Low-Temperature Phases of the Solid Electrolyte $Ag_{26}I_{18}W_4O_{16}$

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Single crystal X-ray diffraction photographs taken with a Buerger precession camera, at temperatures 250, 214, and 122 K, corroborate the existence of three low-temperature phases of $Ag_{26}I_{18}W_4O_{16}$. These phases are labeled α', β, and γ in order of decreasing temperature. The α' phase is monoclinic, space group $P2_1$, $Z = 2$; the β phase is triclinic, space group $P\bar{1}$ or $P1$, $Z = 2$; and the γ phase is triclinic, space group $P1$, $Z = 1$. Lattice constants at the aforementioned temperatures are given. Twins in the β and γ phases are related by the albite and pericline laws, as are twins in the feldspars. The highest symmetry known to be attained by the $(W_4O_{16})^{8-}$ entity is $2(C_2)$, which, strictly, it must lose at the transition to the α' phase.

1. Introduction

At room temperature and above, crystals of $Ag_{26}I_{18}W_4O_{16}$ belong to space group $C2$, with two $Ag_{26}I_{18}W_4O_{16}$ per unit cell, i.e., one per primitive unit cell. The symmetry of the structure is controlled by the symmetry of the $(W_4O_{16})^{8-}$ entities which are at the corners and C-face centers of the unit cell. The tetratungstate ions are surrounded by a three-dimensional network of iodide and iodide–oxide polyhedra through which the Ag^+ ions move. At room temperature, only 44.5% of the Ag^+ ions are mobile; the remainder are trapped in I–O polyhedra *not* in conduction passageways (*1*). Conductivity vs temperature measurements indicate that essentially no additional mobile carriers are generated at higher temperatures (*2*).

Although it seems that sterically the

$(W_4O_{16})^{8-}$ entity could have symmetry $2/m$, it has only the twofold symmetry C_2 (*1, 3*). The structures of the high-temperature modifications of both $Ag_8W_4O_{16}$ (*3, 4*) and $Ag_{26}I_{18}W_4O_{16}$ could become centrosymmetric if the tetratungstate ion did. The space group of $Ag_8W_4O_{16}$ is $Pn2n$ (*4*) and that of $Ag_{26}I_{18}W_4O_{16}$, $C2$; these would be $Pnmn$ and $C2/m$ if the tetratungstate had $2/m$ symmetry. There are no further crystallographic transitions in either $Ag_8W_4O_{16}$ (*5*) or $Ag_{26}I_{18}W_4O_{16}$ (*2*) above room temperature. It appears that even in the melt, the $(W_4O_{16})^{8-}$ ions are noncentrosymmetric (*5*). It is likely that this ion remains noncentrosymmetric in the low temperature phases investigated.

Two first-order crystallographic transitions at 246 and 197 K were found in the course of conductivity vs temperature measurements (*2*); a second-order transition at 277 K has also been found by differential scanning calorimetry (*6*). The main purpose of the present study was to obtain crystallo-

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graphic data on the low temperature phases.

2. Experimental

An Air Products Cryo-Tip single crystal X-ray diffraction refrigeration system was used for temperature control. A phosphor bronze pin, at the end of which the crystal is glued with Elmer's epoxy glue, is inserted in the refrigerator tip, so that the crystal is cooled by conduction. To hold the pin firmly in place, a copper mounting was installed between the tip and the pin. A thin evacuated beryllium shroud encloses the crystal so that warming by convection is eliminated. To minimize radiation into the chamber, a thin aluminized mylar sheet was wrapped around the shroud, thus requiring less nitrogen pressure to achieve a given low temperature.

The Buerger precession camera and Mo $K\alpha$ radiation were used to obtain all data. A crystal of $Ag_{26}I_{18}W_4O_{16}$ was ground to a sphere of radius 0.08 mm with a sphere grinder (7), similar to that designed by Schuyff and Hulscher (8); the crystal was oriented and transferred by means of a Supper crystal transfer device to the Cryo-Tip pin. Alignment of the crystal along the monoclinic **b** axis made it possible to obtain all reciprocal lattice constants in the triclinic phases except β^*. To obtain β^*, another crystal was mounted along **c**.

