

β AgVO₃ Crystal Structure and Relationships with Ag₂V₄O₁₁ and δ Ag_xV₂O₅

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Received July 27, 1995; in revised form November 27, 1995; accepted December 14, 1995

The structure of β AgVO₃ has been determined on single crystal by X ray diffraction techniques. β AgVO₃ crystallizes in the monoclinic system, space group *Cm*, with $a = 18.106(3)$ Å, $b = 3.5787(7)$ Å, $c = 8.043(3)$ Å, and $\beta = 104.44(4)^\circ$. The acentric character of the structure is discussed on the basis of the atomic positions. The β AgVO₃ structure reveals a rather strong three dimensional network made of the vanadium atoms and three silver atoms with their associated oxygen surroundings, [Ag₃V₄O₁₂]_n⁻. The fourth silver cation, which assumes the electrostatic balance, appears to be inserted in a monocapped trigonal prism allowing its mobility at highest temperatures. Structural relationships between this compound and other silver vanadium oxide bronzes such as Ag₂V₄O₁₁ and δ Ag_xV₂O₅ involves crystallographic shear mechanisms. The existence of a new silver vanadium oxide bronze is discussed. © 1996 Academic Press, Inc.

INTRODUCTION

Investigations on the Ag₂O–V₂O₅–VO₂ system have been reported since the sixties by Andersson in 1965 (1), Casalot and Pouchard in 1967 (2), Raveau in 1967 (3), and later in 1974 by Drozdov *et al.* (4). Nonstoichiometric compounds like vanadates as well as vanadium oxide bronzes (VOB), Ag_{1+x}V₃O₈, β and δ Ag_xV₂O₅ (2), Ag₂V₄O_{11-ε} (3), and Ag_{4-x}V₄O₁₂ ($x = 1.05$) (4) were synthesized and characterized by chemical analysis and powder XRD. The difficulties of crystal growing are revealed by the small amount of available structural information. If the first structure of these compounds was determined by Andersson (1), up to now studies have been performed to specify or to determine the structure of this compounds. Recently, the β Ag_xV₂O₅ structure was precisely refined in order to understand the range of the nonstoichiometry domain (5) and Zandbergen *et al.* used an HREM study to determine the structures of Ag_{2-x}V₄O₁₁ (6), one phase of which is isostructural with Cu_xV₄O₁₁ (7). The study of the derived compound hydrated silver vanadate,

AgVO₃·H₂O (8), reveals that it is isostructural to the corresponding potassium compound, KVO₃·H₂O (9).

The system Ag–V–O exhibits nonstoichiometric features both by silver intercalation and/or extended defects of oxygen. Moreover, in the Ag_{4-x}V₄O₁₂ compound the problem of the silver oxidation state arises.

The existence of new potential applications of lithium doped Ag–V–O compounds in the field of positive electrode materials (10, 11) and our knowledge of the vanadium metal oxide systems (12, 13) have prompted us to start a complete reinvestigation of the system. This study reports the structure of the silver vanadate AgVO₃ and its structural relationships with other silver vanadium oxide compounds. This should provide information about the system evolution versus concentrations of silver and/or oxygen ions.

EXPERIMENTAL SECTION

Synthesis

A β AgVO₃ powder was prepared by heating stoichiometric mixtures of V₂O₅ (99.99% Aldrich) and Ag₂O (99% Aldrich) in a gold crucible at 420°C for 12 hr in an oxygen stream. Reheating in the same conditions was necessary to obtain well crystallized red powder. The compound was then fully characterized by powder XRD and elemental analysis (exp. (calc.); Ag:52.15(52.22); V24.61(24.63)).

