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ASSIGNMENT OF RAMAN SPECTRA AND DYNAMICAL PROPERTIES OF SILVER TETRATUNGSTATE $Ag_8W_4O_{16}$

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Assignment of Raman spectra of $Ag_8W_4O_{16}$ is performed. We assumed $(WO_4)^{--}$ ion as a primitive unit in the big $(W_4O_{16})^{-8}$ ion. The Raman spectra of $Ag_8W_4O_{16}$ from temperature up to and above the melting temperature have been recorded. Temperature dependence of the spontaneous electrical polarization was investigated on several samples from 293 to 623 K in oder to check the Raman spectroscopy results.

1. *Introduction*

Silver tetratungstate $Ag_8W_4O_{16}$ mixed with AgI in ratio 4 : 44[1] is a highly conductive solid electrolyte. Our interest in performing high temperature (293 K to 983 K) Raman spectroscopy on $Ag_8W_4O_{16}$ was to get insight into the possible changes of symmetry at about 573 K[2] and also to obtain information about the structure of the tetratungstate complex $(W_4O_{16})^{-8}$ in the melt.

2. *Crystal structure of* $Ag_8W_4O_{16}$

Research was initiated by Prof. Geller whose group was at the time growing crystals of solid $Ag_{26}I_{18}W_4O_{16}$ in order to perform X-ray structure analysis.

Problems which arised in the attempts to grow this crystal led them to grow $Ag_8W_4O_{16}$ crystal and to solve its structure first. The structure analysis indicated that the $(W_4O_{16})^{-8}$ complexes were the basis for both structures (Fig. 1).

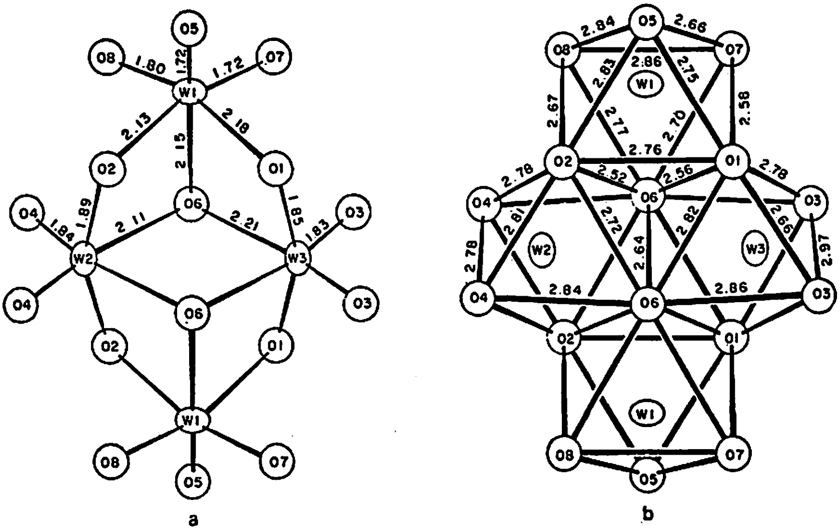

Fig. 1. $(W_4O_{16})^{8-}$ ion showing a) O-O distances, b) W-O distances.

There are two modifications of silver tungstate; the crystal lattice structure is of the symmetry C_{2v}^{10} 3).

The tetratungstate ion is non-centrosymmetric.

However, since the ion positions are close to D_{2h}^{13} symmetry, it was supposed that a piezoelectric-centric phase transition would occur at higher temperatures. An electric field of 40 kV/cm was applied to crystal at room temperature3) and spontaneous polarization did not change. These unsuccessful attempts to switch the spontaneous polarization led those authors to assume that the $(W_4O_{16})^{-8}$ ion would not become centric under any conditions. This assumption had to be proved by Raman spectroscopy. The large crystals of $Ag_8W_4O_{16}$ have been grown from the melt. By Raman spectra of the crystal and the melt we are hoping to show that the $(W_4O^1{}_6)^{-8}$ complex will probably be acentric even in the melt.

3. *Experimental results*

3.1. *Raman spectra of* $Ag_8W_4O_{16}$

The detection of a continuous phase transition to a structure in which $(W_4O_{16})^{-8}$ ions are centric, by means of an X-raf structure analysis, requires considerable work and would not readily give the transition temperature anyway. An alternative powerful method for such detection is that of Raman spectroscopy4).

