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High Ionic Conductivity in Some Lithium Halide Systems

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Introduction. High ionic conductivity has been reported in a wide range of crystalline materials,[1−11] including metal phases (Table 1). Room-temperature conductivity as high as 0.3 S/cm can be achieved with silver and copper(I) halide systems. For example, $RbAg_4I_5$ exhibits Ag^+ conductivity of 0.2 S/cm at 20 °C,[5] and $Rb_4Cu_{16}I_7Cl_{13}$ exhibits Cu^+ conductivity of 0.34 S/cm at 25 °C.[9] The high mobility of Ag^+ and Cu^+ ions is often attributed to their high polarizability, which may facilitate diffusion through bottlenecks. A related factor may be the low cation coordination numbers of Ag^+ and Cu^+, e.g. 2, 3, or 4, which may reduce the activation energy for ion diffusion because the bottlenecks are often envisioned to be low coordination sites. Unfortunately, Ag^+ and Cu^+ are readily reduced, so there are few technical applications for silver or copper(I) electrolytes. By contrast, there is considerable interest in lithium ion conductors because the high reduction potential and low equivalent mass of Li^+ lead to favorable power densities; however, simple lithium halide systems typically exhibit low conductivity.[12,13] In the present study, high ionic conductivity was observed for some binary lithium halide systems.

Experimental Section. Impedance spectroscopy was performed with an HP 4192A impedance analyzer or a Solartron 1250 analyzer. A weighed amount of alkali halides was ground, pressed into pellets under a pressure of 5×10^8 Pa, and annealed at 220 °C under high vacuum for 3−4 days; these pressed pellets were loaded in airtight cells under dry nitrogen, sandwiched between gold foil electrodes. The temperature of the conductivity cell was controlled with a Sun System environmental chamber. DSC data were collected at a heating rate of 40 °C/min on a Perkin-Elmer Pyris 1 DSC. Powder X-ray data were collected on a Rigaku powder diffractometer. Analytical-grade chemicals from Aldrich were dried under high vacuum ($\approx 10^{-5}$ Torr) at 200 °C for at least 3 days and handled in a glovebox filled with dry nitrogen.

Table 1. Conductive Halide Complexes

substance	mobile ion	conductivity (S/cm) at *T* (°C)	*T*	reference
$RbAg_4I_5$	Ag^+	0.2	20	5
KAg_4I_5	Ag^+	0.2	20	5
$Me_4NAg_7I_8$	Ag^+	0.04	25	6
KCu_4I_5	Cu^+	0.6	270	15
$CuPb_3Br_7$	Cu^+	0.03	200	7
$Tl_3Cu_2Cl_5$	Cu^+	0.02	100	8
$Rb_4Cu_{16}I_7Cl_{13}$	Cu^+	0.34	25	9

Following the discovery of high Ag^+ conductivity in $RbAg_4I_5$, many highly conductive solid electrolytes with the general formula MAg_nI_{n+1} were found;[2,4−6,9] examples include KAg_4I_5,[5] $(C_5H_5NH)Ag_5I_6$,[1] and $(Me_4N)Ag_6I_7$.[6] Subsequently, highly conductive halide systems with Cu^+ as the mobile ion were discovered,[7−9,14,15] such as $RbCu_3Cl_4$4 and $Rb_4Cu_{16}I_7Cl_{13}$.[9] These developments encouraged our search for highly conductive halide complexes containing Li^+ or Na^+ as the mobile ion. Because the radius of Li^+ (0.73 Å) is similar to that of Cu^+(0.74 Å) and the radius of Na^+ (1.16 Å) is close to that of Ag^+(1.15 Å), we replaced Ag^+ and Cu^+ by Na^+ and Li^+, respectively, to form analogues of conductive silver and copper(I) halide complexes. Sodium halide compounds, such as MNa_nI_{n+1}, were prepared as analogues of MAg_nI_{n+1}, and related lithium halide compounds, $RbLi_3Cl_4$, $Rb_4Li_{16}I_7Cl_{13}$, and $Rb_4Li_{16}I_7Cl_{13}$, were prepared as well. None of these alkali halide systems exhibit conductivity as high as that of the corresponding silver or copper(I) halide complexes. For example, $Rb_4Li_{16}I_7Cl_{13}$ exhibits a conductivity of 10^{-7} S/cm, which is significantly lower than that of $Rb_4Cu_{16}I_7Cl_{13}$, 0.34 S/cm, at room temperature. In the present research, high conductivity is demonstrated for the technologically more interesting LiI−MI systems, where M is K, Rb, or Cs.

RbI−LiI Systems. Of the compositions studied here, conductivities as high as 10^{-2} S/cm at 65 °C were obtained when the lithium iodide content was 40 or 50 mol % (Figure 1). The impedance data were collected periodically as the sample was slowly heated or cooled at 0.2 °C/min. Between 60 and 80 °C (Figure 1), samples of $(LiI)_{0.4}(RbI)_{0.6}$ and $(LiI)_{0.5}(RbI)_{0.5}$ show a conductivity drop of more than 3 orders of magnitude, indicating a transition between a highly conductive phase and a resistive phase, and DSC data (Figure 2) confirms the presence of this phase change. As shown in Figure 3, there is some hysteresis in this transition. An endotherm occurs for $(LiI)_{0.4}(RbI)_{0.6}$ at 79 °C, which is close

