Raman spectroscopy of structural phase transitions in Ag$_{60}$I$_{18}$W$_4$O$_{16}$

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Raman spectra of single crystals of silver iodide tetratungstate (Ag$_4$I$_4$W$_4$O$_{16}$) have been obtained as a function of temperature from 77 to 350 K. These data indicate the presence of structural phase transitions near 199 and 285 K. Dielectric and conductivity measurements perpendicular to the unique twofold axis confirm the presence of these two transition temperatures. Plots of log ($\sigma$T) versus 1/T reveal three distinct regions of linearity with activation energy 2.4 eV below 199 K; 0.07 eV between 199 and 285 K; and 0.42 eV above 285 K.

I. INTRODUCTION

Solid state materials which exhibit high ionic conductivity are commercially attractive elements for a variety of electronic applications.1–1 The high ionic conductivity in these substances arises from a network of mobile ions which partially occupy a linked interstitial space. These ions move in a diffusive manner; an ion spends a certain average time (called the dwell time) in one available site before hopping to another. Both the vibrations of small amplitude of these ions about their equilibrium positions and their translations between available sites produce fluctuations in the polarizability of the crystals with frequency components in the range $10^9$ to $10^{11}$ Hz. This makes Raman spectroscopy a very suitable tool for the investigation of ionic motion in solid electrolytes.6

In this paper we report the first Raman spectra of single crystals of Ag$_{60}$I$_{18}$W$_4$O$_{16}$, a material of commercial utility selected for application by Sanyo. Evidence for two structural phase transitions is obtained; these transitions are confirmed by electrical measurements. The dynamics of these transitions are interesting and unusual, in comparison with those in AgI and other silver electrolytes, in that the phenomena associated with the transitions evolve in a highly continuous way. The two transition temperatures inferred are $T_1 = 199$ and $T_2 = 285$ K. Above $T_2$, the sublattice of Ag$^+$ ions "melts" and the silver ions become mobile, producing high ionic conductivity. Our Raman and electrical measurements are discussed below in terms of current theories of light scattering in solid state electrolytes and of phase transitions in such systems.

II. EXPERIMENTAL

A. The crystal structure of silver iodide tetratungstate

The structure of crystalline Ag$_{60}$I$_{18}$W$_4$O$_{16}$ was determined by Chan and Geller.6 The formula for this crystal was first reported as Ag$_{60}$I$_4$WO$_4$.7 However, single crystal x-ray data and density measurements revealed that the correct formula is Ag$_{60}$I$_{18}$W$_4$O$_{16}$. The structure of this crystal has point group symmetry $C_2v$ and space group symmetry $C_{2v}^3$. It contains two Ag$_{60}$I$_{18}$W$_4$O$_{16}$ formula groups per unit cell. The cell is monoclinic with $a = 16.73 \pm 0.03$ Å; $b = 15.52 \pm 0.03$ Å; $c = 11.81 \pm 0.02$ Å; and $\beta = 103.9 \pm 0.1^\circ$. The crystal structure is rather complex, and we shall not attempt to describe it fully here. (The paper by Chan and Geller contains a detailed description with several figures showing the possible conduction paths.) Some important features will be summarized below, however.

