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Phase transition and the Ag^+-ion diffusion in AgI: Effect of homovalent Br^--ion substitution

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The incorporation of Br^- ions in β-AgI leads to an *anomalously* large increase in the ionic conductivity (σ_{Ag^+}) and hence in the self-diffusion coefficient of Ag^+ ions (D_{Ag^+}) as well as a *substantial* decrease in the first-order (β-α) phase-transition temperature (T_c). The effect of substitution is found to be qualitatively analogous to that of pressure (P), and is attributed to purely elastic displacement (lattice distortion) caused by the "wrong" size of the substituent ($r_{Br^-} < r_{I^-}$). It is concluded that the order-disorder transition is essentially driven by a critical concentration of Frenkel defects (n_{ci}) beyond which the hexagonal β-AgI becomes unstable and transforms to disordered bcc α-AgI, a behavior consistent with the theory of Rice, Strassler, and Toombs of phase transitions to superionic conductors.

INTRODUCTION

A large number of solids are now known to exhibit ionic conductivities comparable to those of melts or liquids (~1 $ohm^{-1} cm^{-1}$). These so-called superionic conductors (SIC's) or solid electrolytes have received widespread attention mainly for two reasons: (1) they promise applications in high-energy-density batteries and (2) they exhibit unusual transport behavior. Of these, Ag^+-ion conductors are most numerous and also of special interest. Most of the Ag^+-ion based SIC's undergo unique order-disorder (or insulator → SIC) transitions.[1] Some of these are first order while others are second- or higher-order transitions.

Despite the substantial effort in the past decades, α-AgI (stable ≥ 147 °C) remains the best SIC available. Moreover, a number of puzzling features are still not understood. For example, in order for α-AgI (or for that matter any SIC) to exhibit a $\sigma \sim 1\ ohm^{-1} cm^{-1}$, almost all of the Ag^+ ions present in the crystal, according to one estimate,[1] must move and contribute to conductivity. Then the question is, does the classical concept of interstitials and vacancies still apply? There is no widely accepted point of view. The extensive microwave, ir, and neutron diffraction measurements[2] point out that the mobile ions actually spend less time in a particular lattice site than they do during hopping between different sites, i.e., residence time < flight time. A recent extended x-ray absorption fine-structure (EXAFS) study[3] does not necessarily support the above view. A close inspection of the entropies of melting and some of the solid → solid transitions strongly suggests[4] the molten or liquidlike sublattice of the mobile species in the SIC phase.

Another question is why some of the SIC's undergo phase transitions and others do not, and what is the driving force? Pardee and Mahan[5] point out an Ising-type behavior for, e.g., the second-order 208-K transition in $RbAg_4I_5$ while Salamon[6] suggests a Jahn-Teller-type transition. Regarding the first-order (e.g., at 420 K in AgI) transitions, Rice, Strassler, and Toombs (RST)[7] proposed that the interaction between the (Ag^+) interstitials and the strain field they produce by emptying the regular lattice sites, essentially drives the transition. This model requires unusually large values of activation volumes (ΔV) of the defects below T_c, and is approximately satisfied for AgI. ΔV is given by

$$\Delta V = \tfrac{1}{2}\Delta V_f + \Delta V_m , \qquad (1)$$

where ΔV_f and ΔV_m are, respectively, the activation volumes of formation and migration of the defects, and both are derived from σ versus pressure (P) measurements. Recently Allen and Lazarus[8] have extended the σ vs P studies to $RbAg_4I_5$ and also supplemented the earlier data on AgI and found some interesting results, including the unusually large activation volume for γ-$RbAg_4I_5$ which supports the RST model.[7] Furthermore, Fujimoto *et al.*[9] studied T_c as a function of P for KAg_4I_5 and $NH_4Ag_4I_5$. While T_c's show substantial dependence on P, σ's vary only a little[8] (~10% in 6 kbar) with P, as expected, especially in SIC phase where almost all Ag^+ ions are already disordered and contributing to conduction; therefore additional forces (such as pressure, etc.) cause only nominal changes. Applying pressure causes the lattice parameters to contract, thus allowing the short-range forces to interact more closely. The effect of substituting Br^- (or Cl^-) ions in AgI is similar and therefore the effect of this substitution on the T_c and diffusivity of the Ag^+ ions in AgI was studied.