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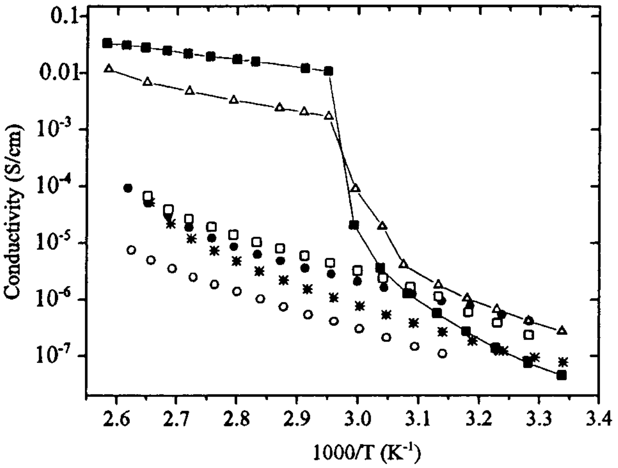

Figure 1. Temperature-dependent conductivity of the LiI–RbI system. (■) 40% LiI; (△) 50% LiI; (□) 67% LiI; (●) 80% LiI; (★) pure LiI; (○) 33% LiI.

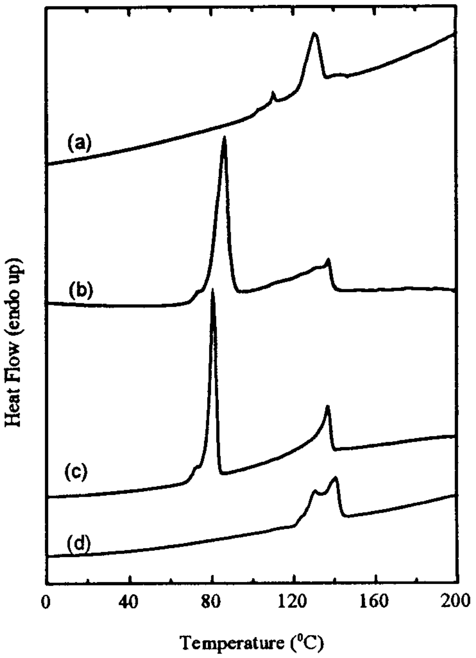

Figure 2. DSC curves of the LiI–RbI system: (a) 67% LiI; (b) 50% LiI; (c) 40% LiI; (d) 33% LiI.

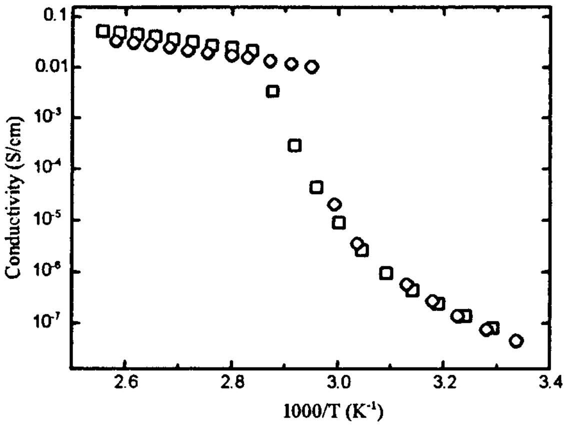

Figure 3. Comparison of the conductivity of $Li_2Rb_3I_5$ upon (□) heating and (○) cooling. .

to the transition temperature, 75 °C, suggested by the conductivity. The small discrepancy may result from the difference the heating rate in the two measurements. The heating rate of the conductivity measurement was 0.2 °C/min while it was 40 °C/min for the DSC measurement. At a heating rate of 5 °C/min, the endotherm is found at 76 °C. For comparison, the published phase diagram for LiI/RbI has a paratectic transition between 40 and 50 mol % RbI.[17] Transitions between conductive and resistive phases have been observed with other halide systems.[5,7,8,14–16] For example, $RbAg_4I_5$ undergoes a transition from a conductive phase to a resistive phase at −155 °C[5] and $Tl_3Cu_2Cl_5$ becomes conductive above 95 °C.[8] The room-temperature conductivity of the LiI–RbI systems is similar to that of pure lithium iodide. Power X-ray diffraction patterns indicate that LiI–RbI consists of a mixture of the two salts at room temperature.

Other Systems. LiI in combination with other halides, KI, CsI, TlI, BaI_2, RbBr, and SrI_2, were investigated. As with the LiI–RbI system, the X-ray powder diffraction patterns indicate that these systems are simple salt mixtures at room temperature; however, conductive phases were found at elevated temperature. For example, $(LiI)_{0.33}(CsI)_{0.67}$ exhibits conductivity close to 10^{-3} S/cm at 120 °C, and the conductivity of $(LiI)_{0.33}(KI)_{0.67}$ is 10^{-4} S/cm at 70 °C. All of these systems revert to resistive phases upon cooling. The temperatures of these phase changes were replicated by DSC data.

For silver and copper(I) halide systems, high Ag^+ and Cu^+ conductivity is usually observed in the complexes with a high proportion of Ag^+ or Cu^+, typically 70–90 mol %.[1,4–6,9] For example, $RbAg_4I_5$ consists of 80 mol % Ag^+, and $RbCu_3Cl_4$ consists of 75 mol % Cu^+. By contrast, the lithium halide systems described here exhibit high ionic conductivity at lower Li^+ concentrations, usually 30–50 mol %. For example, highly conductive phases have the following compositions: $(LI)_{0.4}$-$(RbI)_{0.6}$ (40 mol % Li^+) and $(LiI)_{0.33}(KI)_{0.67}$ (33 mol % Li^+).

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