Ag$_{60}$I$_{18}$W$_4$O$_{16}$ belongs to a family of silver iodides in which some of the iodine ions are replaced by tungstate ions. In Ag$_{60}$I$_{18}$W$_4$O$_{16}$, the tungstate complex is an octahedrally coordinated W$_4$O$_{12}$ ion which lies on twofold axes at the corners and c-face centers of the unit cell. These W$_4$O$_{12}$ ions are separated by a three-dimensional network of face-sharing iodide polyhedra through which Ag$^+$ ions can move. There are 90 iodide polyhedra (88 tetrahedra and two octahedra) per unit cell. Surrounding each tetratungstate ion are 60 polyhedra (120 per unit cell) formed from both I ions and oxygen ions. Eight of these are octahedra, all of which are permanently occupied by Ag$^+$ ions. The remaining 112 iodine-oxygen polyhedra are either tetrahedra or five-cornered polyhedra. Eightysix of these polyhedra are vacant, and the remaining 28 have a high probability of occupancy and are not in conduction passageways. Table III of Ref. 6 gives a complete list of Ag$^+$ ion sites and their association with conduction passageways. The number of mobile Ag$^+$ ions in Ag$_{60}$I$_{18}$W$_4$O$_{16}$ is rather high—about 44.5% of the total. This fact, together with the existence of a complex network of conductivity routes, makes this crystal a very good solid state electrolyte. The fact that the conduction tunnels propagate in three dimensions has an additional favorable effect on the current-carrying properties of this solid; one or two dimensionally interconnecting pathways are less favorable to high ionic conductivity.6

B. Experimental methods

We studied three samples, with identical results in each case. The samples were single crystals study which generally were not oriented. Because of the low $(C_2)$ point group symmetry, x-ray orientation was not important for the Raman measurements. Samples $3 \times 3$ mm in cross section and 2.5 mm thick were mechanically polished and then mounted with General Electric varnish on a copper block in a conventional low-temperature cryostat. The sample temperature was measured using a calibrated platinum thermometer imbedded in
the copper block. The sample chamber was evacuated and helium gas introduced for heat exchange. The block temperature was controlled to ±0.5 K. The samples were studied from 77 to 350 K.

A right-angle scattering geometry was employed, with the 514.5 nm line of a single-moded, argon ion laser, as the exciting source. The laser power was limited to 50 mW to prevent damage. (Higher powers produce photoexcited electrons, which react with Ag ions and deposit neutral Ag at sample surfaces.) The scattered light was analyzed by means of a 0.65 m double grating spectrometer and a cooled RCA31034A phototube and ratemeter. To probe the region of wavenumber near the exciting line, an iodine absorption cell was used with stabilized temperature.

Silver electrodes were attached to the sample for conductivity/capacitance measurements. These measurements were obtained using a Wayne-Kerr B221 ac bridge with a General Radio tuning filter #4469 as a null detector. The bridge was excited using a General Radio 1311A oscillator at frequencies of 1 and 10 kHz. Conductivity and capacitance data were collected using the same cryostat as was used for the Raman measurements; in fact, simultaneous Raman and electrical measurements were made.

III. RESULTS AND DISCUSSION

A. Raman spectra

For point group symmetry $C_4$, the mode symmetries are designated $A$ and $B$, where the $A$ symmetry representation is symmetric with regard to the $C_4$ symmetry operation. Using a standard group theoretical calculations for the $C_4$ space group, we find that the 192 degrees of freedom are divided into three acoustic modes and 94 $A + 94 B$ optical modes, all of which are Raman active.

The Raman spectra of $\text{Ag}_2\text{I}_{18}\text{WO}_{16}$ at 80 and 296 K are shown in Fig. 1. Only a small percentage of the group theoretically predicted vibrations was observed. Modes below 100 cm$^{-1}$ were found to be temperature dependent and will be discussed in more detail. The modes above 100 cm$^{-1}$ were not temperature dependent, except that they broadened, as expected, with increasing $T$. The most intense modes above 100 cm$^{-1}$ lie at 855 and 882 cm$^{-1}$. They are assigned as simple W-O stretching vibrations. Similar modes around 900 cm$^{-1}$ have been observed in $\text{Ag}_2\text{W}_{18} \text{O}_{46}$ and in scheelite structure tungstates.$^{11}$