EXPERIMENTAL

High-purity (99.999%) AgI and AgBr from Apache Chemicals were used as received. Because of the high plasticity of AgBr, it was extremely difficult to pulverize it to obtain a fine powder. The appropriate amounts of AgI and AgBr were therefore directly transferred from the weighing paper to the quartz tube, sealed under vacuum (~ 10^{-3} mm Hg), heated to melt (at ~ 600 °C), shaken a number of times to ensure the homogeneity of the samples, followed by quenching to room temperature. When the sample was largely AgI ($\geq$ 80 mole%, the range investigated in this paper), it was easily separated from the quartz container, possibly because the 6% volume expansion on going from α to β (low-temperature) phase, and also an unusual negative expansion coefficient of hexagonal β-AgI resulted in the breaking of the quartz tube. The AgBr-rich compositions were not only difficult to pulverize but also difficult to remove from the container. The powdered sample was compressed at pressures of the order of 70 to 80 kpsi in a nickel-plated steel die at room temperature. The pellets thus obtained had an area of 0.71 cm^2 and thickness of 4 to 6 mm. High-purity silver paint (Structure Probe, Inc.) was used as electrodes which provided highly reproducible conductance data (±5%). The impedance meter and its supplemental frequency generator and matching null-point detector, the furnaces, and the temperature control and measurement systems are described in detail elsewhere.[10] The temperature control was better than ± 0.5 °C over extended periods of time (4–6 hours). Since the conductivity changes discontinuously (first order T_c) by a factor of about 10^4 at the T_c, a careful and controlled measurement of σ vs T leads to the accurate determination of T_c's. Approximate values of T_c were first determined in a rapid heating and cooling run. In the following run T_c was then approached at extremely slow heating and cooling rates ($\leq$ 0.5 °C per minute), slow enough to ensure that there is no thermal lag between the sample and the measuring thermocouple, while the change in conductivity was constantly watched. A stage was eventually reached when the conductivity continued to increase while the temperature was practically constant. This temperature was recorded as T_c and the corresponding conductivity as σ_c. The heating-cycle data yielded a higher T_c than those in cooling cycle, as usual, by ~ 2 °C. The actual T_c was obtained by averaging the T_c's of several heating and cooling cycles and on different sets of samples. The absolute values of T_c are accurate to within ± 1 °C while their relative values are much more accurate (± 0.2 °C).

Several samples before and after experiments were examined by x-ray diffraction and the results revealed that the hexagonal β-AgI dissolves $\leq$5 mole% NaCl-type AgBr at 25 °C, while σ vs T studies indicated a solubility of up to 10 mole% near T_c (128 °C). The σ of AgI and AgI-AgBr mixed crystals was also measured as a function of frequency (ω) in the range 50 Hz to 50 kHz at three different temperatures. The $\sigma(\omega)$ dependence was found very nominal, e.g., σ at 50 kHz was ~ 25% higher than at 50 Hz for all compositions (pure AgI or AgI containing Br^-), suggesting that the grain-boundary conduction is not significant.

RESULTS AND DISCUSSION

The self-diffusion coefficient (D) is related to the ionic conductivity (σ) by the simple Einstein equation

$$D_{\text{Ag}^+} = \frac{kT}{nq^2}\,\sigma_{\text{Ag}^+}\,, \qquad (2)$$

where k is the Boltzmann constant, T the absolute temperature, q the electronic charge, and n the concentration (per cm^3) of the defects, which in AgI are the cationic Frenkel defects, hence the subscript Ag^+. Thus any change in σ, which is rather simple to measure, directly reveals the

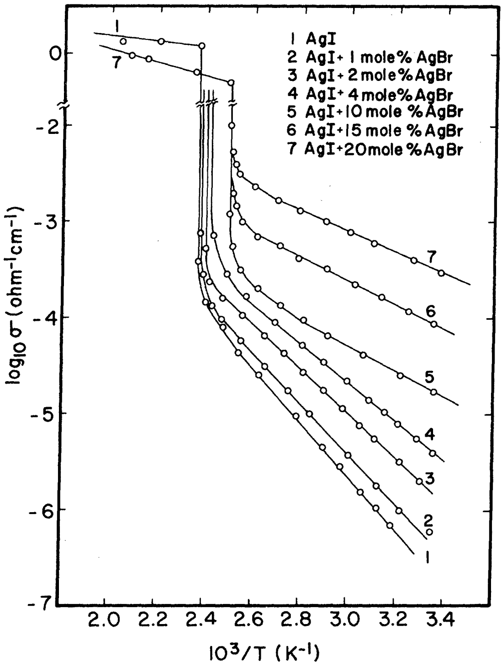

FIG. 1. Logarithm of conductivity ($\log_{10}\sigma$, measured at 1 kHz) as a function of the inverse absolute temperature (K) for AgI and AgI containing 1-, 2-, 4-, 10-, 15-, and 20-mole% AgBr. The compositions AgI + AgBr ($\leq$5 mole%) form complete solid solutions over the entire temperature range investigated, while those AgI + AgBr (between 5 and 10 mole%) do so only at elevated temperatures but below T_c. Note that there is no further decrease in T_c with more addition of AgBr than 10 mole %, indicating that the upper solubility limit of AgBr (in β-AgI) is limited to ~10 mole% at $T \leq 128$ °C.

