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Silver niobium trioxide, $AgNbO_3$

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The present structure determination of silver niobium trioxide at 291 K was performed on a twinned single crystal with a predominant presence [about 93 (1)%] of one twin domain. The sample contained traces of V (about 1 atomic %). This study confirms that the room-temperature phase of $AgNbO_3$ is isostructural with the room-temperature phase of $NaNbO_3$, *i.e.* it is a tilted perovskite. Structural deviation in $AgNbO_3$ from centrosymmetry was not detected in this study and its structure was refined in *Pbcm*, though a previous study indicated ferroelectricity below 350 K, in contrast with $NaNbO_3$.

Comment

The room-temperature phase of $AgNbO_3$ belongs to the perovskite family and is closely related to the room-temperature phase of $NaNbO_3$. Both compounds undergo a number of phase transitions when cooled down from the prototypic cubic phase. The concomitant distortions of the prototypic structure result in the formation of superstructures and symmetry changes which give rise to twins. Some of the phases and the pertinent phase transitions in $AgNbO_3$ and $NaNbO_3$ correspond to each other (Kania *et al.*, 1984; Łukaszewski *et al.*, 1983; Pawełczyk, 1987; Glazer & Megaw, 1973; Verwerft *et al.*, 1989).

The room-temperature phase of $NaNbO_3$ is antiferroelectric (Cross & Nicholson, 1955) and its structure has been determined by a single-crystal experiment on a moderately twinned crystal using film techniques [Sakowski-Cowley *et al.* (1969); this reference was listed in the Inorganic Structure Database (Bergerhoff *et al.*, 1983)]. The other structure determination of the room-temperature phase of $NaNbO_3$, from neutron powder data, was carried out by Hewat (1974); *cf.* the (+)-variant given in Table II of that article. These two structural models are slightly different, though their tilting scheme is the same.

In both the above descriptions, the structure is orthorhombic (*Pbcm*), with the lattice parameters $a_o \sim b_o \sim 2^{1/2}a_p$ and $c_o \sim 4a_p$ (hereafter the subscript '*p*' denotes the primitive pseudocubic unit cell, while the subscript '*o*' denotes the orthorhombic unit cell.) The room-temperature phase of $AgNbO_3$ has the same type of lattice distortion as the room-temperature phase of $NaNbO_3$ (Verwerft *et al.*, 1988).

$AgNbO_3$ is reported to be ferroelectric below 350 K, in contrast with $NaNbO_3$. The transition was detected by X-ray diffraction and dielectric measurements on both single-crystal and polycrystal samples of $AgNbO_3$, by Łukaszewski *et al.* (1983). However, Pawełczyk (1987) did not observe a change in distortion of the pseudoperovskite unit cell at about 350 K. Similarly, Verwerft *et al.* (1989), using electron diffraction and imaging techniques, did not observe a transition at about 350 K. Kania (1998) reported that X-ray diffraction experiments (the Bond method) detected no change of the lattice parameters at about 350 K, although a broadening of the lines took place. Nor did Raman spectroscopy give clear indications of the ferroelectric phase transition in $AgNbO_3$ (Kania, 1998). Nevertheless, in ceramic samples of $AgNbO_3$, a spontaneous polarization below 350 K was measured by Kania *et al.* (1984). Its value ($P_s \sim 0.04\ \mu\mathrm{C\ cm^{-2}}$ at 293 K) is about three orders of magnitude lower than in $KNbO_3$, $BaTiO_3$ or $PbTiO_3$ (Jona & Shirane, 1962), for example.

Verwerft *et al.* (1988) suggested two space groups for $AgNbO_3$, *Pbcm* or $Pbc2_1$, as well as a tilt scheme of NbO_6 octahedra, which was determined from high resolution electron microscopy experiments. The tilt scheme transformed into the basis applied in this article is $(a_p^- a_p^- c_p^+)_1^2$ $(a_p^- a_p^- c_p^-)_2^3$ $(a_p^- a_p^- c_p^+)_3^4$ [for the adopted notation see Glazer (1972)].

