Ferroelectric phase transition in the superionic conductor Ag$_{29}$I$_{18}$W$_4$O$_{16}$

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An analysis of the dielectric measurements for the ferroelectric phase transition in the superionic conductor Ag$_{29}$I$_{18}$W$_4$O$_{16}$ is reported. The transition is interpreted as being slightly first order, with a hysteresis region less than 2.5°C in width. The system obeys Curie-Weiss dependences in both phases, with the dielectric constant satisfying the equation

$$\varepsilon^{-1}(T) = 0.94 \times 10^3 (T - 160°C)$$

in the paraelectric phase and

$$\varepsilon^{-1}(T) = 1.38 \times 10^2 (200.5°C - T)$$

in the ferroelectric phase. The ferroelectric transition is of the order-disorder-type and involves mobile silver ions. The frequency dependence of ionic conductivity has been measured in the high temperature phase. From 0.5 to 10.0 kHz it satisfies $\sigma(\omega)$ proportional to $\omega$ in contrast to the $\omega^2$ dependence predicted by Lines.

**INTRODUCTION**

Recently we reported the presence of a ferroelectric phase transition in the superionic conductor Ag$_{29}$I$_{18}$W$_4$O$_{16}$. The dielectric measurements included in that paper showed that the transition at about 199 °K was ferroelectric, with a lambda-shaped divergence in the 1 kHz dielectric response; accompanying Raman spectroscopic data showed further that the transition was of the order-disorder character, as manifest by the overdamping of a low energy silver ion vibration at 199 °K and by the lack of any "soft" mode characteristic of displacive phase transitions.

In our earlier paper we reported that all of the data, including Raman spectra, electrical conductivity, and dielectric measurements, were compatible with interpretation of the phase transition as second-order. In the present work we provide a more detailed analysis of the dielectric data. It shows that the phase transition is slightly first-order, with a transition temperature of 199.0 °K encountered upon heating and a transition temperature of about 198.0 °K upon cooling. Curie-Weiss dependences are observed in both ferroelectric and paraelectric phases.

This is the first ferroelectric phase transition known to the authors to be reported for a superionic conductor. The observation may be of some practical importance to the authors to be reported for a superionic conductor. Inasmuch as Ag$_{29}$I$_{18}$W$_4$O$_{16}$ has room temperature ionic conductivities comparable to those in RbAg$_{4}$I$_{5}$, and chemical stability suitable for device fabrication; in fact, Sanyo markets this material as the electrolyte in its "Memoriode" batteries used for memory and timing application. In addition, because the order-disorder phase transition involves the silver ions, its analysis plays a key role in understanding the conduction mechanism in this electrolyte; further, our analysis shows that Ag$_{29}$I$_{18}$W$_4$O$_{16}$ cannot possibly function as a solid state ionic conductor below $T_e=199$ K, which may be of interest in designing solid state batteries with lower operating temperatures.

Because of the difficulty in demonstrating switching of spontaneous electric polarizations in conducting ferroelectric crystals, we employ in the present work the microscopic definition of ferroelectricity based upon lattice dynamical properties (in particular, the instability of a polar optical phonon). This definition has also been applied in the case of several ferroelectric metals, notably the tungsten bronzes, for which the usual technique of demonstrating ferroelectricity via applied electric switching fields is impossible.

The phase transition near 199 °K to be analyzed below is very nearly second-order. For such transitions in ionic conductors Lines' recent theories predict a diverging conductivity. In Ref. 1 we found increases in ionic conductivity of more than one order of magnitude in Ag$_{29}$I$_{18}$W$_4$O$_{16}$ at each of two transitions (near 199 and 285 °K). The theory of Ref. 4 predicts a conductivity divergence proportional to $(T_e-T)^{-1}$; the data of Ref. 1 are in only rough accord with this hypothesis below $T_e=199$ °K, and show no decrease above $T_e$.

The conductivity data were shown to be of form $\sigma(T) = (\sigma_\theta/T)e^{E/4T}$ in Ref. 1 with $E=2.4$ eV and $\sigma_\theta=5 \times 10^2$ (K ohm$^{-1}$ cm$^{-1}$) below $T_e=199$ °K. Plots of $\sigma^2(T)$ vs $T$, which in Lines' theory yields a straight line, show that the dependence is of Arrhenius form and not Curie-Weiss.