Using this technique we undertook the project of seeing whether the prediction of Skarstad and Geller was correct.

The samples were grown by the Czohralski technique[5]. Specimens 2.5 × × 2.5 mm in cross section and 2.0 mm thick were cut and polished for Raman spectroscopic purposes and 0.2 mm thick for electric polarization measurements. Samples were X-ray oriented and afterwards polished. The crystal *b*-axis, which is the polar axis, was perpendicular to the 2.5 × 2.5 mm plane. Raman spectra were excited by a a few hundred milliwatts of 514.4 nm or 488 nm radiation from an argon ion laser. A right angle scattering geometry was employed in Raman spectra measurements. Only a small percentage of the group-theoretically predicted long wavelength phonons was observed. We have simply lebelled modes as A_1, A_2, B_1, or B_2 according to whether the ZZ, XY, XZ or YZ scattering tensor was most intense. The Raman spectra of $Ag_8W_4O_{16}$ are shown in Fig. 2. The frequencies of these modes and their probable symmetries are listed in Table 1.

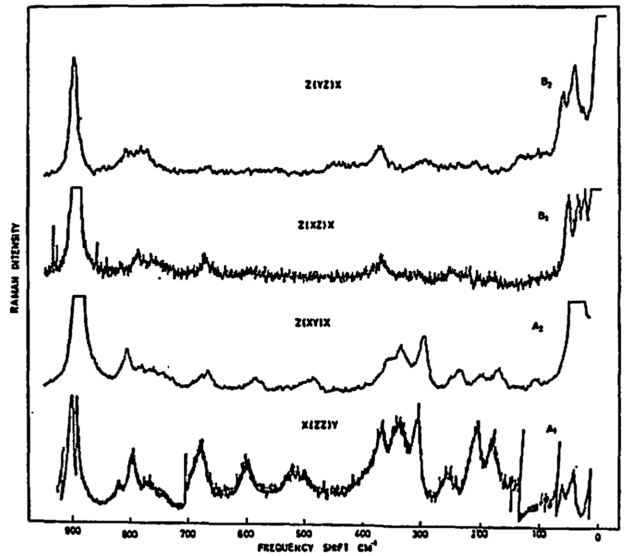

Fig. 2. Raman spectra of $Ag_8W_4O_{16}$ at room temperature.

TABLE 1

Probable symmetry species:	A_1	B_1	A_2	B_2
	44	32	182	116
	60	92	208	488
	366	248	306	510
	590	629	336	546
	778	667		754
	800	730		
	884			

Observed phonon frequencies in $Ag_8W_4O_{16}$ crystal at 293 K $(cm)^{-1}$.

Raman spectra were measured at temperatures from 293 K to 905 K. Using an anology with the work Porto and Scott[6,7] on assignment of Raman spectra tungstates, we assumed $(WO_4)^{--}$ ion as a primitive unit in the large $(W_4O_{16})^{-8}$ ion. In these conditions the splitting of the free tetrahedral levels are due to presence of four $(WO_4)^{--}$ ions in each $(W_4O_{16})^{-8}$ ion, which has C_{2v} symmetry. The crystal field further removes some of the degeneracies, due to the presence of the two $(W_4O_{16})^{-8}$ ions per unit cell. A few different correlations of ion, site and factor-group symmetry had been attempted. The successful one, regarding realistic number of vibrations comparing to experimental values, was the correlation using C_{2v} symmetry of $(W_4O_{16})^{-8}$ ion. Correlation of ion, site and factor-group symmetry is given in Table. 2.

TABLE 2

Ion group isolated tetrahedron $(WO_4)^{--}$ T_d	Site symmetry group $4(WO)_4^{--}$ in $(W_4O_{16})^{-8}$ C_{2v}	Factor group $2(W_4O_{16})^{-8}$ per unit cell C_{2v}^{10}
E $8C_3$ $3C_4$ $6S_4$ $6\sigma_d$	E C_2^b $\sigma_v(cb)$ $\sigma_v(ab)$	E C_2 σ_v σ_v
A_1 *Ram* — —	A_1 (T_b) — $A_1(T)$ —	— A_1 2 A_1 (T) *Ram*
A_2 —	A_2 R_b — A_2 (R) —	— A_2 2 A_2 (R) *Ram*
E *Ram* — —	B_1 $(T_c)(R_a)$ — A_1+A_2 —	— B_1 $2(A_1+A_2)$ *Ram*
F_1 (R) —	$A_2+B_1+B_2(R)$	— $2(A_2+B_1+B_2)(R)$ *Ram*
F_2 (T) *Ram* — —	B_2 $(T_a)(R_c)$ — $A_1+B_1+B_2(T)$ —	— B_2 $2(A_1+B_2+B_2)(T)$ *Ram*

T — translational motions of tetrahedrons

R — rotational motions of tetrahedrons

Ram — Raman active vibrations

Correlation of ion, site and factor-group symmetry.