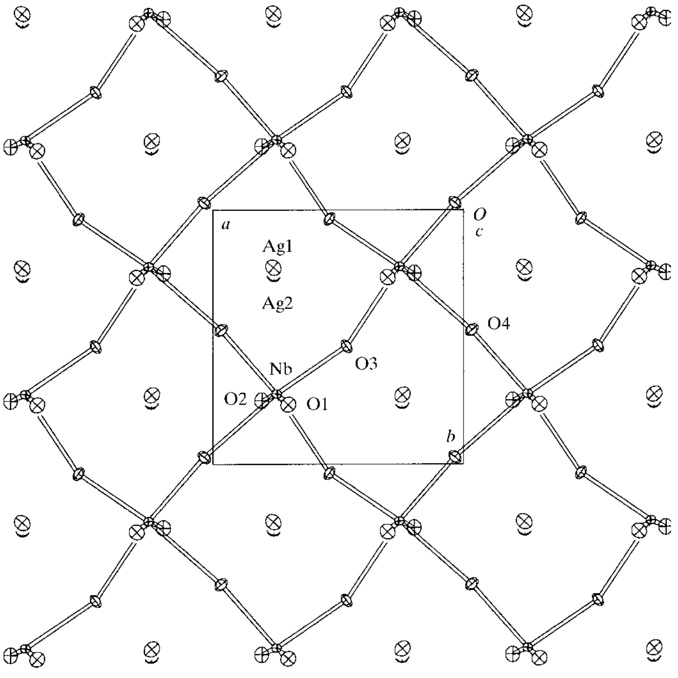

Figure 1
A view of the third layer [$z \in (0.50,0.75)$] of $AgNbO_3$ along the *c* axis, showing 50% probability displacement ellipsoids (*ORTEP*III; Burnett & Johnson, 1996).

Verwerft *et al.* (1988) also pointed out that the crystals of $AgNbO_3$ contained planar faults perpendicular to $[001]_p$.

$AgNbO_3$ tends to form non-stoichiometric phases with a lower content of Ag. This deficiency of Ag is supposed to be accompanied by oxygen reduction (Łukaszewski *et al.*, 1983). The precipitation of Ag was also observed by Verwerft *et al.* (1989). Matsumoto *et al.* (1992) observed the deficiency of Ag, as well as the release of O, during heating of sintered powder samples. From the dependence of electronic conductivity on the content of Ag in the bulk, these last authors concluded the existence of some Nb atoms in valences lower than +5.

The principal result of the present study is the confirmation of a model given by Hewat (1974), both for $AgNbO_3$ and $NaNbO_3$ (we collected single-crystal data on a sample of $NaNbO_3$, the structure of which is not published here due to the high proportion of a second domain). The relevant interatomic distances are given in Table 1 and the structure is depicted in Fig. 1. The tilt scheme is the same as that determined for $NaNbO_3$ by Sakowski-Cowley *et al.* (1969) and Hewat (1974), and that suggested for $AgNbO_3$ by Verwerft *et al.* (1988).

This study could not distinguish between the centrosymmetric and non-centrosymmetric space groups *Pbcm* and *Pbc*2$_1$. Refinement in $Pbc2_1$ was hindered by high correlations, so the structure is reported in *Pbcm*.

Referring to the reported ferroelectricity in $AgNbO_3$, it should be remembered that the spontaneous polarization observed in $AgNbO_3$ is about three orders of magnitude lower than that in $KNbO_3$ or $BaTiO_3$ (Jona & Shirane, 1962). The displacements of non-O atoms do not exceed several tenths of an Å in the latter compounds (Katz & Megaw, 1967). Consequently, the displacements of non-O atoms in $AgNbO_3$ should be duly smaller. These small displacements hinder the detection of deviation from centrosymmetry.

Experimental

The preparation of both single crystals and ceramic polycrystal samples of $AgNbO_3$ is described by Łukaszewski *et al.* (1983). Single crystals were grown by the molten salt method (solvents $8Ag_2O$:$5V_2O_5$ and Ag_2SO_4). Traces of V observed in the single crystals (concentration ~ 1 atomic %; Kania, 1998) come from the V_2O_5 in the solvent. Single crystals of $AgNbO_3$ are usually twinned; the domains in $AgNbO_3$ can be created by external stress. Among the crystals of $AgNbO_3$ available for the present work, one crystal was found with only a small fraction of a second domain, and this was used for the present X-ray structure determination.