Crystal Growth

Fleury and Kohlmuller (14) have shown that AgVO₃ exists under three prototype structures according to the temperature of synthesis. Although the β variety transforms into the γ variety at 420°C, it can exist as a metastable phase up to 480°C, its melting temperature. The β AgVO₃ powder has been heated under O₂ in a gold crucible at 500°C for 10 hr, then slowly cooled to 450°C (cooling speed 2°C/hr) and finally quenched to room temperature. Microscopy examination of the obtained red acicular crystals shows that they easily divide into fibers, which infers bad crystallinity and consequently difficulties in structure de-

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TABLE 1
Physical Properties and Parameters Pertinent to Data
Collection and Refinement

Formula	AgVO ₃
Mol. wt. (g)	206.81
Cryst. system—Space group	monoclinic— <i>Cm</i>
<i>a</i> (Å)	18.106(3)
<i>b</i> (Å)	3.5787(7)
<i>c</i> (Å)	8.043(3)
β (°)	104.44(4)
<i>V</i> (Å ³)	504.69(1)
<i>Z</i>	8
<i>d</i> _{calc} (g/cm ³)	5.45(1)
<i>F</i> (000)	752
Crystal shape	Red Needle
faces	{1 0 0} {0 1 0} {1 0 1}
distances (cm)	0.001 0.008 0.002
<i>Parameters of data collection and refinement</i>	
λ (Å)	0.71073
Scan type	$\omega/2\theta$, step scan
Scan width (°)	1.83 + 1.33 tan θ
<i>hkl</i> range	<i>h</i> : -11 → 0; <i>k</i> , -5 → 0; <i>l</i> -25 → 25
θ range (°)	3–30
Number of meas. refl.	1625
Absorption correction	
μ (MoK α) (cm ⁻¹)	104.63
Gaussian grid	4 40 14
transmission factor	0.61 0.84
Number of unique refl.	632
$R_{\text{ave}} = \sum (I - I_{\text{ave}}) / (\sum I)$	0.030
Number of variables (<i>NV</i>)	94
Number of refl. with $I > 3\sigma$ (<i>NO</i>)	588
Weighting scheme	$w = \{\sigma^2(I) + 0.0006 * I^2\}^{-1/2}$
Highest peak in last difference Fourier (<i>e</i> /Å ³)	2.9 -2.6
$R = (\sum F_{\text{obs}} - F_{\text{calc}}) / (\sum F_{\text{obs}})$	0.051
$wR^2 = [\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2 / \sum w(F_{\text{obs}}^2)]^{1/2}$	0.0572
$s = [\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2 / (NO - NV)]^{1/2}$	1.02

termination. Knowing that, we performed several measurements on various crystals of different sizes. We present further the best result obtained.

All physical and technical data about the compound and the measurement as well as structural refinement parameters are summarized in Table 1.

CRYSTALLOGRAPHIC STUDY—STRUCTURE DETERMINATION

A preliminary crystallographic study by Laue and Weissenberg techniques revealed that the β AgVO₃ phase crystallizes in the monoclinic system with possible space groups *C2/m*, *Cm*, or *C2*. Using a CAD4 Enraf Nonius automatic diffractometer with MoK α radiation, the cell parameters were determined and refined after the centering of 25 *hkl* reflections in the 5°–24° θ range. The intensity of the *hkl*

reflections was then measured and corrected for Lorentz and polarization factors. Numerical absorption corrections have been performed (Table 1). The atomic scattering factors with their anomalous dispersion coefficients taken for every Ag, V, and O atoms are those given by Cromer and Waber (15). The calculations using SHELX-86 (16) and drawings with ORTEP (17) were performed on the super minicomputer ALLIANT VFX 80 at the laboratory.

Assuming the centrosymmetric space group *C2/m*, the heavy atoms (Ag, V) have been located by direct methods and the oxygen atoms by difference Fourier synthesis. Every atom being refined with isotropic thermal parameters, the solution gave a high value to the reliability factor, $R = 0.14$. In order to decrease this factor, the noncentrosymmetric space groups *Cm* and *C2* have been tried. The best solution is obtained by using the *Cm* space group, driving the R value down to 0.07. The Hamilton test confirms the validity of this solution at the 0.0005 level. Each atom is found to be located in the mirror plane {0 1 0}. The origin of other coordinates (*x* and *z*) are fixed, assuming Ag1 to be locked in the position $x = 0$ and $z = \frac{1}{2}$. Final Fourier difference synthesis confirms that not an atom is displaced out of the mirror plane. The size and the morphology of the crystal make it quite impossible to index its faces so that the shape of the crystal was modeled according to the visual observation and the orientation of the crystal on the diffractometer. Although the absorption correction was tested on specially measured equivalent reflections, absorption corrections make the R factor to decrease of only 0.015. As a consequence, during the transformation of the thermal displacement parameters from isotropic to anisotropic, the $U(2, 2)$ parameters of the atoms V3, O1, O3, O6, O8, and O9 become negative, so the thermal displacement of these atoms were kept isotropic. The final R factor is 0.05. This result and the problems encountered with the displacement parameters confirm that this best crystal is of relatively poor quality. The large values of the silver thermal displacement parameters and the strongest electron density residues observed around each silver atoms imply that the thermal motions of these atoms are not well modeled; perhaps anharmonic motion treatment could be performed as Kato *et al.* do for Cu_xV₂O₅ (18).