Figure 3 shows approximate forms of vibrations of WO_4^{--} ion of T_d symmetry.

Two groups of vibrations are of interest in regard to their temperature dependences. First, the modes varying from 40 to 65 cm^{-1} are very intense and are not present in other tungstates, such as $CaWO_4$, $SrWO_4$, $BaWO_4$, or $ZnWO_4$[7]. These are obviously due to motion of the heavy Ag^+ ions. Figure 4 shows the temperature dependence of Raman active Ag^+ — ion vibrations.

The second frequency region of interest is around 900cm^{-1}, where the energy of the assigned totally symmetric modes, those which corresponds to the W-O stretching mode is usually found in tungstates, e. g., the scheelites[7] 912 cm^{-1}, 925 cm$^{-}{}_{1}$, 878 cm^{-1}, 887 cm^{-1} and $ZnWO_4$ [7] 900 cm^{-1}. The latter contains octahedrally coordinated W[8] though unlike that in $Ag_8WO_4O_{16}$.

The following assignment of observed Raman spectra is proposed in Table 3.

TABLE 3

Vibrational mode and symmetry				
Isolated tetrahedrons	Tetrahedrons in ion $(W_4O_{16})^{-8}$	Tetrahedrons in lattice	Observed wave number (cm^{-1})	Assignment
Td ion group	C_{2v} site group	C_{2v}^{10} factor group		
$\nu_1 (4A_1)$	$\nu_1 (4A_1)$	$\nu_1 (A_1)$	884 (*ww*) A_1	W-O stretch totally symm.
	$\nu_3 (4A_1)$	$2\nu_3 (4A_1)$	800 (*ww*) A_1	W-O stretch
			778 (*m*) A_1	W-O stretch
	$\nu_3 (4B_1)$	$2\nu_3 (4B_1)$	730 (*w*) B_1	W-O stretch
			667 (*w*) B_1	W-O stretch
$\nu_3 (4F_2)$	$\nu_3 (4B_2)$	$\nu_3 (8B_2)$	754 (*w*) B_2	W-O stretch
	$\nu_4 (4A_1)$	$\nu_4 (8A_1)$	590 (*w*) A_1	W-O
	$\nu_4 (4B_1)$	$\nu_4 (8B_1)$	629 (*vw*) B_1	bending
				bending
$\nu_4 (4F_2)$	$\nu_4 (4B_2)$	$2\nu_4 (4B_2)$	546 (*ww*) B_2	bending
			510 (*vw*) B_2	bending
				W-O
	$\nu_2 (2A_1)$	$\nu_2 (4A_1)$	366 (*w*) A_1	bending
$\nu_2 (4E)$	$\nu_2 (2A_2)$	$2\nu_2 (2A_1)$	336 (*w*) A_2	bedinng
			306 (*w*) A_2	bending
Rotation	$\nu_R (4A_1)$	$2\nu_R (4A_2)$	208 (*w*) A_2	rotation
	$\nu_R (4B_1)$	$\nu_R (8B_1)$	182 (*w*) A_2	
$(4F_1)$	$\nu_R (4B_2)$	$\nu_R (8B_2)$	248 (*vw*) B_1	
			116 (*w*) B_2	
			92 (*w*) B_1	

$(WO_4)^{--}$ vibrations in Raman spectra of $Ag_8W_4O_{16}$.

The vibrational modes of Ag^+ ions are presented in Table 4.

TABLE 4

Species:	A_1	B_1
	44	32
	60	

Ag^+-ion vibrations of $Ag_8W_4O_{16}$ in $(cm)^{-1}$.