corresponding change in D. Figure 1 shows the $\log_{10}\sigma$ (at 1 kHz) vs $10^3/T$ plot for the AgI-AgBr system. The results for pure AgI (viz., $\sigma \sim 2.5 \times 10^{-7}$ ohm^{-1} cm^{-1} at 25°C and an activation energy ΔE_a of ~0.56 eV) are very close to those from previous investigations on polycrystals, and also to single-crystal data.[1] β-AgI dissolves up to 5 mole% at 25 °C, so that the compositions AgI + AgBr ($\leqslant 5$ mole%) correspond to a single-phase hexagonal β-AgI (I, Br) mixed crystal throughout the stable temperature range. Since Br^- and I^- ions possess the same charge (so-called homovalent ions), the substitution of one for the other is not expected to have profound effect on the σ (and hence D) or related properties. But, instead, the effects are dramatic (Fig. 1). For instance, the σ of AgI + 4 mole% Br^- is more than an order-of-magnitude larger than that of pure AgI at 25 °C. Equivalent amounts (or even more) of AgCl in AgBr have been found to cause a relatively negligible change[11] in the σ, possibly because both AgCl and AgBr have the same fcc structure and the sizes of Cl^- and Br^- are so close. The effect of further ($\geqslant 5$ mole %) addition of AgBr in AgI leading to *two-phase* mixtures is even more dramatic (~10^3 times enhancement in σ) but is not within the scope of this paper and therefore will appear elsewhere.

The effect of the substitution of I^- ions in AgBr (Ref. 12) is similar but less pronounced. This unusual behavior is attributed to purely elastic displacement (lattice distortion) caused by the very "wrong" size of the substituents leading apparently to lattice "loosening" and consequently to a decrease in the melting point of the mixed crystals, as is generally supported by the experiments. This implies also a decrease in the formation enthalpy (ΔH_f) of the defects, making more defects available, and hence a larger D (or σ). The order (s) of magnitude increase in the σ due to the possible increase in the mobilities (μ) rather than densities (n) of the defects is highly unlikely because the former (μ) is, in general, least affected by such physical forces as those created by pressure, substitutions of aliovalent or homovalent ions, etc. Furthermore, the fact that the σ's have very nominal dependence on frequency (~25% in the range 50 Hz to 50 kHz) for all compositions–pure AgI or AgI + AgBr—indicates perhaps that the grain-boundary conduction also cannot account for the large increase in the σ. Thus it is believed that homovalent (like aliovalent) ions also enhance the σ largely by increasing the defect population, but via lattice strain (or distortion) rather than charge compensation mechanism.

Table I summarizes the T_c's and the ΔE_a's for Ag^+-ion diffusion in AgI:Br^- mixed crystals. As the concentration of Br^- ions increases, the AgI lattice contracts[13] ($r_{Br^-} < r_{I^-}$) leading to increased concentration of Frenkel defects and hence an increased σ. Note also the corresponding decrease in the overall activation energy ΔE_a. This must reflect a decrease in the ΔH_f, because

$$\Delta E_a = \tfrac{1}{2}\Delta H_f + \Delta h_m , \qquad (3)$$

where the migration energy of the defects (Δh_m) is usually small (~15 to 20% ΔH_f), especially in silver halides. The effect of pressure is qualitatively similar to Br^--ion substitution. For quantitative comparison, while 1-kbar pressure increases σ by ~19% at 400 K and ~38% at 294 K, the 1-mole% Br^- increases σ by ~13 and 100%, respectively, at the same temperatures which also reflects the relative difference in their temperature dependences.