**EXPERIMENT AND ANALYSIS**

The experimental details were provided in Ref. 1. Measurements were made from 0.5 to 10 kHz. Data provided in Ref. 1 and in the present work were obtained from small single crystals. The point group

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symmetry in this material is quite low; even in the paraelectric phase it is \(C_2\), and in the ferroelectric phase there are probably no symmetry elements (\(C_1\) point group). Measurements were made along directions perpendicular to the \(C_2\) axis of the paraelectric phase of the crystals. These data are summarized in Fig. 1. This figure shows that the dielectric data in each phase obey a Curie-Weiss dependence. Below 199 \(^\circ\) K the observed dependence is given by Eq. (1),

\[ \varepsilon^{-1}(T) = 1.38 \times 10^{-2} (200.5 \, ^\circ\text{K} - T) \]  

The dependence above 200 \(^\circ\) K is given by Eq. (2)

\[ \varepsilon^{-1}(T) = 0.94 \times 10^{-3} (T - 160 \, ^\circ\text{K}) \]  

where the capacitance \(C(T)\) is proportional to the dielectric constant \(\varepsilon(T)\). That is, the Curie temperature is 160 \(^\circ\) K. Despite the large difference between the extrapolated temperatures at which the dielectric constants would diverge in the paraelectric and ferroelectric phases (160 and 200.5 \(^\circ\) K), there is no direct evidence of hysteresis in our work. Nevertheless, the data show that the system cannot be described as a second-order, mean-field phase transition. Whereas the critical exponents given empirically in Eqs. (1) and (2) are mean-field, viz.,

\[ \varepsilon^{-1}(T) = A(T - T_\varepsilon)^\gamma \]  

exhibits \(\gamma = 1.0\), in accord with predictions, the coefficients \(1.38 \times 10^{-2}\) and \(0.94 \times 10^{-3}\) are not in the right relationship (mean-field theory requires\(^5\) a ratio of 2.0, in contrast to the observed ratio of 16.7), and the extrapolated Curie temperatures of 160 and 200.5 \(^\circ\) K are very different.

These are interpreted in terms of a first-order, mean-field transition in Fig. 1. There are a total of four characteristic temperatures in this description. The temperature \(T_P = 200.5 \, ^\circ\text{K}\) is the transition temperature extrapolated from the ferroelectric phase, assuming a second-order phase transition. Similarly, \(T_E = 160 \, ^\circ\text{K}\) is the transition temperature extrapolated from the paraelectric phase, assuming a second-order phase transition. \(T_H\) is the observed phase transition temperature upon heating, equal to 199.0 \(^\circ\) K in our samples. \(T_S\) is the observed phase transition upon cooling. It depends upon the cooling rate and therefore is difficult to measure accurately experimentally. We assign it as 198.0 \(^\circ\) K, the temperature at which the dielectric constant extrapolated from the paraelectric phase equals that at the same temperature in the ferroelectric phase. This temperature is necessarily a lower bound upon the actual value of \(T_S\) and corresponds to infinitely slow cooling; the hysteresis width has an upper limit of 2.5 \(^\circ\) K for the actual region of coexistence of paraelectric and ferroelectric domains, from 198.0 to 200.5 \(^\circ\) K.

**FREQUENCY DEPENDENCE**

In two recent papers\(^4\), \(^5\) Lines has presented the models for the frequency dependences of the dielectric response and ionic conductivity of ionic conductors. At low frequencies his theory predicts, for systems like ours with blocking contacts (we used gold electrodes), that the dielectric constant will be independent of frequency and that the conductivity will be proportional to frequency squared. Above a characteristic frequency designated \(\omega_U\) in his theory the ionic conductivity saturates at a constant bulk value, whereas the dielectric constant drops rapidly from its blocked, low frequency value with a \(\omega^{-\delta}\) dependence.

The data required to verify Lines' theory for a particular ionic conductor are capacitance and conductivity data over many decades of frequency. In the present study we were able to make such measurements only from 500 Hz to 1 kHz. These data are presented in Fig. 2. The data in Fig. 2 are for the highest temperature employed in our work (310 K). At this temperature the ionic conductivity of powdered specimens of \(\text{Ag}_2\text{Rb}_3\text{W}_{18}\text{O}_{46}\) is about 0.08 (ohm cm\(^{-1}\)).

The conductivity data in Fig. 2 may be fitted to a power law dependence of form \(\sigma(\omega) = a \omega^b\); the exponent \(b\) is found to average 0.8 \pm 0.1 over the range 500 Hz to 1 kHz and to be 1.0 \pm 0.1 in the small frequency limit. This is in contrast to the predicted value of 2.0 for the low frequency region in Lines' theory.\(^5\) The same value of 1.0 was found experimentally for \(\text{Ag}_2\text{Rb}_3\text{W}_{18}\text{O}_{46}\) in the work of Armstrong and Taylor\(^1\) and attributed by Lines\(^5\) to be due to a dominance of a resistive surface layer in the measured admittance of the system. The conductivity data of Fig. 2 show a slight rounding; that is, the frequency dependence becomes sublinear at the highest frequencies.