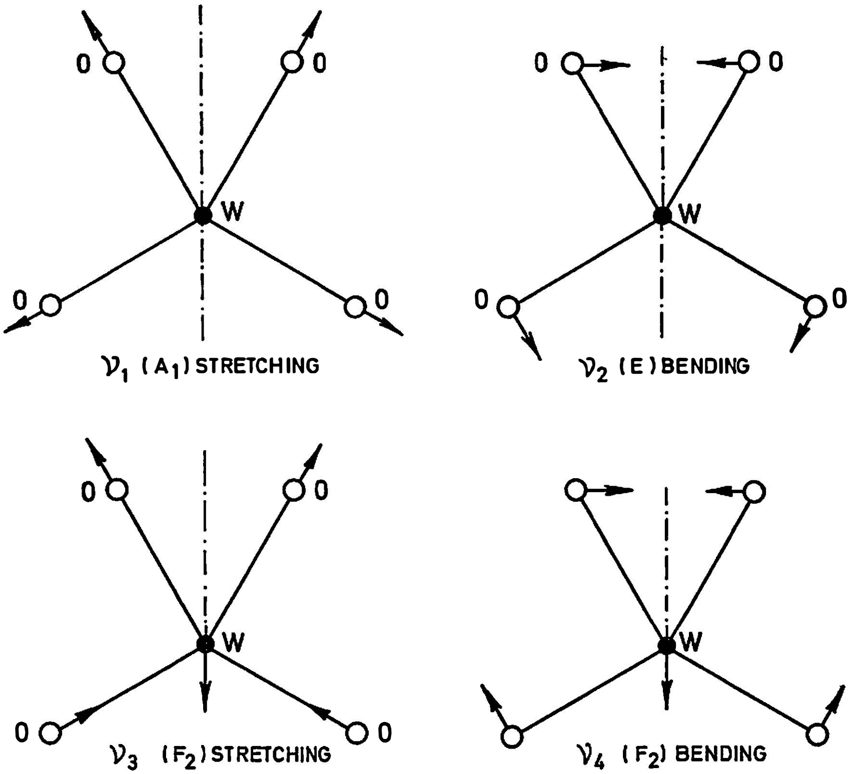

Fig. 3. Vibrations of $(WO_4)^{--}$ ion of T_d symmetry.

Representative spectra obtained at 293 K, 759 K in crystal and at 905 K in the melt are shown in Fig. 5.

These data were obtained in air at atmospheric pressure. The data display a number of important characteristics. First, the bands broaden very rapidly as the sample is heated; this is often taken as characteristic of the onset of disorder in crystals. The low frequency modes corresponding to silver ion motion in the 50—65 cm^{-1} energy region do not shift or »soften« as the temperature is raised. They show no anomaly in the 573 K region in which Takashi et al.[2] find a conductivity anomaly, but they do abruptly disappear as the sample melts (top trace in Fig. 5). This is to be expected because the Ag^+ ions should be mobile in the melt. Melting in our samples occurred between 853 and 943 K furnace temperature; these values depended upon sample and upon laser power and wavelength. The samples became opaque when heated to high temperature in air. Actual sample temperature in the illuminated region may be 50 K above that of the furnace, because of absorption of the laser light. The melting point of $Ag_8W_4O_{16}$ reported by Takahashi et al.[9] is 993 ± 5 K. The frequencies and intensities in the high energy region (500—800 cm^{-1}) do not change abruptly upon melting, indicating that the $(W_4O_{16})^{-8}$ ion remains unchanged in the melt, as previously suggested by Skarstad and Geller[3].