The crystals used in this investigation were obtained from large specimens grown (9) for directional conductivity measurements (2).

3. Results and Discussion

3.1 α' Phase

At room temperature, the Laue symmetry of $Ag_{26}I_{18}W_4O_{16}$ is $2/m$. Absent ($h\ k\ l$) reflections are those with ($h + k$) odd for the C centering. At 250 K, the Laue symmetry is still $2/m$, but low-intensity reflections with ($h + k$) odd are observed. Thus the unit cell becomes primitive with $Z = 2$.

The ($0\ k\ 0$) reflections with k odd are still absent; thus the probable space groups are $P2_1$ or $P2_1/m$. The α–α' transition cannot be seen in the conductivity vs temperature measurements (2) and differential scanning calorimetry suggests a second-order transition at 277 K (6). A second-order transition can occur only if the new space group is a subgroup of the former (10). Of the two probable space groups, only $P2_1$ is a subgroup of $C2$. Therefore, the most probable space group is $P2_1$. See Table I for the lattice constants of the α' phase at 250 K.

The space group of the α' phase does not contain twofold rotation axes. Strictly, then, the tetratungstate ions can no longer have a twofold axis. Very likely, the atomic displacements relative to the α phase are very small.

Greer et al. (6) claim that $Ag_{26}I_{18}W_4O_{16}$ becomes a solid electrolyte, i.e., a "fully disordered three-dimensional silver ion conductor at 277 K." Because the structure determination of the α phase (1) shows that only 44.5% of the Ag^+ ions are mobile at room temperature, the crystal cannot possibly be "fully disordered" at 277 K. The question of whether the $\alpha \rightarrow \alpha'$ transition involves ordering of the Ag^+ ions can be answered best by a structure determination. However, the conductivity data (2) preclude any significant ordering at temperatures down to the α'–β transition at 246 K. Furthermore, they show unequivocally that the material is a solid electrolyte as defined by Sato (11), down to 246 K: the directional enthalpies of activation of motion of the α and α' phases are essentially the same (see also Section 4).

3.2 β and γ Phases

3.2.1 The unit cells and space groups.

TABLE I

LATTICE CONSTANTS AND SPACE GROUPS OF THE MONOCLINIC OR PSEUDOMONOCLINIC CELLS OF THE FOUR PHASES OF $Ag_{26}I_{18}W_4O_{16}$

Phase	α	α'	β	γ
Temperature (K)	293	250	214	122
Space group	$C2$	$P2_1$	$C1$ or $C\bar{1}$	$C1$
Unit cell description	monoclinic	monoclinic	pseudomonoclinic	pseudomonoclinic
Formula units per cell, Z	2	2	4	2
a (Å)	16.76	16.71	16.64	16.53
b (Å)	15.51	15.48	15.45	15.47
c (Å)	11.81	11.80	23.54	11.70
α	90°	90°	89.3°	88.8°
β	103.9°	103.9°	103.9°	103.7°
γ	90°	90°	92.8°	93.5°
Volume (Å³)	2980	2963	5868	2901

The reflections with $(h + k)$ odd that appeared in the α' phase do not appear in the β and γ phases. In the β phase, the directions of a and c (pseudomonoclinic description) are unchanged, and b rotates 2.8° in the (0 0 1) plane. In the γ phase, c rotates 0.2° in the (0 1 0) plane; b rotates 3.5° from its former α-phase position, and moves slightly out of the former (0 0 1) plane.

In the β phase many new low-intensity reflections appear in rows halfway between the rows of the "α-phase reflections" perpendicular to c^*, indicating a doubling of c. Thus the volume of the pseudomonoclinic cell is doubled and contains four formula units. In the γ phase these new reflections do not appear; thus c returns to (approximately) its α-phase length, although the direction of c^* changes slightly. Thus the pseudomonoclinic cell of the γ phase contains two formula units. Lattice constants of the pseudomonoclinic cells are given in Table I; corresponding volumes of the cells decrease with decreasing temperature.