**FIG. 1.** Reciprocal dielectric susceptibility as a function of temperature for \(\text{Ag}_2\text{Rb}_3\text{Ag}_2\text{W}_{18}\text{O}_{46}\) for both ferroelectric and paraelectric phases. The solid lines are theoretical mean-field predictions from Eqs. (1) and (2). The observed value of the transition temperature upon heating is 199.0 \(^\circ\) K and is only slightly less than the extrapolated Curie temperature of 200.5 \(^\circ\) K. The estimated transition temperature upon cooling is 198.0 \(^\circ\) K and is taken as the temperature at which dielectric constants in the paraelectric and ferroelectric states would become equal; it is significantly higher than the value \(T_P = 160 \, ^\circ\text{K}\) extrapolated as the Curie temperature from dielectric data in the paraelectric \(C_2\) symmetry phase.
measured frequencies. This is compatible with the measured decrease (of 30% from 0.5 to 10 kHz) in the dielectric constant; in Lines' theory both effects indicate that applied frequencies are approaching the characteristic frequency $\omega_0$ at which the capacitive response becomes unblocked. Our data suggest that $\omega_0$ lies at a frequency of order 50 kHz in $\text{Ag}_2\text{6I}_{18}\text{W}_{40}\text{16}$ at 310 K. Approximately the same value has been reported for $\text{Ag}_4\text{RbI}_{18}$.

The fact that Lines' theory yields $\sigma \propto \omega^{2}$, whereas the data for both $\text{Ar}_2\text{6I}_{18}\text{W}_{40}\text{16}$ and $\text{Ag}_4\text{RbI}_{18}$ yield $\sigma \propto \omega^{4}$, seems to us to be too great a difference to be accidental. In very recent work one of us has shown, using response theory, that the imaginary part of the susceptibility $\chi^{''} (\omega)$ for solid electrolytes will vary as $\omega^4$ with $n \approx 1$ under certain reasonable conditions. $n$ is exactly equal to 1.0 under the assumptions that energy diffusion is dominated by exchange of energy within the system of mobile ions (and not with their surroundings) and that the frequency range measured has a maximum $f$ less than a characteristic length given by

$$f \ll D / l^2$$

where $D$ is the silver ion diffusion coefficient (about $10^{-4}$ cm$^2$ sec$^{-1}$ for $\text{Ag}_2\text{6I}_{18}\text{W}_{40}\text{16}$ at 350 K) and $l$ is the ion jump length, estimated from Raman data [Eq. (5) of Ref. 1] as 3 Å. Thus, for $f \ll 10^{11}$ Hz in our system we expect to observe $\chi^{''} (\omega)$ proportional to $\omega$, and $\sigma (\omega)$ proportional to $\omega^{2}$, in agreement with Lines'. This, however, is an upper limit on the frequency exponent and can be reduced but not increased by boundary conditions and dimensionality of the local system. Under the assumptions that energy exchange between silver ions and their surroundings is dominant, and where the silver ion diffusion is highly anisotropic Habbal obtains $\chi^{''} (\omega) = \text{const}$ and thus $\sigma (\omega)$ proportional to $\omega^{1.5}$, in accord with the data of Fig. 2 and Ref. 7.

**SUMMARY AND CONCLUSIONS**

A quantitative analysis of the observed dielectric data in $\text{Ag}_2\text{6I}_{18}\text{W}_{40}\text{16}$ shows that the transition is slightly first-order. The hysteresis region inferred from the analysis is 198.0 to 200.5 K. This region is small, even in comparison with transitions such as that in quartz where historically there was doubt concerning the order of the transition. This (the hysteresis region is approximately 3 K in quartz).

The system appears to be mean-field in both paraelectric and ferroelectric phases. In disagreement with Lines' theory, the ionic conductivity near $T = 200.5$ K diverges not as $(T_p - T)^{-\alpha}$, but as $\sigma (T) = (\sigma_0 / T) e^{-E/RT}$.

The frequency dependence of the conductivity in the high temperature conducting phase yields $\sigma$ proportional to $\omega$, as in $\text{Ag}_4\text{RbI}_{18}$, in contrast to the $\omega^2$ dependence predicted in Lines' theory. This agrees with the theoretical results of Habbal.

**ACKNOWLEDGMENT**

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2See J. F. Scott, Rev. Mod. Phys. 48, 83 (1974). The term "ferroelectric metal" was originally suggested by B. Matthias, private communication.