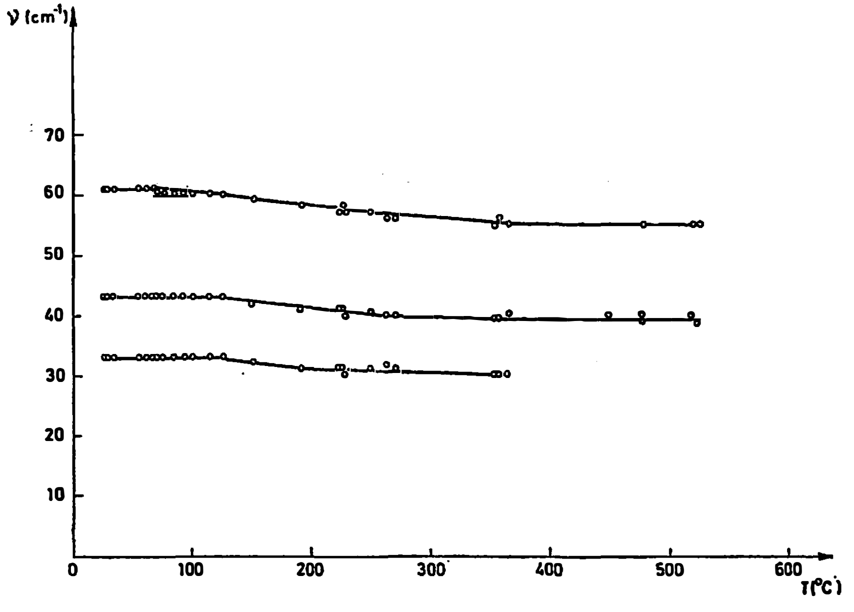

Fig. 4. Raman active Ag$^+$ — ion vibrations as a function of temperature.

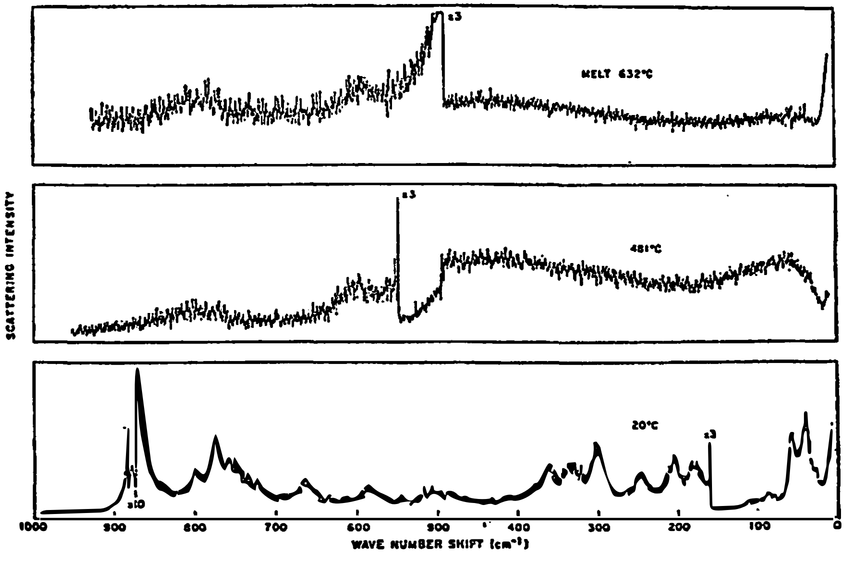

Fig. 5. Raman spectra in air at 20, 481 and 632 °C.

Most unusual is the temperature dependence of the A_1 mode at 884 cm^{-1}. This is the most intense scattering feature in the crystal at room temperature, but its intensity decreases drastically within creasing temperature. As mentioned previously, this mode is assigned as a totally symmetric W-O stretching vibration. In Fig. 6, we have plotted the intensity of this mode relatively to that of a 44 cm^{-1} Ag mode I (884)/I (44), versus furnace temperature. An approximatively linear decrease in intensity with temperature is shown from 293 K to 523 K, above this temperature