Final atomic coordinates and corresponding isotropic thermal parameters are given in Table 2. A selection of interatomic distances is gathered in Table 3.

STRUCTURE DESCRIPTION

A projection of the structure onto the (010) plane is presented in Fig. 1. It must be noted that only the Ag4 atoms impose the loss of the symmetry center. All other atoms can be related by a symmetry center (average deviation 0.4 Å). Using the centrosymmetric space group *C2/m*, the Ag4 site (*4m*) is found to be half occupied.

TABLE 2
Final Least-Squares Atomic Parameters with Estimated
Standard Deviations for β AgVO₃

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$
Ag1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.34(8)
Ag2	0.5526(3)	0	0.8663(6)	1.4(1)
Ag3	0.4496(3)	0	0.1406(6)	1.5(1)
Ag4	0.2550(3)	0	0.9616(6)	1.8(1)
V1	0.1316(4)	0	0.2308(9)	0.7(1)
V2	0.3214(4)	0	0.4436(9)	1.1(1)
*V3	0.1805(4)	$\frac{1}{2}$	0.5640(8)	0.1(1)
V4	0.3725(4)	$\frac{1}{2}$	0.7754(8)	0.5(2)
*O1	0.037(1)	0	0.232(2)	0.5(3)
O2	0.125(1)	0	0.014(3)	0.9(3)
*O3	0.265(1)	0	0.243(2)	0.6(3)
O4	0.404(2)	0	0.403(3)	1.9(4)
O5	0.349(2)	0	0.719(3)	1.2(4)
*O6	0.194(1)	0	0.500(3)	0.6(3)
O7	0.090(1)	$\frac{1}{2}$	0.589(2)	0.9(3)
*O8	0.152(1)	$\frac{1}{2}$	0.295(3)	0.4(3)
*O9	0.314(1)	$\frac{1}{2}$	0.514(3)	1.1(3)
O10	0.465(1)	$\frac{1}{2}$	0.764(3)	1.8(5)
O11	0.377(2)	$\frac{1}{2}$	0.980(3)	1.6(2)
O12	0.240(1)	$\frac{1}{2}$	0.762(3)	1.3(4)

Note. $B_{eq} = 8\pi^2/3 \sum_i \sum_j U(i, j) a_i^* a_j^* a_i a_j$, a^* reciprocal parameter;

* = atoms refined isotropically.

TABLE 3
Selected Interatomic Distances (\AA) for β AgVO₃

Atoms	Distance (\AA)	Atoms	Distance (\AA)
Ag1-O10	2.37(3)	Ag1-O7'(a,b)	2.41(1)
Ag1-O1'	2.41(2)	Ag1-O4(a,b)	2.48(2)
Ag2-O10	2.40(2)	Ag2-O2''(a,b)	2.36(1)
Ag2-O7'	2.49(2)		
Ag3''-O1'''(a,b)	2.38(1)	Ag3''(a,b)-O11	2.40(1)
Ag3''-O4''	2.45(3)		
Ag4-O3''	2.22(2)	Ag4-O12(a,b)	2.37(2)
Ag4-O2''	2.50(2)	Ag4-O11(a,b)	2.81(2)
Ag4-O5	2.89(3)		
V1-O2	1.71(2)	V1-O3	2.39(2)
V1-O1	1.71(2)	V1-O6	2.18(2)
V1-O8(a,b)	1.874(6)		
V2-O3	1.68(2)	V2-O4	1.61(3)
V2-O5	2.15(2)	V2-O6	2.45(2)
V2-O9(a,b)	1.891(8)		
V3-O7	1.70(3)	V3-O8	2.10(2)
V3-O9	2.55(3)	V3-O12	1.68(2)
V3-O6(a,b)	1.896(8)		
V4-O9	2.11(2)	V4-O10	1.69(3)
V4-O11	1.63(2)	V4-O12	2.38(3)
V4-O5(a,b)	1.868(7)		

Note. Symmetry operators: ' : $\frac{1}{2} + x, \frac{1}{2} + y, z$; '' : $x, y, 1 + z$; ''' : $\frac{1}{2} + x, \frac{1}{2} + y, 1 + z$. a and b show atoms related by translation $y = 1$.

