0.005$	$3.4 \pm 1.2$

#### DESCRIPTION OF THE STRUCTURE

There are two independent vanadium atoms,  $V_1$  and  $V_2$ , each one having five nearest oxygen neighbours at the corners of a somewhat distorted trigonal bipyramid. The  $V_1$ —O distances within the trigonal bipyramid vary between 1.49—1.95 Å, and the corresponding distances for the  $V_2$  atom vary between 1.54—2.10 Å. For both  $V_1$  and  $V_2$  there is one further oxygen at the distances 2.43 and 2.35 Å, respectively completing two very distorted octahedra. This is a rather common feature for vanadium and has been observed in several compounds.<sup>7-12</sup> The silver atom has an approximately fivefold coordination, with the Ag—O distances varying between 2.48 and 2.68 Å.

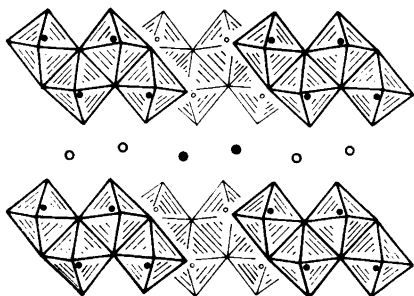


Fig. 1. The crystal structure of  $Ag_{1-x}V_xO_5$ . Large circles are silver atoms, small circles are vanadium atoms.

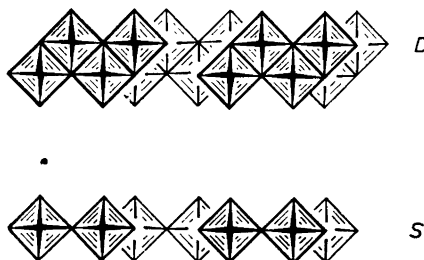


Fig. 2. Double zig-zag ribbons of octahedra having edges in common. These are called D units (upper), and consist of two single, or S sheets (lower) joined together by common edges.

Table 3. Interatomic distances in  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$ 

		Mean value	
		Trigonal bipyramid	Octahedron
$\text{V}_1 - \text{O}_1$	$1.85 \pm .04$	1.82	1.92
$2 \text{V}_1 - \text{O}_3$	$1.90 \pm .02$		
$\text{V}_1 - \text{O}_3$	$1.95 \pm .04$		
$\text{V}_1 - \text{O}_5$	$1.49 \pm .05$		
$\text{V}_1 - \text{O}_2$	$2.43 \pm .04$		
$\text{V}_2 - \text{O}_1$	$1.78 \pm .04$	1.84	1.92
$\text{V}_2 - \text{O}_2$	$2.09 \pm .04$		
$2 \text{V}_2 - \text{O}_3$	$1.89 \pm .02$		
$\text{V}_2 - \text{O}_4$	$1.54 \pm .04$		
$\text{V}_2 - \text{O}_1$	$2.35 \pm .04$		
$2 \text{Ag} - \text{O}_4$	$2.54 \pm .04$		
$2 \text{Ag} - \text{O}_5$	$2.48 \pm .05$		
$1 \text{Ag} - \text{O}_5$	$2.68 \pm .05$		

The structure consists of layers which are built up of very distorted  $\text{VO}_6$ -octahedra sharing edges and corners. The layers have the composition  $\text{V}_2\text{O}_5$  and are held together by means of  $\text{Ag}^+$  ions (Fig. 1). Each layer consists of double zig-zag ribbons of octahedra having edges in common. Such a layer was described for the structure of the sodium titanium oxide bronze and was then called a D unit.<sup>13</sup> Each such unit can be divided up to S sheets as is

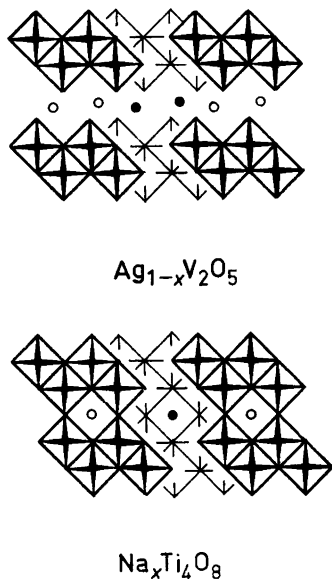


Fig. 3. The structure of  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$  as compared with  $\text{Na}_x\text{Ti}_4\text{O}_8$ .

demonstrated in Fig 2. In  $\text{Na}_x\text{Ti}_4\text{O}_8$  the D units have corners in common and the structure could thus be represented by the sequence



A logical representation of  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$  using this symbolism would therefore be:

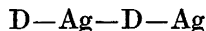


Fig 3 shows how the layers of a  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$  structure type can be united to form a structure of the  $\text{Na}_x\text{Ti}_4\text{O}_8$  type. In this way a sequence series is formed, analogous to what earlier has been observed for the sodium titanates<sup>14,15</sup> and the potassium titanoniobates.<sup>16</sup> This sequence series has only three possible members of which two are thus known.

The crystal structure of  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$  has some similarities with the structures of the two earlier known vanadium oxide bronzes,  $\text{Li}_{1-2}\text{V}_3\text{O}_8$  and  $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$ , as worked out by Wadsley.<sup>8,9</sup> In all the three compounds the  $\text{VO}_6$ -octahedra are very distorted and approach five coordination. Both  $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$  and  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$  are also layer structures. The crystal chemistry and the physical properties of bronzes in general were recently discussed in a review by Wadsley.<sup>17</sup>

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