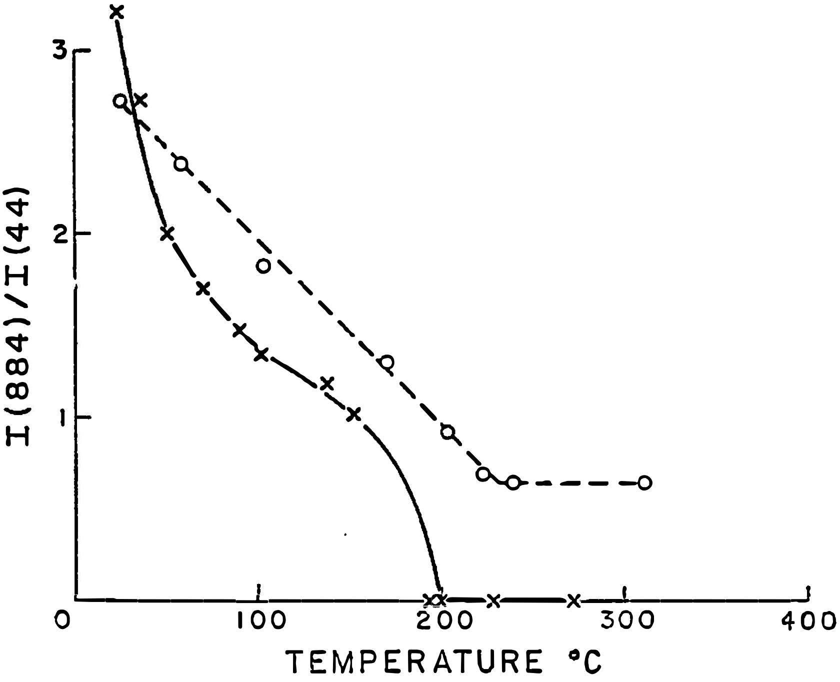

Fig. 6. Plot of intensity of the 884 cm^{-1} symmetric W-O stretching mode in $Ag_8W_4O_{16}$, relative to the intensity of the Ag^+ — ion translational mode at 44 cm^{-1}, versus temperature. Dashed line, in oxygen; solid line, in air.

no measurable change is observed. This could suggest a change in crystal structure at a sample temperature of roughly 573 K. This is in a quite good agreement with the temperature at which Takahashi et al.⁹⁾ found changes in conductivity of Ag_2WO_4. When the Raman measurements were repeated in an oxygen atmosphere, less changes were observed in the spectrum with increasing temperature. In particular, the change in intensity of the 884 cm^{-1} W-O stretching mode was not as large as previously.

3. 2. Electrical polarization measurements

Measurements of the spontaneous electrical polarization as function of temperature were performed on several samples in air atmosphere and at different temperatures ranging from 293 to 573 K. The circuit used is shown in Fig 7. Throughout the text term polarization will be used to denote electrical polarization.

The *b*-faces of the samples were spring-contacted with copper or gold electrodes. The spontaneous polarization observed was of order 0.3 $\mu C/cm^2$, which is a relatively small value. The »apparent« spontaneous polarization decreased as shown in Fig. 8, reaching an unmeasurably small value at about 556 K. We refer to this as apparent spontaneous polarization because of the following: In all our measurements at high temperatures, whether optical or electrical, the sample surfaces dar-

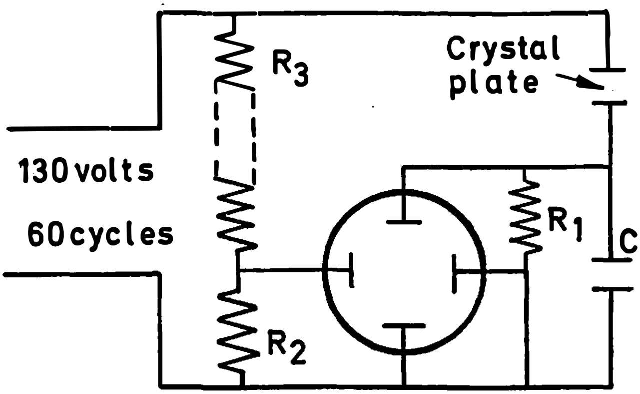

Fig. 7. Circuit for polarization measurements.