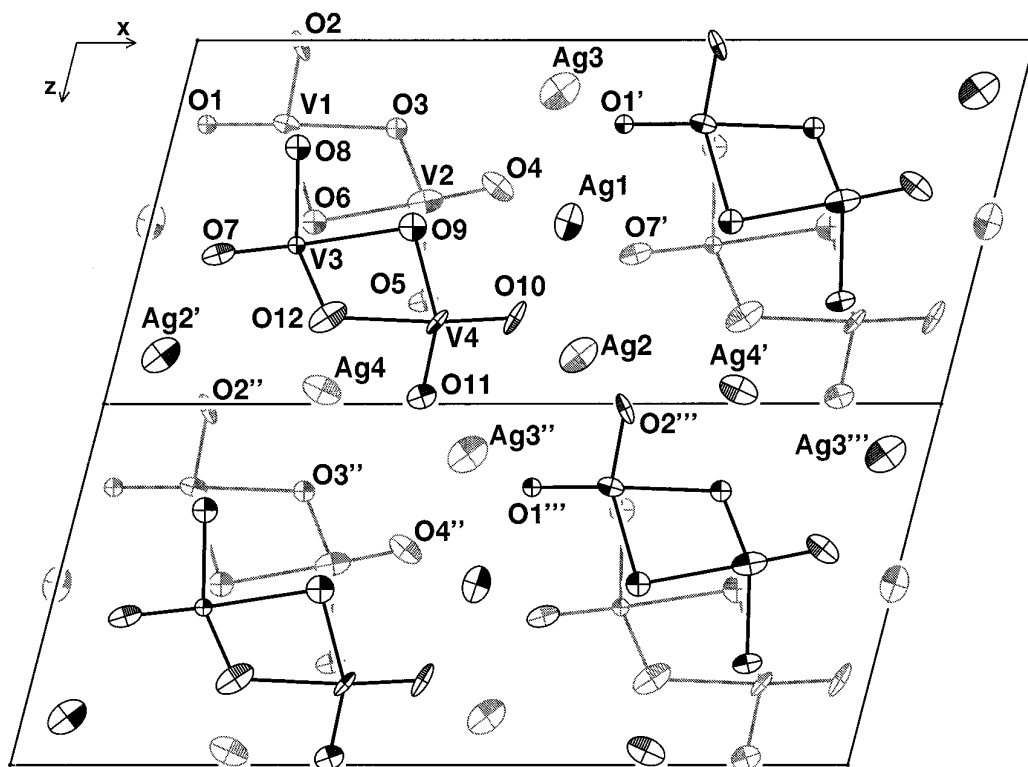


FIG. 1. Projection onto the (0 1 0) plane of two cells showing the labeling of atoms. Grey drawing corresponds to level $y = 0$ and the black one to level $y = 0.5$. The displacement thermal parameters are drawn at the 50% probability level. Symmetry operators are indicated in Table 3.

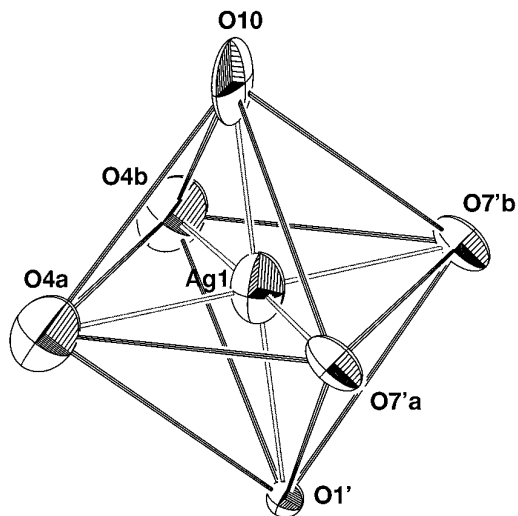


FIG. 2. View of the Ag1 coordination polyhedra. Displacement thermal parameters are drawn at the 66% probability level.