The low frequency modes are quite intense and exhibit strong temperature dependences. These modes are not observed in nonconducting tungstates such as $\text{CaWO}_4$, $\text{BaWO}_4$, $\text{SrWO}_4$, or $\text{ZnWO}_4$. However, they are observed in $\text{Ag}_2\text{W}_{18} \text{O}_{46}$, where they were assigned as vibrations of silver ions.$^{10}$ Similar low-frequency modes have been observed in $\text{AgI}^{12,13}$ and $\text{RbAgI}_4$. It is expected that these low energy vibrations are associated with heavy, loosely bound silver ions in a variety of solid state electrolytes. For this reason, we concentrated our attention on these modes and their $T$ dependences in $\text{Ag}_2\text{I}_{18}\text{WO}_{16}$. Figure 2 illustrates the low energy region of the Raman spectrum of this crystal at various temperatures. At low temperatures, there are two well-defined modes peaking at about 20 and 35 cm$^{-1}$. The spectra of these modes were computer fitted to a

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model of noninteracting damped harmonic oscillators. At \( T = 199 \) K, the mode at 35 cm\(^{-1}\) becomes unresolvable, and an increase in quasielastic scattering becomes noticeable, leading to an apparent increase in the peak frequency for the lower energy mode near 20 cm\(^{-1}\).

By "quasielastic scattering," we refer to that portion of the spectrum below 20 cm\(^{-1}\) which does not exhibit intensity maxima, i.e., the "wings" of the laser line. At low temperatures, this quasielastic scattering (present in all crystals) commonly arises from optical defects in the specimens studied, e.g., voids, inclusions, sample strain, and other inhomogeneities of size comparable to or larger than a wavelength of the laser light used. However, in Ag\(_{25}\)I\(_{18}\)WO\(_{45}\), as the temperature approaches 199 K, there is a noticeable increase in the quasielastic, low-frequency scattering: we believe that this scattering is dynamic in origin and arises from silver ion tunneling between adjacent sites.

We will call the temperature \( T_1 \) at which the 35 cm\(^{-1}\) peak disappears the first phase transition temperature in Ag\(_{25}\)I\(_{18}\)WO\(_{45}\). As \( T \) is further increased to about 285 K, the other low-energy vibration (near 20 cm\(^{-1}\)) becomes diffusive and exhibits no peak. This disappearance is quite continuous with increasing \( T \) (see Fig. 2), in contrast to systems such as AgI. The low-frequency portion of the Raman spectra becomes broader as \( T \) is increased further above 300 K.

The transition temperatures of 199 and 285 K were determined simply by observing the temperatures at which distinct maxima in intensity disappeared for the low frequency spectral lines. Computer curve fitting gave the same results (to \( \pm 5 \) K) as were obtained by visual inspection of the data, some of which are shown in Fig. 2. Both methods of estimating transition temperatures agreed well with the electrical measurements discussed in the following section.

These observations are independent of temperature cycling and led us to hypothesize that a phase transition exists near 199 K and that ionic conductivity should be very small below this temperature. We therefore carried out some electrical measurements, which are summarized in Sec. III, B below. It is worth emphasizing that the spectral evolution which we observe in Fig. 2 is qualitatively different than that observed in other silver compounds. For example, in AgI, the transition from \( \alpha \)-AgI to \( \beta \)-AgI is very sharp, and the disappearance of the low-frequency mode at 17 cm\(^{-1}\) occurs within 1 K. However, gradual changes in Raman spectra have been observed in other solid state electrolytes, such as SrCl\(_2\), PbF\(_2\), and Ag\(_{25}\)I\(_{18}\)WO\(_{45}\).

To investigate further the nature of the changes in the Raman spectra as a function of \( T \), we examine the reduced Raman intensity. This is done in Fig. 3. The reduced Raman intensity \( I_{\text{red}} \) is calculated from the Raman spectra using the equation

\[
I_{\text{red}} = \frac{\omega}{1 + n(\omega, T)} I_{\text{Ram}}(\omega, T), \tag{1}
\]

where \( I_{\text{Ram}} \) is the experimentally observed Stokes Raman data and \( n(\omega, T) \) is the Bose-Einstein factor.

