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Defects and Ionic Conductivity in TlCl, TlBr, and TlI at High Pressure and Temperature

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High-pressure and temperature experiments of ionic conductivity and crystal structure of TlCl, TlBr, and TlI reveal discontinuous and reproducible increases in conductivity on heating at constant pressure but no evidence for structural change from high-pressure and -temperature X-ray diffraction data. For each compound, the pressure-dependent solid–solid boundary between the low- and the high-temperature conductivity regions extrapolates to a 1-atm temperature value, which coincides with its 1-atm melting temperature to within 15 K. This behavior is discussed in terms of solid state partial disorder, caused by a sudden increase in defects, and is linked to the highly polarizable Tl$^+$ site. Concomitant increases in charge carrier concentration and mobility and decreases in activation energy without structural transformation emphasize the importance of nonstructural factors in fast-ion conduction. © 1998 Academic Press

Solid-state fast-ion conduction is characterized by ionic conductivity values comparable to those of liquids ($\sim 1\ \Omega^{-1}\ \mathrm{cm}^{-1}$). Fast-ion conductors have been the focus of much attention in view of their potential use as solid electrolytes in various electrochemical devices such as solid state batteries, chemical sensors, and smart devices (1–4). The relationship between fast ionic conductivity and structural factors, including lattice free volume, has been well established by investigations of systems undergoing temperature-induced structural phase transformation accompanied by lattice expansion and by incorporating various isovalent guest cations and anions (5–9). However, in cases where a phase transition involves lattice contraction, as in TlI, the accompanying jump in conductivity at the transition suggests a significant contribution by other, nonstructural factors. Here, we report on high-pressure and -temperature experiments of ionic conductivity and crystal structure of TlCl, TlBr, and TlI. We find modest, yet discontinuous and reproducible, increases in conductivity on heating at constant pressure but no evidence for structural change from high-pressure and -temperature X-ray diffraction data. For each compound, the pressure-dependent boundary between the low and high temperature conductivity regions extrapolates to a 1-atm temperature value which is identical with its 1-atm melting temperature to within 15 K. This collective behavior is suggestive of a sudden increase in Frenkel defects on the highly polarizable Tl$^+$ site with concomitant increases in charge carrier concentration and mobility. Temperature modulation of ionic conductivity at high pressure by controlling defect concentration, combined with the stabilization of a high conductivity phase by incorporation of guest ions (10), thus provides potential new pathways for optimization of fast-ion conductor properties.

Several fast-ion conducting compounds, such as mixed alkali cation sulfates, iodides, and Li_2MCl_4 spinels, undergo solid–solid phase transitions to a high temperature phase accompanied by a large jump in ionic conductivity, up to a factor of 10^4 as in the archetypal fast-ion conductor AgI (11). Many 1-atm studies, in which temperature and chemical composition were systematically varied, have clearly shown a qualitative resemblance of the logarithm conductivity (σT) versus T^{-1} plot to the site percolation probability function (12, 13), suggesting a percolation model for ion transport. However, the conductivity jump–free volume correlation is not observed in the β–α transitions of AgI and TlI. In AgI and TlI, the phase transition is accompanied by a volume decrease where the structure changes from shared corners and/or edges of coordination polyhedra to shared faces, resulting in a significant increase in the number of accessible sites for the mobile ion with lower activation energy. Recent studies of the combined effects of pressure and temperature on ionic conductivity of crystalline and amorphous materials (14, 15) have shown that conduction in some fast-ion conductors depends on a combination of a number of factors in addition to lattice free volume

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including activated ion concentration, ion size, bottleneck size, vibrational amplitudes of neighboring ions, rotational motion of complex ions, lattice compressibility, electron configuration of the mobile ion, ion–ion interaction or bonding characteristics, electronegativity, and cation polarizability. The thallium halide system, containing high polarizability Tl^+, provides an opportunity to investigate the effects of structure, lattice volume, and bonding and their changes with pressure and temperature in a common cation system.

Yellow β-TlI, a double-layered distorted NaCl-type orthorhombic structure undergoes a temperature-induced transformation to red α-TlI, a *Pm*3*m* CsCl-type cubic structure, the room-temperature stable structure of TlCl and TlBr. The β–α transition occurs at 172°C at 1 atm and is accompanied by a jump in conductivity (16) of $> 10^2$ and a reduction in lattice volume by 3.3% (17).

The conductivity experiments in this study were carried out on both powder and fused disk samples compressed and cored, respectively, from 99.999% purity compounds. Both ac and dc conductivity measurements were made in an evacuated ("1 atm") apparatus using a guarded two-electrode technique described in detail elsewhere (16) and in a high-pressure cubic anvil apparatus using conductivity measuring techniques previously described (15). The high-pressure, -temperature crystal structure experiments were carried out in a DIA-6 cubic anvil apparatus using energy dispersive X-ray diffraction spectra collected at the superconducting wiggler beamline (X17B1) at BNL-NSLS and the experimental details are described elsewhere (18, 19).