Assuming that silver atoms occupy every second equivalent ($4m$) site infers that Ag4 atoms being in the 2a sites of the Cm space group.

The β AgVO_3 structure consists of infinite chains of formula $[\text{V}_4\text{O}_{12}]_n$ which develop along the $[010]$ direction, the silver ions ensuring the cohesion of the chains. These chains of zigzag shape are double and constituted of edge-shared VO_6 octahedra.

As shown in Table 3, the VO_6 octahedra are distorted; the six V–O bonds of each vanadium are distributed in four domains, two short distances (1.67(4) Å), two middle ones (1.88(1) Å), a longer one (2.13(3) Å), and a longest one (2.44(8) Å). Such a distribution of the distances is generally observed in vanadium oxide compounds (19).

The four silver atoms, which lie in the mirror plane, are distributed among three types of surroundings, as the Ag–O distances reported in Table 3 show. The Ag1 atom is sixfold coordinated, the oxygen atoms being at the apices of a regular octahedron (Fig. 2). The six Ag1–O distances are of the same order of magnitude (2.43(4) Å), leading to a weak distortion. Ag2 and Ag3 atoms are fivefold coordinated with surrounding square pyramidal oxygen (Fig. 3). The similarities of Ag2–O and Ag3–O distances can be explained if we remember that, assuming the $C2/m$ space group, they are related to each other by the symmetry center. Ag4, which is responsible for the lack of a symmetry center, is sevenfold coordinated in a $(\text{O}12, \text{O}11)_2, \text{O}2'', \text{O}3''$ and O5 monocapped trigonal prism (Fig. 4). The Ag4–O distances, which are the longest Ag–O distances, reveal that the Ag4 site is the largest one. The displacement thermal parameter of Ag4 atom which is greater than the one of the other silver atoms can explain such extend. The

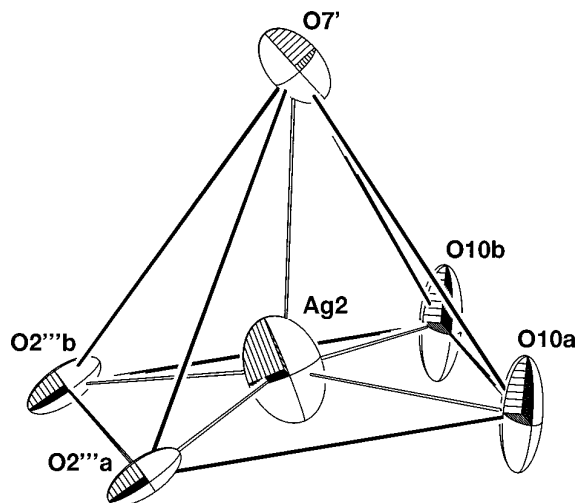


FIG. 3. View of the Ag2 coordination polyhedra. Displacement thermal parameters are drawn at the 66% probability level.

Ag4O₇ monocapped trigonal prisms share faces along the $[010]$ direction developing a kind of tunnel. This and the large thermal displacement parameter favor a possible mobility of the Ag4 cations.

Finally, β AgVO_3 consists in a rather strong three dimensional network: $[\text{V}_4\text{O}_{12}]$ double chains held together in the $[100]$ direction by Ag1O₆ octahedra making a kind of a thick layer $[\text{AgV}_4\text{O}_{12}]_n$ parallel to the (001) plane, themselves firmly interconnected by Ag2 and Ag3 in their oxygenated square pyramids. This three dimensional structure has the following formula: $[\text{Ag}_3\text{V}_4\text{O}_{12}]_n^{n-}$. The electrostatic balance of the full network is assumed by silver ions inserted in the prismatic tunnels giving the formula $\text{Ag}[\text{Ag}_3\text{V}_4\text{O}_{12}]$, i.e., β AgVO_3 .