Both the β and γ pseudomonoclinic cells are C centered; thus the primitive cells contain two and one formula units, respectively. The transformation from the pseudomonoclinic to the primitive cells, for both the β and γ phases, is

$$\mathbf{a}_p = \tfrac{1}{2}(\mathbf{a}_s - \mathbf{b}_s)$$

$$\mathbf{b}_p = -\mathbf{c}_s$$

$$\mathbf{c}_p = \tfrac{1}{2}(\mathbf{a}_s + \mathbf{b}_s)$$

where the subscripts p and s refer to the primitive and pseudomonoclinic cells, respectively. This transformation retains a right-handed system in which $c < a < b$, and α, β, and γ are acute. The chosen cell is in accord with a type I normal representation (12). Lattice constants for the primitive cells are given in Table II.

It has been shown above that in the α' phase, the $(W_4O_{16})^{8-}$ ion no longer has a twofold axis, i.e., its symmetry is one. The β-phase primitive cell contains two $Ag_{26}I_{18}W_4O_{16}$, which implies that this phase could belong to space group $P\bar{1}$ with the two $(W_4O_{16})^{8-}$ ions related by a center of symmetry. This would, of course, require shifts of Ag^+ and I^- ions, such that they arrange themselves in pairs related by a center of symmetry. Because the α phase is nearly centrosymmetric, as can be seen by referring to Table I of Ref. (1), this possibility is plausible. The γ-phase primitive cell contains one formula unit; therefore $P1$ is the most probable space group. Based on the pseudomonoclinic C centered cell,

TABLE II

QUANTITATIVE DESCRIPTION OF THE TRICLINIC
CELLS OF THE β AND γ PHASES COMPARED WITH
THAT OF THE PRIMITIVE CELL OF THE α PHASE

Phase	α	β	γ
Temperature (K)	293	214	122
Space group	$C2$	$P1$ or $P\bar{1}$	$P1$
Z, per triclinic cell	1	2	1
a (Å)	11.42	11.63	11.66
b (Å)	11.81	23.54	11.70
c (Å)	11.42	11.07	10.97
α	79.8°	80.1°	80.3°
β	85.6°	85.7°	86.2°
γ	79.8°	79.6°	79.8°
Volume (Å^3)	1490	2934	1451

the β phase belongs to $C1$ or $C\bar{1}$ and the γ phase to $C1$.

Unlike the case of β-RbAg$_4$I$_5$ (13), the β and γ structures of Ag$_{26}$I$_{18}$W$_4$O$_{16}$ could be ordered with respect to Ag$^+$ ions. However, this is not a requirement. The γ phase in RbAg$_4$I$_5$ could be ordered, but probably is not (13–15). Nevertheless, high enthalpies of activation of motion (2) (~0.3 eV in the β phase and ~0.55 eV in the γ phase) make it seem likely that these phases are more nearly ordered than is γ-RbAg$_4$I$_5$. Structure determinations would elucidate the nature of the ordering in the β and γ phases. Especially because of the twinning and also because of the large number of data required to give reasonable estimates of all the parameters, the task is a formidable one.

3.2.2 Twinning. Twinning laws of Ag$_{26}$I$_{18}$W$_4$O$_{16}$ in the β and γ phases are the same as those of triclinic microcline (KAl Si$_3$O$_8$). Microcline occurs in a transition from a monoclinic modification, orthoclase; orthoclase belongs to space group $C2/m$. As already mentioned, Ag$_{26}$I$_{18}$W$_4$O$_{16}$ would belong to $C2/m$ if the tetratungstate were centrosymmetric ($2/m$). There is evidence for an intermediate state of KAlSi$_3$O$_8$ belonging to $P2_1/a$ (16), while α'-Ag$_{26}$I$_{18}$W$_4$O$_{16}$ belongs

to $P2_1$. The space group of microcline is $C\bar{1}$, while β-Ag$_{26}$I$_{18}$W$_4$O$_{16}$ belongs to either $C1$ or $C\bar{1}$. However, the structures of these seemingly analogous crystals are unrelated and other features of the phases and transitions are different. KAlSi$_3$O$_8$ has diffuse reflections for $(h + k)$ odd in $P2_1/a$, whereas those of α'-Ag$_{26}$I$_{18}$W$_4$O$_{16}$ are sharp. In the KAlSi$_3$O$_8$ case, the transition of $P2_1/a$ is associated with ordering of the Al and Si atoms. Also, complete transition of orthoclase to $C\bar{1}$ is very sluggish (17); all the Ag$_{26}$I$_{18}$W$_4$O$_{16}$ transitions are rapid.