The use of \( I_{\text{red}} \) was found to be useful in several studies. By eliminating the thermal occupation, \( I_{\text{red}} \) involves density of states and frequency dependent matrix elements. Another feature of \( I_{\text{red}} \) is that it is related to the frequency dependent conductivity \( \sigma(\omega) \), a quantity which has been determined theoretically for different models. Both \( \sigma(\omega) \) and \( I_{\text{Ram}} \) of transverse polar phonons are related to the imaginary part of the response function. From the fluctuation-dissipation theorem, we have

\[
\sigma(\omega) = \frac{\omega}{4\pi} \epsilon''(\omega) \tag{2}
\]

and the Raman intensity is given by

\[
I_{\text{Ram}} = A(1 + n(\omega, T))\epsilon''(\omega), \tag{3}
\]

where \( A \) is a constant to a good approximation under nonresonant conditions. From Eqs. (1)–(3), one finds

\[
\sigma(\omega) = \frac{\omega}{4\pi A} I_{\text{Ram}} - \frac{1}{4\pi A} I_{\text{red}}. \tag{4}
\]

This relation between \( \sigma(\omega) \) and \( I_{\text{red}} \) is not only useful for comparing the Raman results with theoretically determined \( \sigma(\omega) \), but it also reveals an important feature for \( I_{\text{red}} \). It is trivial to show that if \( \epsilon''(\omega) \) is the response function of a harmonic oscillator with damping \( \Gamma \) and harmonic frequency \( \omega_0 \), then, from Eq. (2), \( d\sigma/d\omega = 0 \)

![FIG. 3. Reduced Raman spectra for low energy modes of Ag\(_{25}\)I\(_{18}\)WO\(_{45}\).](image-url)
at \( \omega = 0, \pm \omega_0 \). Therefore, \( I_{\text{red}} \) peaks at \( \omega_0 \) regardless of \( T \). The analysis of \( I_{\text{red}} \) can be useful in determining whether the modes soften or overdamp.

Since no infrared intensity data exist for Ag\(_{26}I_{16}\)WO\(_{16}\), we cannot evaluate the coefficient of proportionality between conductivity \( \sigma(\omega, T) \) and \( I_{\text{red}}(\omega, T) \), and we cannot examine the hypothesis that the two low-frequency modes shown in Fig. 2 produce most of the ionic conductivity. Note in Fig. 3 that there is a third low-frequency mode near 50 cm\(^{-1}\) below \( T_2 = 285 \) K. This mode is quite weak and not noticeable in Fig. 2. Figure 3 shows one important point: The dominant temperature effect in the low frequency response of Ag\(_{26}I_{16}\)WO\(_{16}\) is an increase in damping \( \Gamma(T) \) with increasing \( T \); there is no significant "softening" of the mode frequency \( \omega(\Gamma) \) with temperature changes near \( T_1 \) or \( T_2 \). This indicates that the individual potential wells in which Ag\(^+\) ions sit do not change much with \( T \), but that the tunneling probability from well to well increases dramatically as \( T \) increases, i.e., the dwell time decreases. This phase transition is thus of the order–disorder variety, or, more correctly, disorder–disorder, since the Ag\(^+\) ions are disordered in all phases, but the degree of disorder increases with increasing \( T \).

There are two separate contributions to the quasielastic scattering in ionic conductors. When \( T \) increases and the energy barrier between Ag\(^+\) sites decreases, the Ag\(^+\) sublattice becomes more disordered. Vacancies and interstitials change the polarizability of nearby ions and produce a \( T \)-dependent defect-induced Raman spectrum.\(^{21}\) This is essentially a static effect. A second source of this scattering is a dynamical contribution due to the motion of Ag\(^+\) ions between vacant sites.\(^{22,23}\) These fluctuations in polarizability are due to particle diffusion and yield a linewidth for quasielastic scattering related to the diffusion constant \( D \) and the hopping distance \( l \) by:\(^{22,24}\)

\[
\Gamma(T) = 1/T_{\text{rel}} = 2D/l^2.
\]