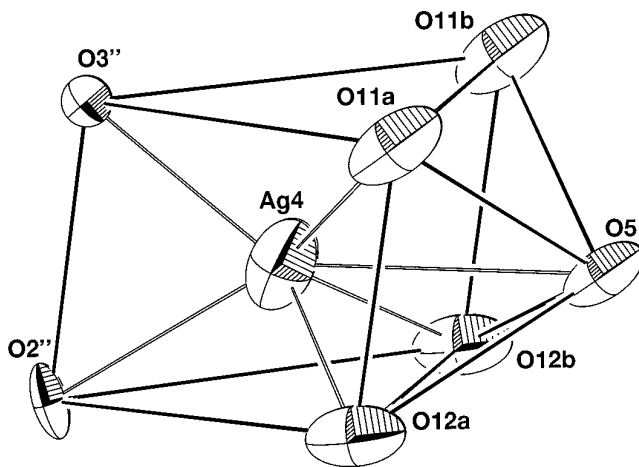
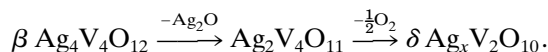


FIG. 4. View of the Ag4 coordination polyhedra. Displacement thermal parameters are drawn at the 66% probability level.

type layers can be viewed as V_4O_{12} strings linked together by edge sharing. Comparing these structures with the presented one, we can note that they are built with the same quadruple $[V_4O_{12}]_n$ chains, isolated in β $AgVO_3$ ($Ag_4V_4O_{12}$), corner shared in $Ag_2V_4O_{11}$ and edge shared in δ $Ag_xV_2O_5$ ($Ag_2V_4O_{10}$). The “chemical equation” relating these structures could be written:



We have then tried to find a mechanism which could enlighten such relations.

The transition β $AgVO_3 \rightarrow Ag_2V_4O_{11}$ can be explained by crystallographic shear CS following the “departure” of Ag_2O (Fig. 5a). In β $AgVO_3$, when suppressing these Ag_2O units, oxygen vacancies appear and, with the loss of silver cations, it infers a possibility to connect $[V_4O_{12}]_n$ chains. That can be achieved if we consider $CS \frac{1}{12}[1\ 0\ 6](-2\ 0\ 1)$, i.e., crystallographic shear applied in the plane $(-2\ 0\ 1)$ with periodicity $\frac{1}{12}$ in the $[1\ 0\ 6]$ direction. The structure obtained after reorganization of the silver cations is the known $Ag_2V_4O_{11}$ structure. Another loss of oxygen, corresponding to the equation $Ag_2V_4O_{11} \rightarrow Ag_2V_4O_{10}$, implies oxygen vacancies which could drive to the $CS \frac{1}{6}[0\ 9\ 2](1\ 0\ 0)$, as described in the Fig. 5, option a. Unfortunately, this mechanism leads to a structure which is different from δ $Ag_xV_2O_5$ and up to now unknown. In order to obtain the δ $Ag_xV_2O_5$ structure, another shearing mechanism has been found. It occurs in two steps as represented in Fig. 5, option b. First, due to oxygen vacancies and loss of silver cations, the $CS \frac{1}{3}[1\ 0\ 0](0\ 0\ 1)$ leads to an unknown structure of formula $Ag_2V_4O_{11}$. A new loss of oxygen in this last structure could then induce a second $CS \frac{1}{18}[1\ 0\ -3](1\ 0\ 0)$. Such mechanism drives to the known δ $Ag_xV_2O_5$ structure.

It is interesting to note that the main difference between the two $Ag_2V_4O_{11}$ structures is only due to the oxygen connecting the V_4O_{12} blocs. A rearrangement by crystallographic shears, inferred by stability conditions, could ex-

plain that the second $Ag_2V_4O_{11}$ structure has never been observed. This fact is supported by the appearance of the known $Ag_2V_4O_{11}$ structure when oxidation of δ $Ag_xV_2O_5$ is made at $500^\circ C$. In order to verify the growth of the hypothetical $Ag_2V_4O_{11}$ structure, HVTEM (High Voltage Transmission Electron Microscopy) observations, using a special micro chamber allowing *in situ* experiments under a flow of oxygen, of the different steps of the δ $Ag_xV_2O_5$ oxidation are in progress. These experiences could make it possible to characterize this unstable $Ag_2V_4O_{11}$ variety and the rearrangement occurring at high temperature, or during the cooling, to form the known one.

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