Crystal data

$AgNbO_3$
$M_r = 248.77$
Orthorhombic, *Pbcm*
$a = 5.5462$ (3) Å
$b = 5.6028$ (4) Å
$c = 15.6365$ (13) Å
$V = 485.90$ (6) Å^3
$Z = 8$
$D_x = 6.799$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 5$–$33°$
$\mu = 12.492$ mm^{-1}
$T = 292$ (1) K
Prism, light brown
$0.31 \times 0.17 \times 0.09$ mm

Data collection

Hilger & Watts diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (Templeton & Templeton, 1978)
$T_{min} = 0.130$, $T_{max} = 0.356$
5156 measured reflections
1689 independent reflections
1497 reflections with $I > 3\sigma(I)$

$R_{int} = 0.025$
$\theta_{max} = 30°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -21 \rightarrow 22$
3 standard reflections every 30 reflections intensity decay: 7.0%

Refinement

Refinement on *F*
$R = 0.034$
$wR = 0.053$
$S = 2.84$
1689 reflections
52 parameters
$w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2]$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 1.20$ e Å^{-3}
$\Delta\rho_{min} = -3.65$ e Å^{-3}
Extinction correction: type II (Becker & Coppens, 1974)
Extinction coefficient: 2.28 (4) $\times 10^{-4}$

The structure is a twinned fourfold superstructure related to the perovskites. Due to imperfect superposition, reflections were only averaged through inversion. Those reflections which were partially overlapped were discarded from the calculations. The Fourier maps were therefore biased, either because not all reflections were used or because the $|F_o|$ values were not directly available. The deepest electron-density minima are ~ 0.6 Å from Ag1, Ag2 and Nb. Being a ferroelastic superstructure, there are pseudosymmetry properties. We attempted to refine the occupancy of Ag under the assumption that the occupancy of Ag1 is equal to that of Ag2. The occupancy of the O atoms was constrained in order to keep the charge balanced. The number of constraints was 15. The indicators of refinement decreased to the values $R_{obs} = 0.0316$, $wR_{obs} = 0.0477$, $R_{all} = 0.0357$, $wR_{all} = 0.0357$ and $S = 2.42$, and the composition resulted in $Ag_{0.9802(2)}Nb_{0.99}V_{0.01}O_{2.9901(2)}$. However, trying to include the refinement of the occupation of Nb/V was hindered by high correlations and resulted in unrealistic occupancies for all the heavy atoms. Therefore, the model with the ideal formula $AgNbO_3$ is reported here. The differences between the pertinent positional parameters which resulted from the refinement assuming the ideal non-stoichiometric compositions were as much as five times the respective s.u.'s. A full discussion of the treatment of twinning is available in the archived CIF; see the deposition footnote for access details.

Data collection: *HW* (Petříček, 1996); data reduction: *JANA*98 (Petříček & Dušek, 1998); program(s) used to solve structure: *TILT*

Table 1
Selected geometric parameters (Å).

Nb—O1	1.9866 (3)	Ag1—O1^{vii}	3.028 (1)
Nb—O2	1.9876 (3)	Ag1—O3	3.211 (1)
Nb—O3	1.8811 (9)	Ag1—O3^{viii}	3.211 (1)
Nb—O3^{i}	2.121 (1)	Ag2—O2^{iii}	2.8144 (1)
Nb—O4^{ii}	1.878 (1)	Ag2—O2	2.8144 (1)
Nb—O4^{i}	2.1333 (9)	Ag2—O2^{ix}	2.442 (1)
Ag1—O1^{iii}	2.604 (1)	Ag2—O2^{x}	3.105 (1)
Ag1—O1^{iv}	2.536 (1)	Ag2—O3	2.8597 (9)
Ag1—O3^{iv}	2.719 (1)	Ag2—O3^{x}	2.444 (1)
Ag1—O3^{v}	2.720 (1)	Ag2—O3^{iv}	2.444 (1)
Ag1—O4^{ii}	2.503 (1)	Ag2—O3^{xi}	2.8597 (9)
Ag1—O4^{vi}	2.503 (1)	Ag2—O4^{ii}	2.762 (1)
Ag1—O4^{iv}	2.721 (1)	Ag2—O4^{xii}	2.762 (1)
Ag1—O4^{v}	2.721 (1)	Ag2—O4^{x}	3.081 (1)
Ag1—O1	3.038 (1)	Ag2—O4^{iv}	3.081 (1)

Symmetry codes: (i) $1-x, \frac{1}{2}+y, z$; (ii) $1+x, y, z$; (iii) $x, y-1, z$; (iv) $1-x, y-\frac{1}{2}, z$; (v) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (vi) $1+x, y, \frac{3}{2}-z$; (vii) $2-x, y-\frac{1}{2}, z$; (viii) $x, y, \frac{3}{2}-z$; (ix) $2-x, 1-y, 1-z$; (x) $1-x, 1-y, 1-z$; (xi) $x, \frac{1}{2}-y, 1-z$; (xii) $1+x, \frac{1}{2}-y, 1-z$.

(Fábry, 1998); program(s) used to refine structure: *JANA*98; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *JANA*98.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1290). Services for accessing these data are described at the back of the journal.

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