The Arrhenius plot in Fig. 1 shows examples of the high-pressure conductivity behavior for TlCl, TlBr, and TlI on heating in comparison with the 1-atm conductivity of TlI. The β–α transition in TlI at 1 atm is clearly shown by the abrupt jump in conductivity at a $10^3/T$ value of 2.25. In all data sets, conductivity increases with temperature followed by a jump in conductivity. The curvature in the temperature-dependence of conductivity in the low-temperature regions of each data set suggests a temperature-dependent activation energy of conduction. However, in the temperature regions just below and above the conductivity jump, the linear trends indicate a single activation energy. Comparison of the activation energy values calculated for temperature regions just below and above the conductivity jump, as plotted in Fig. 2, shows that in all three compounds the activation energy is lower in the high-temperature state for all compounds and pressures plotted except for TlBr at $P < 3$ GPa. Both the conductivity jump and the decrease in activation energy are consistent with an increase in charge carrier concentration and/or an increase in charge carrier mobility. An increase in carrier mobility implies a sudden change in one or more of the factors that control conduction discussed above.Therefore, we explored the possibility of abrupt changes in lattice volume and ion–ion interactions by investigating the high-pressure and -temperature of structure each halide. Figure 3 shows typical diffraction patterns for TlCl at a pressure of 4.2 GPa at three temperatures below and at one temperature (500°C) above the conductivity jump. Apart from small shifts in peak positions to lower energies expected from temperature-induced lattice dilatation, these patterns clearly do not show any evidence of a structural change at temperatures straddling the conductivity jump in the pressure and temperature ranges investigated. This confirms previous structural studies of their pressure and temperature phase diagrams (17, 20–23). Based on the structural and conductivity evidence, we interpret the temperature-induced conductivity jump to result from a sudden increase in the number of Frenkel defects in the cation sublattice as further discussed below.

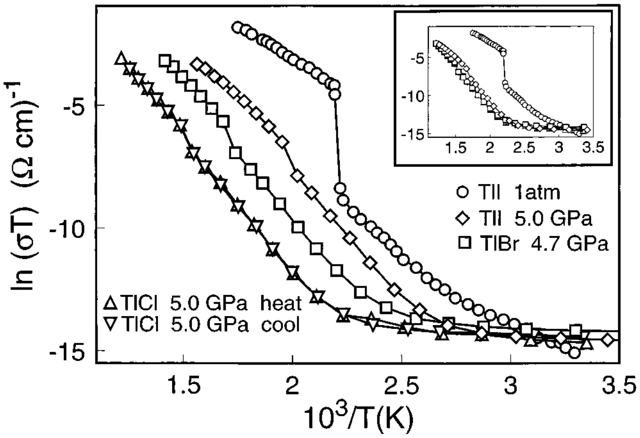

FIG. 1. Arrhenius plots of conductivity of TlCl on heating and cooling at 5.0 GPa, for TlBr on heating at 4.7 GPa, and for TlI on heating at 1 atm and 5.0 GPa. The high-pressure TlI and TlBr data have been shifted to the right 0.2 and 0.3 units, respectively, for clarity. All data are plotted in their unshifted positions in the inset.

An important factor in the formation of defects, and thus in ionic conductivity, is polarizability. It is known that next to Cs^+, Tl^+ has the highest dielectric polarizability of any atomic cation and in TlCl, TlBr, and TlI, its polarizability values are 5.1, 5.2, and 5.4 A^3, respectively (24, 25). Polarizability is anticorrelated with the energy of defect formation because the larger the dielectric constant of an ionic crystal, the lower the energy of formation of lattice defects (26). Since the temperature derivative of polarizability is positive (27) the T-induced increase in Tl^+ polarizability leads to a decrease in the defect formation enthalpy. The total activation energy of conduction is the sum of the activation energy of migration plus one-half of the activation energy of defect formation. The larger activation energy values before the conductivity jump are consistent with the additional energy term of defect formation.

While the formation of defects provides a significant contribution to the ionic conductivity of these thallium halides,