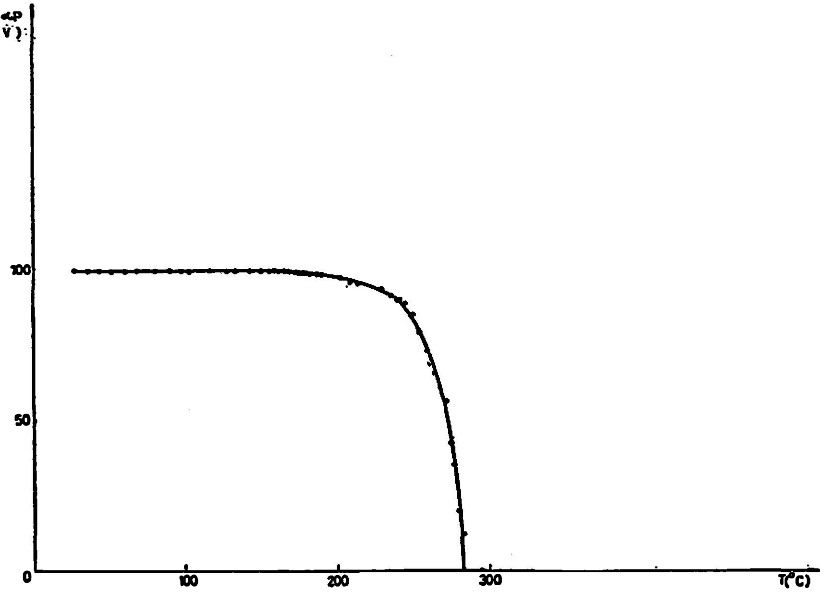

Fig. 8. Apparent spontaneous polarization of $Ag_8W_4O_{16}$ versus temperature. Measurements made in air with heating rate approximately 1°/C/min. Specimen in air. Upon cooling, the apparent spontaneous polarization remained at zero.

kened considerably. This process was irreversible and rendered the samples visually opaque and appeared to give substantially increased absorption of X-rays untill polished off. It occurred to us that the altered surface (or bulk) could provide a conducting short in the circuit by which we measured the apparent spontaneous polarization; this would yield the same kind of data as shown in Fig. 6, that is, not requiring a contiouous phase transition, if the changes in the sample were caused by a thermally activated process.

A clue that this might be the right explanation was afforded by the shape of the »polarization« curve in Fig. 8.

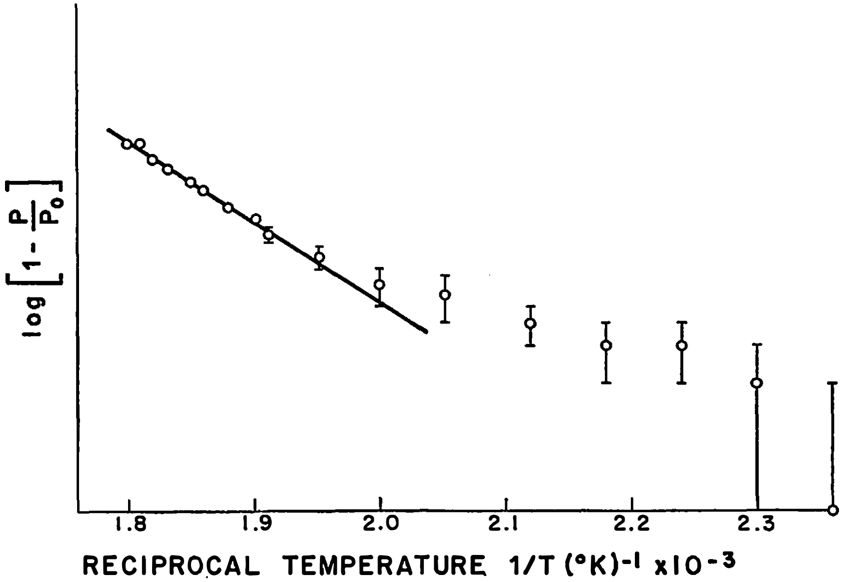

Fig. 9. Plot of log (1 − P/P_0) versus $1/T$ for $Ag_8W_4O_{16}$, where P is the apparent spontaneous polarization at temperature T, and P_0 is the spontaneous polarization at low temperatures. Specimen in air.

As shown in Fig. 9, a graph of the apparent spontaneous polarization, normalized to the room-temperature value, yields a straight line when log $(1 - P/P')$ versus $1/T$ is graphed. Here P is the apparent polarization at temperature T, and P' is the value of P at room temperature. This is the behaviour expected for a thermally activated process with a well defined activation energy, in this case, 0.03 eV. This graph therefore supports the interpretation that our spontaneous polarization measurement actually measures sample conductivity, and that this conductivity increases with sample temperature through a thermally activated transport mechanism. These, thermally activated increase in conductivity, could be surface effects, bulk effects, or both.

4. Analysis of data

We have considered two possible explanations of the phenomenon reported above: 1) that the effect is due to the loss of oxygen at the sample surface upon heating; and 2) that the effect is due to migration of Ag to the surface. Several experiments were performed in an attempt to determine which process occurs. First, the polarization experiments summarized in Figs. 8 and 9 were repeated in conditions where pure oxygen was flowing over the sample. Under these conditions the metallic build-up on the surfaces lessened somewhat and no decrease in apparent spontaneous polarization was noted up to 567 K, in complete contrast to the data shown in Fig. 8. Raman data taken under conditions of flowing oxygen also showed less pronounced decreases in the intensity of the 884 cm^{-1} W-O stretch with temperature than did those taken in air. Both of these experiments suggest that an overpressure of oxygen impedes the metallic surface layer formation in $Ag_8W_4O_{16}$ at high temperatures; note that the Raman measurements are not made at the surface.