Twins related by the albite and pericline laws are present in both the β and γ phases. The albite law relates twins by a mirror plane perpendicular to the *former* twofold b axis (discussion in this section refers to the pseudomonoclinic cells), the pericline law by a twofold rotation about the *former* b axis. X-ray diffraction results displaying albite and pericline twinning were first correctly interpreted by Laves (18), who also used the precession method. Laves pointed out that these twinning laws exist in microcline only because it formed first from monoclinic orthoclase. Ideal albite and pericline twinning in the reciprocal lattice, and some of the important deviations from ideality, are described by Laves (18). Smith (19) discusses other deviations.

As seen in Fig. 1, four reflections appear in place of each general $hk0$ α-phase reflection. Two are albite reflections which split parallel to b* from the original $hk0$ reflection. The other two are small rotations of albite reflections about an irrational axis and are related by the pericline law. The rotation takes the reflections out of the (001) reciprocal lattice plane, and pericline reflections are therefore not well focused when the albite twins are aligned. This can be seen in Fig. 1, in which pericline reflections are not related by a center of symmetry.

In the β phase, pericline reflections are derived from albite reflections by a rotation of ~2.8° about an irrational direction near
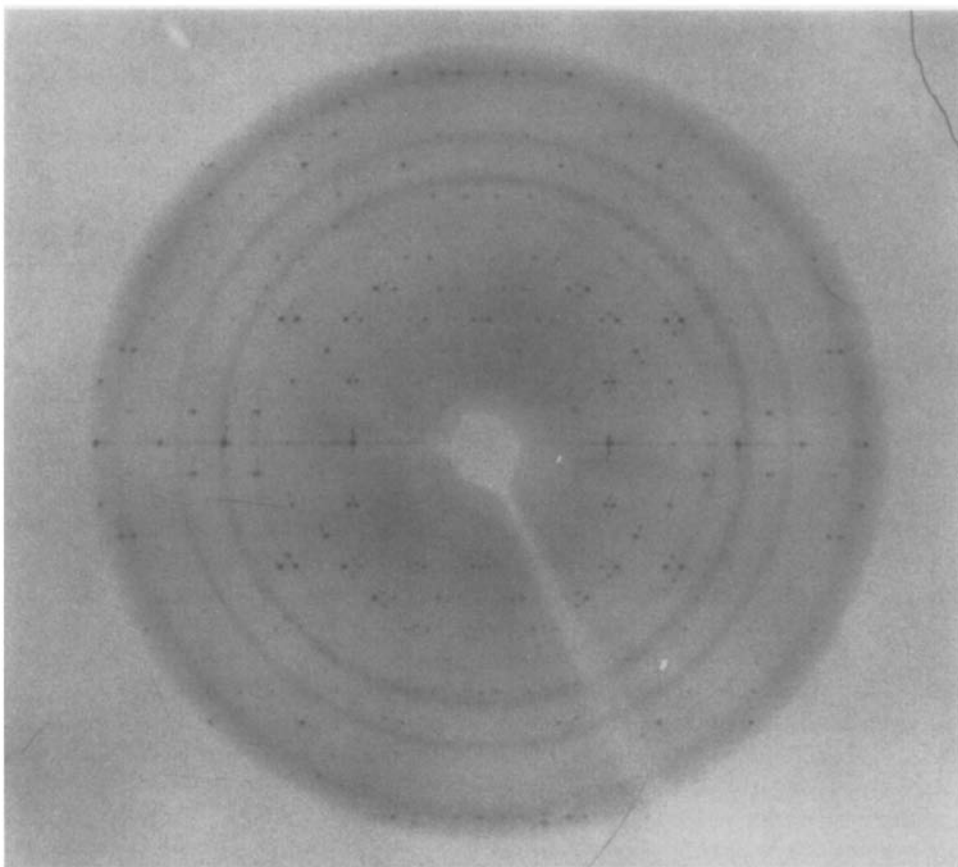
FIG. 1. 0-layer c axis precession photograph at 122 K. The splitting of $h\,k\,0$ reflections from the albite twins is horizontal (parallel to $\mathbf{b}^*$). The pericline reflections are small rotations of albite reflections in opposite directions roughly about the c axes of the albite twins. (The diffraction rings are from the beryllium shroud.)