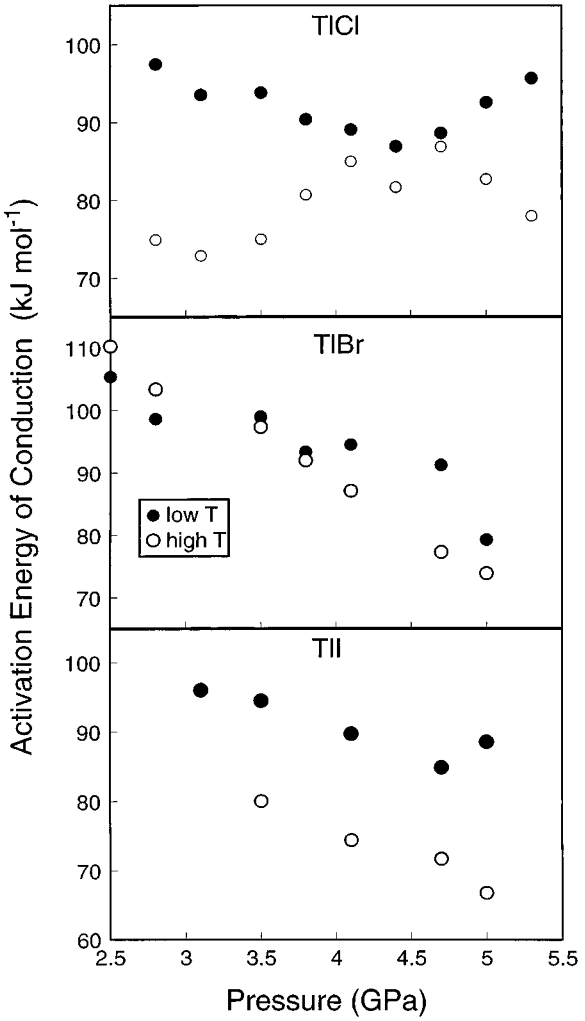

FIG. 2. Activation energy of conduction for temperature regions below (low temperature, solid circles) and above (high temperature, open circles) the conductivity jump for TlCl, TlBr, and TlI at pressures between 2.5 and 5.5 GPa.

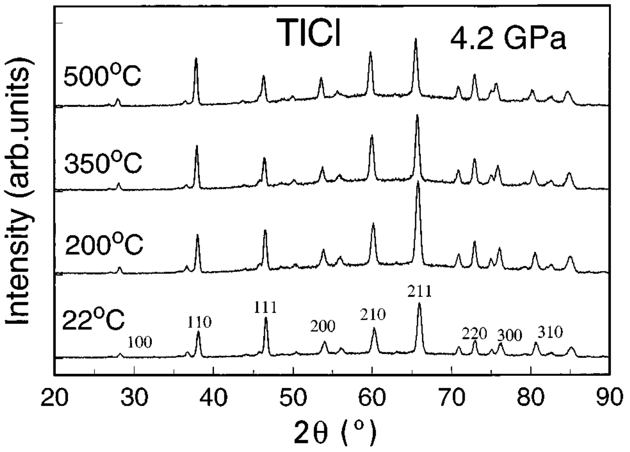

FIG. 3. X-ray diffraction patterns of TlCl at 4.2 GPa at three temperatures below and at one temperature (500°C) above the conductivity jump.

the X-ray diffraction data convincingly show that the increases in defect concentration are below X-ray detection and thus can be explained only by a partial disordering. The sudden increase in disorder may be viewed, however, as a temperature threshold that is crossed at constant pressure. It is of interest therefore to plot the pressure dependence of the temperatures of the jumps in defect population for each compound as shown for pressures above 2.5 GPa in Fig. 4. Linear extrapolations of each data set back to 1 atm for all three compounds show almost perfect coincidence with their respective 1-atm melting temperatures. On this basis, and consistent with the accepted understanding of melting as an order–disorder transformation, this correlation strongly supports our interpretation of a temperature-induced, solid state, partial disorder phenomenon in this system. The concept of a threshold temperature at which step changes in solid state defect population can be brought about in systems containing high polarizability ions presents the intriguing possibility of discretized states of solid disorder preceding catastrophic disordering at the melting transition. When viewed within the framework of their respective high-pressure melting phase lines, all of which have a *positive* pressure dependence (although not shown in Fig. 4 for clarity) and which mark the onset of complete long range atomic positional disorder, we hypothesize that the single solid state partial disorder boundary found for each material in this study may belong to a family of such boundaries, each pinned at some (common?) pressure and each representing progressively increasing, but discrete,

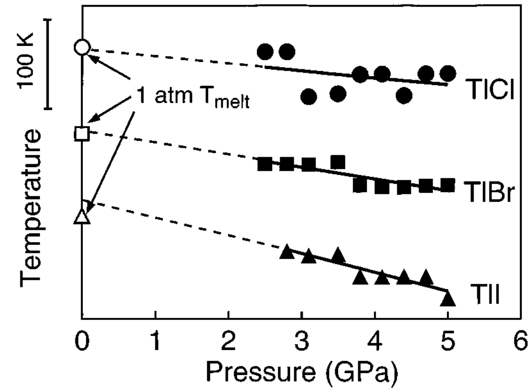

FIG. 4. Pressure dependence of the temperature of the conductivity jumps for TlCl, TlBr, and TlI. For clarity, the three datasets have been shifted vertically and are shown on a relative temperature scale. The solid lines are fits to the data (solid symbols) above 2.5 GPa and the dashed lines are backward extrapolations for comparison with the 1-atm melting temperatures of TlCl, TlBr, and TlI (matching open symbols) of 704, 733, and 715 K, respectively. The solid–liquid boundary for each compound (not shown) has a positive pressure dependence.

states of solid disorder. If borne out by future experimental data in other systems which would indicate general behavior, this speculative but intriguing possibility would cast constraints on defect-mediated melting theories founded on continuous changes in the solid defect concentration up to some critical concentration (28).

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