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Makariy A. Tanatar [a b]

[a] Institute of Surface Chemistry, N.A.S. of Ukraine, Kyiv, 252026, Ukraine

[b] Dept. of Physics, Kyoto University, Kitashirakawa, Sakyoku, Kyoto, 606-8502, Japan

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Light Interference Study of Superionic Transition in Synthetic Metal – Solid Electrolyte Hybrid $(BEDT\text{-}TTF)_3Ag_xI_8$

MAKARIY A. TANATAR*

Institute of Surface Chemistry, N.A.S. of Ukraine, Kyiv, 252026 Ukraine

First order phase transition at 163–172 K is found in the $(BEDT\text{-}TTF)_3Ag_xI_8$ compound in close vicinity to the temperature range of superionic conductivity. This observation indicates formation of the mobile silver ions in the salt as a consequence of sublattice melting.

Keywords: superionic conductors; phase transition; birefringence; BEDT-TTF

INTRODUCTION

The charge transfer salt $(BEDT\text{-}TTF)_3Ag_xI_8$ [BEDT-TTF, or ET, is bis(ethylenedithio)tetrathiafulvalene] is known as the first synthetic metal exhibiting properties of a solid electrolyte [1,2]. At room temperature Ag^+ ion conductivity σ_i of the salt is in the $10^{-3}\,\Omega^{-1}cm^{-1}$ range, while the electronic conductivity σ_e is 7 to $10\,\Omega^{-1}cm^{-1}$. Both σ_i and σ_e are sensitive to the stoichiometry index x.

The mechanism of superionic state formation in the salt is not known at present. At room temperature Ag ions fill randomly only a part of available positions, forming silver ion sublattice in the crystal lattice [1]. It is not clear, however, whether this disorder in distribution is retained at low temperature (as in point-defect superionics [3]), or it is created only on heating, as a result of a phase transition (so called sublattice melting [3]). Existing data does not allow

* Address at present: Dept. of Physics, Kyoto University, Kitashirakawa, Sakyoku, Kyoto 606–8502, Japan

discrimination of these possibilities. σ_i was detected above ca 180 K via resistance transient [2], however its behavior at lower temperatures can be obscured by $\sigma_e >> \sigma_i$. On the other hand, $\sigma_e(T)$ dependence shows slope change at ca 160 K, indicative of a possible phase transition [2]. These measurements are rather indirect, since the change in the ion system is probed through associated change in the electronic properties, caused by local variation of stoichiometry and disorder. The results of the study of superionic phase transition in the salt with the help of temperature dependence of refractive index and its anisotropy (birefringence) are presented in this article. We show that the salt undergoes first order phase transition very close in temperature to first manifestation of superionic properties, implying superionic state formation through sublattice melting.

EXPERIMENTAL

The refractive index n is an important parameter characterizing a material. It has a specific value for a pure substance and is widely used in analytical chemistry for identification of products, analysis of binary mixtures and study of phase transitions [4]. A birefringence is a difference of the refractive indices for extraordinary n_e and ordinary n_o rays, $\Delta n = n_e - n_o$, in an anisotropic medium, and thus in an analytical sense is identical to the refractive index. However, a measurement of birefringence is characterized by high precision due to interference effects involved. It easily gives an accuracy, hardly obtained for n, especially for small size single crystals. Both techniques are based on an analysis of refractive index temperature dependence. In case of first-order phase transitions $n(T)$ shows jump-like changes. For the second-order transitions slope changes should be observed.

Crystals of the $(ET)_3Ag_xI_8$ were grown by a standard electrochemical technique [2]. Thin samples appeared as dark-red. The absorption within the sample is anisotropic, we designate the directions of high and low absorption as $\parallel$ and $\perp$ in the following.

The birefringence studies were performed in 4.2 to 300 K range by a standard compensation technique [5] at 632.8 nm, corresponding to the transparency window in the crystal absorption. The temperature variation of the refractive index was estimated from the interference maxima position change with temperature [6]. Due to low absorption in the sample, especially in the near infrared region, the reflectance is dominated by interference of radiation

reflected on the front and the rear sample surfaces. This results in an interference structure of periodic maxima and minima [Fig.1(a)], most notable for low absorption $\perp$ polarization. The positions of these maxima are determined by relation $2nd+\phi=m\lambda$, here d is sample thickness, m is integer, λ is wavelength of light, and ϕ is an additional phase shift between the front and the rear sample surfaces, caused by absorption in the sample. Thus, positions of these maxima reflect temperature dependence of n, and their variation with temperature can be used for the study of phase transition.

RESULTS AND DISCUSSION

Fig.1(b) shows change of the position of interference maximum, denoted by arrow in Fig.1(a), with temperature. The dependence is not monotonic and shows two slope changes, indicating phase transitions at around 140 and 200 K. However, the experimental scatter of the data is rather large, since the maximum is not quite sharp.

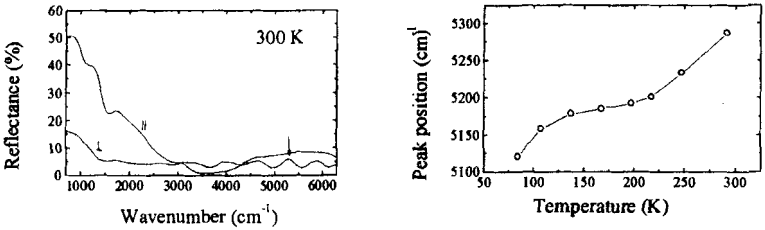
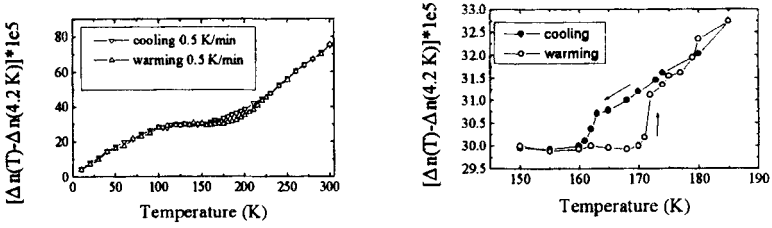


FIGURE 1 Room temperature polarized reflectance spectra for the $(ET)_3Ag_xI_8$ thin crystal (a) and temperature dependence of the interference maximum position (b).

More precise picture can be obtained from the birefringence studies (Fig.2). In the vicinity of the superionic transformation $\Delta n(T)$ is sensitive to the thermal

cycle, namely to the temperature sweep rate and direction [Fig.2(a)]. Fig.2(b) was obtained in the quasi-equilibrium conditions. The data were taken after holding the sample for 15 min at each temperature. In this case Δn(T) shows two hysteresis branches and jump-like changes above (at ca 172 K on warming) and below (at ca 163 K on cooling) real transition. The behavior is typical to the first order phase transition. Since the superionic conductivity appears at temperatures above this transition, and disorder in the Ag sublattice is observed by X-ray at room temperature [1], it is natural to relate the transition with the silver sublattice melting.



(a) (b)

FIGURE 2 Temperature dependence of birefringence measured on cooling and warming (a) and expanded transition region measured in quasi-equilibrium conditions (b).

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