[1 0 3]. In the γ phase, a rotation of $\sim$3.5° about an irrational direction near [1 0 4] relates albite to pericline twins. The composition plane for all albite twins is the (010) plane of the α phase. The composition plane of the pericline twins is the rhombic section (20) with indices ($h\,0\,l$). According to Friedel (21), the following equation holds:

$$(h:k:l) = a\,\cos\,\gamma:0:c\,\cos\,\alpha.$$

For the β (at 214 K) and γ (at 122 K) phases, the composition planes are ($\bar{3}\,0\,1$) and ($\bar{4}\,0\,1$), respectively.

If the absence of a center of symmetry in pericline twins is caused by poor alignment, proper alignment of one of the twins should result in the appearance of a center for the particular twin. One of the twins was brought into alignment; it was found to have a center, while the lattices of the three other twins did not in this photograph.

Precession photographs of feldspars often show diffuse streaks between reflections of pericline and albite twins. The presence of streaks is attributed to domains of cells which have transformed only partially from orthoclase to microcline (adularia is a

common intermediate metastable state) (*16*). No such diffuse streaks in the β and γ phases were observed in orientation photographs of $Ag_{26}I_{18}W_4O_{16}$ taken immediately after cooling. This indicates that the phase transitions are rapid and complete.

An interesting feature of the twinning in our samples is that the ratio of albite to pericline twinning was observed to change with temperature and specimen. A change in this ratio at a given temperature was also permanently induced. In the first specimen, pericline reflections were very weak in the β phase. However, at 160 K, the intensity ratio of albite to pericline reflections was much less than one. In our other specimen, pericline reflections were also initially very weak in the β phase. Even at 160 K in the γ phase, pericline intensities were low. At 122 K they became more intense, but still did not approach the intensity of albite reflections. The specimen was bathed in liquid nitrogen for a 2-hr period; when a photograph was taken of the β phase, pericline reflections were nearly of the same intensity as albite reflections. This new twinning ratio persisted after cycling several times from room temperature (where the structure is still the same) and back, and was apparently permanently induced. The ratio of pericline to albite twins is probably related to crystal defects.

4. Appendix (by S.G.)

To complete the work on $Ag_{26}I_{18}W_4O_{16}$, it is necessary to comment on the declamation by the authors of Ref. (*6*) on the nonlinearity of the $\log_{10}(\sigma T)$ vs T^{-1} data above 246 K (the $\alpha'-\beta$ transition temperature) reported in Ref. (2). The authors (*6*) assert that the nonlinearity is simply caused by the transition at 277 K which was not observed in Ref. (2). This implies that they are asserting that the $\log_{10}(\sigma T)$ vs T^{-1} data are linear above 277 K (the $\alpha-\alpha'$ transition temperature). This, of course, is not the case.

Although because of the high density of data in Fig. 3 of Ref. (*2*), it may be somewhat difficult to see the nonlinearity of the $\log_{10}(\sigma T)$ vs T^{-1} plots *above* the transition temperature of 277 K, it is absolutely obvious in Fig. 4 (*2*), which is a plot of $\log_{10}(\langle\sigma\rangle T)$ vs T^{-1}. It is also obvious for the results of directional measurements given in Table II (*2*), in which for 25-K increments in the temperature range 273–473 K, the values calculated from the parabolas, fitted to the data, are in excellent agreement with the observed values measured in four separate crystals in four different directions. The data between 277 and 246 K have no more than a minor effect on the parabolic fits as should also be obvious from Table II and Fig. 4 (*2*).

Acknowledgment

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