Application of Eq. (5) to our data at \( T = 350 \) K yields a Ag\(^+\) ion diffusion constant of order \( 10^{-4} \) cm\(^2\)/s, which may be compared with \( 10^{-6} \) in Ag\(_2\)I at 180 °C.\(^{25}\) (This estimate uses a 3 Å jump distance \( l \) and a 15 cm\(^{-1}\) linewidth.) We believe that, in this high-temperature regime, the quasielastic scattering is diffusion dominated, whereas, below room temperature, the quasielastic scattering is primarily static, defect induced. This conclusion follows from the continuous evolution of the low-frequency modes from propagating waves below 200 K to overdamped diffusion above 300 K.

**B. Alternating current conductivity and capacitance measurements**

Measurements of conductivity \( \sigma(T) \) and capacitance \( C(T) \) were done in the temperature range 150–350 K. The results at 1 kHz are shown in Fig. 4. The behavior of \( C(T) \) is rather interesting. \( C(T) \) increases with \( T \), passes through a maximum near 198 K, and then decreases; this is similar to the normal manifestations at a ferroelectric phase transition, and it is quite possible that 198 K is indeed the Curie temperature for an order–disorder transition which can be described as ferroelectric. The decrease in \( C(T) \) persists up to about 240 K, where \( C(T) \) begins to increase again; a rapid divergence is observed above \( T_2 = 285 \) K. The dip in \( C(T) \) is affected by laser irradiation; a deeper dip is observed in the presence of laser light. Presumably, this is due to photoexcited Ag\(^+\) recombination. The conductivity \( \sigma(T) \) exhibits changes with \( T \) similar to those of \( C(T) \), although there is no peak at \( T = 198 \) K, only an inflection point. The ionic conductivity follows an Arrhenius equation

\[
\sigma(T) = (\sigma_0/T)e^{E/RT},
\]

where

\[
\sigma_0 = (1/3b)(Ze)^2\rho\omega_gJ^2
\]

with \( l \) the jump distance, \( \rho \) the concentration of mobile ions, \( \omega_g \) the attempt frequency, and \( k \) is Boltzmann's constant. The activation energy \( E \) can be obtained by plotting \( \log(\sigma T) \) versus \( 1/T \), as shown in Fig. 5. For temperatures below 199 K, we find from Fig. 5 a well-defined activation energy of 2.4 eV. This is a very large energy and is comparable to that observed in ionic insulators. In the intermediate temperature range 199 ≤ \( T \) ≤ 285 K, we find a very small activation energy of 70 meV; this is comparable to the value we observed earlier\(^{19}\) in Ag\(_2\)WO\(_{16}\), which is not an ionic conductor. Above 285 K, we find an activation energy of 0.42 eV, comparable to the value in BaMnF\(_4\) at low temperatures.\(^{26}\) Our value 0.42 eV for the high-temperature activation energy is comparable to the value of \( E = 0.18 \) eV obtained in Ref. 6 from a polycrystalline sample.

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**FIG. 4.** Conductivity and capacitance changes at 1 kHz as functions of \( T \) in Ag\(_{26}I_{16}\)WO\(_{16}\) for 150 ≤ \( T \) ≤ 300 K.
The thermodynamical calculations of Rice et al.\textsuperscript{29} and Huberman\textsuperscript{30} were recently extended by Gurevich and Kharkats,\textsuperscript{31} who distinguished between the number of energetically equivalent interstitial sites $N'$ and the number of sites $N$ of the disordered lattice. Their expression for the concentration of mobile ions $\rho$ is given by

$$\frac{kT}{\lambda} = \frac{\beta - \rho(T)}{\ln[Rp^{-1}(T)](1 - \rho(T))},$$

(8)

where $\beta = \epsilon_0/\lambda$; $R = \prod_{j}(\omega_j/\omega_j')^N/N'$; and $\omega_j$ and $\omega_j'$ are the localized interstitial vibrational frequencies and those of the perfect lattice, respectively. Abrupt changes in $\rho(T)$ occur at phase transitions. $\rho(T)$ and thus $\sigma(T)$ may increase or decrease after passing through transition temperatures. Equation (8) predicts the possibility of two critical temperatures as observed in our experiments; several possible mathematical solutions for $\rho(T)$ are given in Ref. 31.