The Br^--ion substitution, leading to increased σ and hence to increased defects, yields a decrease in T_c. Figure 2 shows the plot of T_c versus concentration of Br^- ions $[x_{Br^-}]$ in AgI. T_c decreases fairly linearly with the increasing $[x_{Br^-}]$ in accord with the following equation:

$$T_c - T_{c0} = \lambda[x_{Br^-}] , \qquad (4)$$

where T_c and T_{c0} (= 420.5 K) are the β-α transition temperatures of AgI containing Br^- and pure AgI,

TABLE I. T_c and activation energy for Ag^+-ion diffusion in AgI:Br^-. The solubility of AgBr in AgI is strongly temperature dependent. The last three compositions form complete solid solutions only at higher temperatures ($T \geqslant 25$ °C) but certainly $\leqslant T_c$.

Composition (mole% Br^- added to AgI)	T_c (K)	ΔE_a (eV)	Temperature range (°C)
0	420.5	0.56	25–110
1	418.5	0.52	25–110
2	416.0	0.46	25–110
4	412.3	0.40	25–110
6	408.3	0.35	25–100
8	402.5	0.30	25– 90
10	401.0	0.26	25– 85

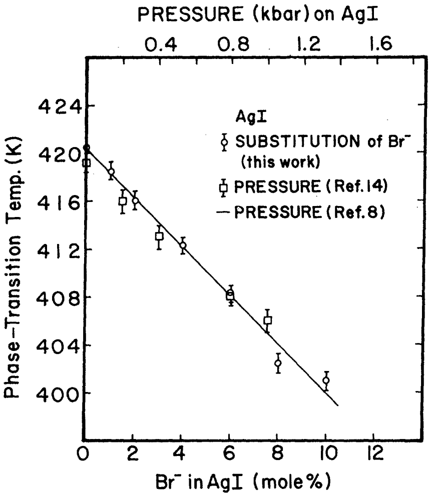

FIG. 2. The first-order (β-α) phase-transition temperature (T_c, K) of AgI:Br$^-$ as a function of the concentration of substitutionally dissolved Br$^-$ ions (mole%) in AgI. T_c's shown above are the averages of T_c's obtained in heating and cooling cycles of conductivity vs temperature measurements (Fig. 1). The vertical bar represents the upper limit of uncertainty (± 1 °C) in the absolute values of T_c. The relative values of T_c are accurate to within ± 0.2 °C. Decreasing T_c with increasing concentration of Br$^-$ ions is perhaps evidence of the fact that the order-disorder transition is essentially driven by a critical concentration of Frenkel defects ($n_{ci} \sim 10^{20}$ cm^{-3}, see the text) which is consistent with the RST model (Ref. 7) of phase transitions to superionic conductors (SIC's). The pressure dependence of T_c is also shown for comparison (Refs. 8 and 14).

and the slope $\lambda = -1.95$ K/mole%. Thus, each mole% of substituted Br$^-$ ions lowers the T_c by ~1.95 K, a total of 19.5 K by about 10-mole% Br$^-$. It should be noted that although hexagonal β-AgI dissolves only ~5-mole% AgBr at 25 °C, its dissolution is much higher (~10 mole%) near T_c (128 °C). The effect of pressure on T_c is also remarkably analogous to that of substitution (see Fig. 2); T_c decreases linearly[8] with P in view of the following equation:

$$T_c - T_{c0} = \lambda P \tag{5}$$

in units of kbar, where the slope $\lambda = -15.66$ K kbar^{-1}. Thus it is believed that the β-α transition is driven by a critical concentration of the Frenkel defects (n_c), beyond which hexagonal β-AgI fails to sustain its form and transforms to cubic α-AgI. It is also interesting to compare the linear compressibilities (κ) due to Br$^-$-ion substitution[13] and to pressure[15]: $\kappa_{\mathrm{Br}} = (1/a)(\partial a/\partial x_{\mathrm{Br}})_{70\,°\mathrm{C}} = 0.46 \times 10^{-3}$ per mole% Br$^-$ and $\kappa_P = (1/a)(\partial a/\partial P)_{25\,°\mathrm{C}} = 1.5 \times 10^{-3}$ kbar^{-1}, which are roughly in the same order as their relative effects on T_c [λ's of Eqs. (4) and (5)].

