Fast ionic conductivity of ternary iodides in the systems LiI-M^III_2 (M^II = Mn, Cd, Pb)

H.D. Lutz, Z. Zhang and A. Pfitzner
University of Siegen, Anorganische Chemie I, Postfach 101240, D-5900 Siegen, Germany

Received 4 February 1993; accepted for publication 22 March 1993

The phase relationships and electric conductivities of the ternary iodide systems LiI-M^III_2 (M^II = Mn, Cd, Pb) have been studied by high-temperature X-ray measurements and impedance spectroscopy methods. Whereas mutual solubility of LiI and MnI2 is negligible at any temperature deficient NaCl-type mixed crystals Li_{1-x}M^{II}I_{x} (M^{II} = Mn, Cd, Pb) are formed at temperature above 540 K, which, however, cannot be quenched to ambient temperature. The solid solutions obtained exhibit high ionic conductivity, e.g. 1 × 10^{-1}, 3 × 10^{-2} and 7 × 10^{-2} S cm^{-1} at 570 K for materials like Li2CdI4, Li2PbI4, and Li4PbI6, respectively.

1. Introduction

Ternary lithium iodides of bivalent metals are scarce. The only compound known so far is olivine-type LiI-ZnI4, which displays fairly high ionic conductivity [1,2]. No compounds have been obtained in the systems LiI-MgI2 [3,4], LiI-CaI2 [4], LiI-CdI2 and LiI-HgI2 [5]. In analogy to the recently established ternary bromides LiI-MgBr4 [6,7], Li2MnBr4 [6,8,9], and Li2CdBr4 [8], the existence of the corresponding iodides was expected. We therefore investigated the systems LiI-MnI2, LiI-CdI2, as well as LiI-PbI2 [10] by X-ray, high-temperature X-ray, and conductivity measurements.

2. Experimental

Polycrystalline samples of the lithium iodides under investigation were prepared by fusing the binary iodides in evacuated sealed borosilicate glass ampoules. Starting materials were LiI·xH2O (purum, Fluka, Buchs), Mn (3N, Strem, Newburyport), I2 (3N, Fluka), CdI2 (reinst, Merck, Darmstadt), and PbI2 (5N, Alfa, Karlsruhe). Commercially available CdI2 and PbI2 were heated at 470 K in a vacuum before use. LiI was dehydrated by reaction with 2,2-dimethoxypropane [1]. MnI2 was prepared by heating stoichiometric amounts of the elements in evacuated sealed quartz glass ampoules of 20 cm in length at temperatures up to 1170 K (with a temperature gradient in order to allow the iodine to condense at the cold site of the ampoule during the reaction [10]) and subsequent sublimation in a vacuum.

The samples obtained were characterized by X-ray powder photographs (Huber-Guinier 600 system, Enraf-Nonius high-temperature Guinier-Simon FR 533 camera), using Cu Kα radiation and α-quartz as internal standard. The sealed quartz capillaries taken as sample holders were protected from reaction with the lithium iodides at elevated temperatures by a thin carbon layer [11]. The unit-cell dimensions were determined by least-squares refinements (LSUCR). The electrical conductivity was determined by the impedance spectroscopy method using a Hewlett-Packard 4192A LF impedance analyzer. Details of the cell and the experimental setup are given in [10,12].

3. Results

3.1. Phase relationships in the systems LiI-M^III_2 (M^II = Mn, Cd, Pb)

LiI and CdI2 form deficient NaCl-type solid solutions at elevated temperatures. Opposite to the results reported in [5] these mixed crystals cannot be
H. D. Lutz, A. Pfitzner/Ternary iodides in the systems LiI-MnI₂

Fig. 1. Unit-cell dimensions of deficient NaCl-type Li₁₋ₓCdₓI₄ (full signs) and Li₁₋ₓPbₓI₄ solid solutions (empty signs) (high-temperature X-ray measurements): (▲) x=0; (●) x=0.2; (●) (□) x=0.33; (arrows) monophase solid solutions.

quenched to ambient temperature. On cooling down they decompose forming LiI and CdI₂ with only small mutual solubility at room temperature. For samples of the composition Li₂CdI₄, a monophase solid solution is obtained above 538 K. On heating, the gradual incorporation of CdI₂ in NaCl-type LiI is revealed from the increase of the cubic lattice constant (see fig. 1). Contrary to LiI and CdI₂, the mutual solid solubility of LiI and MnI₂ is negligible at any temperature below the melting temperature of LiI at 722 K.