Any model calculation we employ for Ag$_{24}W_4$O$_{16}$ should explain the following observations: (1) a peak in the dielectric constant and an inflection point in the conductivity at 199 K; (2) the overdamping of one low-frequency Ag$^+$ vibration at 199 K; (3) a decrease in conductivity in the 200–285 K region when the sample is laser illuminated at 514.5 nm; and (4) diverging conductivity above 285 K, and the overdamping of two low-energy Ag$^+$ modes at that temperature.

It would be desirable, in the attempt to explain the four phenomena above, to obtain the following additional data: (1) specific heat measurements from about 150–350 K; (2) x-ray structural determination of crystal changes near 199 and 285 K; (3) directional measurement of conductivity to reveal anisotropy in $\sigma(T)$ near 199 and 285 K. (The latter measurements are underway.\textsuperscript{29})

In the absence of such independent data, let us consider the origin of the low-frequency vibrations at 20, 35, and 51 cm$^{-1}$ shown in Figs. 2 and 3. The simplest hypothesis is that these modes are translation-like vibrations of the Ag$^+$ ions along three different directions. (The low $C_2$ point group symmetry of the crystal permits no degeneracies, and so three distinct modes would be expected.) Suppose that, at 199 K, the Ag$^+$ ions become free to move along the $x$ axis, but that motion in the $yz$ plane is restricted until 285 K. In this case, the conduction between 199 and 285 K would be relatively independent of temperature, and a "plateau" in the conductivity plot shown in Fig. 5 would be manifest. In addition, this hypothesis would require one Ag$^+$ vibrational mode to become overdamped at 199 K, whereas the other two modes would not become diffusive until 285 K. These predictions are in accord with the Raman measurements summarized in Figs. 2 and 3. If this model is correct, it can be verified by measurements of the anisotropy in electrical conductivity over the temperature range 150–350 K; it predicts that the conductivity anomaly shown in Fig. 4 at 199 K will be much greater along one particular (but undetermined) axis, and that the conductivity divergence above 285 K will be essentially isotropic. The requisite conductivity anisot-

\[\text{FIG. 5. Conductivity at 1 kHz for Ag}_{24}W_4O_{16} \text{ with and without 50 mW laser irradiation at 514.5 nm} \text{ plotted.}\]
ropy measurements to test this hypothesis are underway. An alternative hypothesis is that there are two classes of Ag⁺ sites and that ions at one of these become mobile at 199 K, whereas the others become mobile at ~285 K.

We believe that the decrease in conductivity with laser illumination has a simple explanation. This conductivity decrease is accompanied by visual darkening at high laser powers, and it probably arises from photoexcited electrons which combine with Ag⁺ ions to yield neutral Ag atoms, thus decreasing the number of mobile charged ions in the system.

IV. SUMMARY

We have presented Raman data on Ag₂₅₀₁₆W₄O₄₆ over the temperature range 154–350 K, together with dielectric and conductivity data which confirm the presence of phase transitions in the vicinities of 199 and 285 K. The transitions are of the order–disorder type and appear highly continuous, in contrast to those in other silver-based solid electrolytes. Two hypotheses are suggested as explanations of the data: They assume in one case two separate classes of Ag⁺ ions with different binding energies, or, in the other case, a single class of Ag⁺ ions with highly anisotropic vibrations. Additional experiments are suggested which might permit selection between the two models.

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