When the samples were allowed to cool down to ambient temperatures after being above 573 K, they continued to exhibit the high temperature Raman spectra for hours, or even days, afterwards. After this time, the spectra returned to nearly that obtained before heating, except for some line broadening attributable to irreversible disorder. Such effects show that continuous decrease to zero of the apparent spontaneous polarization in Fig. 8 cannot be due to a second order structural phase transition.

To measure directly any oxygen weight loss occurring upon heating, we weighed $Ag_8W_4O_{16}$ single crystal samples with a microbalance before and after heating for three hours at 623 K. No weight loss was observed. The accuracy of our microbalance allows us to put an upper limit of not more than one oxygen ion per fifty primitive cells lost under these conditions. These measurements are compatible with those of Bottelberghs$^{10)}$, who also failed to find any measurable weight loss in $Ag_8W_4O_{16}$ under similar conditions. An oxygen atmosphere impeded probable decomposition reaction of the $Ag_8W_4O_{16}$ occuring with increasing temperature, what was confirmed by electrical and optical measurements. On the other hand, the negative results of weight loss measurements indicate that the surface effect does not arise simply from loss of oxygen at the surface. The reaction is undoubtedly complex, but some suggestions can be made. Geller$^{11)}$ suggests a possible reduction of a tungsten atom in a complex. With the loss of an oxygen atom, the entire valence of the new complex is remaining the same, e. g.,

$$2\,(W_4O_{16})^{8-} \rightarrow O_2 + 2\,(W_4O_{15})^{8-}.$$

Such an occurrence would not require the reduction of Ag^+ to Ag, and the crystal could preserve its characteristics of ionic conductor with a thermally activated hopping mechanism.

The Raman spectra of the specimens in flowing oxygen show that there is no crystallographic transformation in $Ag_8W_4O_{16}$ up to the melting point. The crystal structure of $Ag_8W_4O_{16}$ is such that ion conductivity is not expected. The temperature dependences of the low-frequency Ag^+ — ion vibrations at 44 cm^{-1} show no anomalies, in agreement with this expectation, and in contrast to observation in other ionic conductors such as α-$AgI^{12)}$ or $PbF_2{}^{12)}$. Furthermore, as mentioned earlier, the spectra of the melt in the 500—800 cm^{-1} region remain essentially unchanged in comparison with those of the solid, indicating that the $(W_4O_{16})^{-8}$ ion exists in the melt too. The results are then in agreement with the predictions made by Skarstad and Geller$^{3)}$.

5. *Conclusion*

All results obtained and discussed up to now indicate that: 1) pure $A_8gW_4O_{16}$ is not a solid electrolyte; electrical and thermal evidence for a conducting phase above 553 K obtained by Takahashi et al.[2] is shown in our work to result from thermally activated, irreversible chemical degradation with a 0.03 eV activation energy 2) the silver ion vibrations in $Ag_6W_4O_{16}$ occur in the 40—60 cm^{-1} region and remain well defined up to the melting temperature at 893 K: 3) the chemical degradation at about 550 K can be minimized by an oxygen pressure of several atmospheres; 4) $(W_4O_{16})^{-8}$ ion is noncentrosymmetric, having the C_2 symmetry which was used as the basis for the assignment of the Raman spectra. In addition the ion remains essentially the same entity in the melt as in the solid.

Acknowledgment

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ASIGNACIJA RAMAN SPEKTRA I DINAMIČNA SVOJSTVA SREBRNOG TETRAVOLFRAMATA $Ag_8W_4O_{16}$

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Izvršena je asignacija Raman spektra $Ag_8W_4O_{16}$. Pretpostavili smo $(WO_4)^{--}$ ion kao manju jedinicu u većem $(W_4O_{16})^{-8}$ ionu. Izmjereni su Raman spektri $Ag_8W_4O_{16}$ od sobne temperature do i iznad temperature taljenja. Mjerenja spontane električne polarizacije kao funkcije temperature učinjena su na nekoliko uzoraka od 293 do 623 K u svrhu provjere rezultata Raman spektroskopskih mjerenja.