The system LiI–PbI₂ is similar to that of LiI–CdI₂.

At ambient temperature mutual solubility is negligible. LiI coexists with CdI₂-type PbI₂ polytypes [13]. On heating initially, i.e. at 508 K, the PbI₂ polytype present is changed to that of 12H type. Above 545 K, Li₁₋ₓPbₓI₄ solid solutions are formed, which cannot be quenched to lower temperatures. They crystallize in the cubic system with a closed-packed arrangement of the I⁻ ions. The lattice constants increase with the increase of lead content (see fig. 1). The temperature of formation of NaCl-type mixed crystals depends only slightly on the composition x.

3.2. Ionic conductivity of NaCl-type Li₁₋ₓMoₓI₄ (M=Cd, Pb) solid solutions

The electric conductivities (Arrhenius plots) of NaCl-type solid solutions with the composition Li₂CdI₄, Li₂PbI₄, and Li₄PbI₆ are shown in fig. 2, respectively. Numerical data are given in table 1.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Li₂CdI₄</th>
<th>Li₂PbI₄</th>
<th>Li₄PbI₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>470 K</td>
<td>3 × 10⁻³</td>
<td>3 × 10⁻³</td>
<td>1.7 × 10⁻⁴</td>
</tr>
<tr>
<td>510 K</td>
<td>5 × 10⁻²</td>
<td>5.3 × 10⁻⁴</td>
<td>1 × 10⁻³</td>
</tr>
<tr>
<td>570 K</td>
<td>1 × 10⁻¹</td>
<td>3 × 10⁻²</td>
<td>7 × 10⁻²</td>
</tr>
<tr>
<td>585 K</td>
<td></td>
<td>3.5 × 10⁻²</td>
<td>9 × 10⁻²</td>
</tr>
</tbody>
</table>
The ionic conductivities of the ternary iodides (Li₂CdI₄, Li₄PbI₆) exceed that of binary LiI up to two orders of magnitude. The Arrhenius plots obtained display the decomposition and formation of the mixed crystals by strong decrease and increase of the conductivity with decreasing and increasing temperature, respectively. The transition temperatures thus established confirm those observed by the X-ray experiments, e.g. 540 K for the ternary lead iodides. The further increase of the conductivity above 655 K (Li₂PbI₄ and Li₄PbI₆) is due to melting of the samples.

4. Discussion

The tendency of formation of compounds between lithium halides and halides of bivalent metals decreases on going from chlorides to iodides. These findings are caused by the lower distortion of the halide ion sublattice on formation of ternary compounds in the case of iodides compared to chlorides and bromides [15]. Thus, the gain of additional cohesive energy is negligible and, hence, outmatched by the lattice energies of the binary iodides.

Among ternary lithium halides of composition Li₂MᵢX₄, the iodides possess the greatest conductivity (see table 2). (The somewhat smaller conductivities of the bromides compared to those of the chlorides are mainly due to the different crystal structures [9].) Because of decomposition of the ternary iodides at temperatures below 500 K ionic conducting lithium iodide material with conductivities quite higher than those of binary LiI doped with small amounts of bivalent metal ions, however, is not available at ambient temperature. The ionic conductivity of the lead compounds decreases on going from Li₄PbI₆ to Li₂PbI₄ (see fig. 2) despite the increase of the unit-cell volumes (see fig. 1). The size of the vacancies in Li₄PbI₆ is probably more appropriate for Li⁺ ion mobility than those in Li₂PbI₄.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References