Ag$^+$ interstitials (in β-AgI) are more mobile than the vacancies,[1,16] and therefore, attributing the conduction to interstitials and using the known temperature dependence[16] of their mobility (μ_i),

$$\mu_i T = 8.3 \times 10^2 \exp(-0.41\ \mathrm{eV/kT}) \tag{6}$$

we get $\mu_{ic} = 2.35 \times 10^{-5}$ cm^2 V^{-1} s^{-1} at $T_c = 420.5$ K in AgI. The σ of AgI just below T_c (Fig. 1) is $\sigma_c = 4.2 \times 10^{-4}$ ohm^{-1} cm^{-1} which, on substitution in $\sigma_c = n_{ci} q \mu_{ic}$, yields the critical concentration of interstitials, $n_{ci} \simeq 1 \times 10^{20}$ cm^{-3}, needed to stimulate the transition. The dissolved Br$^-$ leads to a higher σ and hence higher disorder, and therefore the critical concentration (n_{ci}) is attained at a lower T, i.e., lower T_c. A similar calculation for AgI + 10-mole% AgBr, which transforms at a lower T_c (401 K), leads to a somewhat higher value of $n_{ci} \sim 2.5 \times 10^{20}$ cm^{-3} which is possible in view of the decreased lattice vibrations.

It is interesting to compare the dependence of the σ's and T_c's on pressure[8,9] of SIC's MAg$_4$I$_5$ (M = K, Rb, NH$_4$). MAg$_4$I$_5$ unlike AgI, however, undergo a second-order transition in addition to a first-order transition at lower T. The three different phases, from high T to low, are denoted[8] α, β, and γ. In these systems γ-β is first order while β-α is second order, and therefore it is the former (γ-β) that should be compared with the β-α transition of AgI. In MAg$_4$I$_5$, the (γ-β)T_c is found to be a quadratic function of P; RbAg$_4$I$_5$, for example, satisfies the equation[8]

$$T_c - T_{c0} = aP + bP^2 , \tag{7}$$

where the constants $a = 5.65$ K kbar^{-1} and $b = -0.53$ K kbar^{-2} and other symbols have their usual meaning. Thus T_c increases (opposite that of AgI) initially with increasing P, peaks ~5.33 kbar and then decreases. T_c's of KAg$_4$I$_5$ and NH$_4$Ag$_4$I$_5$ are available over a wider P range and demonstrate further the above [Eq. (7)] behavior. Similarly in Ag$_2$HgI$_4$ the increasing P increases T_c, and hence it appears more common that P increases the T_c's. Equally general seems to be the fact that increasing P usually decreases the σ and hence n, with a few exceptions such as β-AgI. If increasing P decreases the lattice constant, so does the substitution of Br$^-$ in AgI,[13] but they have reverse effects, in general, on σ's and T_c's. This clearly implies that the lattice strain thus produced (leading to volume expansion or contraction) has little influence on T_c's contrary to the previous proposals.[8,9] This could be further verified by studying the T_c versus concentration of other anions larger (in size) than I$^-$ that lead to volume expansion of β-AgI but unfortunately no such anions seem to exist. Alternatively the substitution of different cations (e.g., Na^+, K^+, Rb^+, etc.) should prove useful even if they are known to be "softer" than the anions, and belong to the same sublattice that undergoes the disordering process. However, most of these alkali iodides react with AgI to form such SIC's as KAg_4I_5, $RbAg_4I_5$, etc., rather than forming solid solutions. One is thus left with limited choices, viz., NaI, CsI, etc., provided they dissolve in β-AgI. The ideas presented here and detailed elsewhere[10] predict that the substitutions of foreign ions (larger or smaller than the host ions leading subsequently to expansion or contraction of the lattices) should generally result in lattice distortion leading to more thermal disorder (defects) and hence higher σ's and lower T_c's. Another evidence of this notion is the fact that substitution of Rb^+ in KAg_4I_5 also decreases the T_c (Ref. 17) and so will Na^+, Cs^+, etc., we predict.

In summary, the effects of Br^--ion substitution and pressure in β-AgI are found remarkably similar, i.e., both increase the σ (hence the n) and decrease the T_c, which is compatible with the idea that it is the critical concentration of Frenkel defects (n_{ci}) which is primarily responsible for the first-order phase transitions. To this end, it seems desirable to see if the combined effects of pressure and substitution are additive, which would necessitate the measurement of σ vs P on $AgI:Br^-$ and other mixed crystals. The fact that pressure decreases the σ (hence the n) in γ-$RbAg_4I_5$ (the low-temperature phase), and accordingly increases the T_c's in all three isostructural MAg_4I_5 SIC's provides further support to the above model. It is believed that similar studies on other mixed crystals and of substitution effects in other SIC's (e.g., Ag_3SI, Ag_2HgI_4, MAg_4I_5, etc.), which seem quite feasible, should prove very useful, and would provide further clues to the understanding of the superionic conductivity and the disordering (phase-transition) phenomena.

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