

Fast ionic conductivity of ternary iodides in the systems $\text{LiI-M}^{\text{II}}\text{I}_2$ ($\text{M}^{\text{II}} = \text{Mn, Cd, Pb}$)

H.D. Lutz, Z. Zhang and A. Pfitzner

Universität Siegen, Anorganische Chemie I, Postfach 101240, W-5900 Siegen, Germany

Received 4 February 1993; accepted for publication 22 March 1993

The phase relationships and electric conductivities of the ternary iodide systems $\text{LiI-M}^{\text{II}}\text{I}_2$ ($\text{M}^{\text{II}} = \text{Mn, Cd, Pb}$) have been studied by high-temperature X-ray measurements and impedance spectroscopy methods. Whereas mutual solubility of LiI and MnI_2 is negligible at any temperature deficient NaCl-type mixed crystals $\text{Li}_{1-x}\text{M}_x^{\text{II}}\text{I}$ ($\text{M}^{\text{II}} = \text{Mn, Cd, Pb}$) 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 $7 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 570 K for materials like Li_2CdI_4 , Li_2PbI_4 , and Li_4PbI_6 , respectively.

1. Introduction

Ternary lithium iodides of bivalent metals are scarce. The only compound known so far is olivine-type Li_2ZnI_4 , which displays fairly high ionic conductivity [1,2]. No compounds have been obtained in the systems LiI-MgI_2 [3,4], LiI-CaI_2 [4], LiI-CdI_2 and LiI-HgI_2 [5]. In analogy to the recently established ternary bromides Li_2MgBr_4 [6,7], Li_2MnBr_4 [6,8,9], and Li_2CdBr_4 [8], the existence of the corresponding iodides was expected. We therefore investigated the systems LiI-MnI_2 , LiI-CdI_2 , as well as LiI-PbI_2 [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 $\text{LiI} \cdot x\text{H}_2\text{O}$ (purum, Fluka, Buchs), Mn (3N, Strem, Newburyport), I_2 (3N, Fluka), CdI_2 (reinst, Merck, Darmstadt), and PbI_2 (5N, Alfa, Karlsruhe). Commercially available CdI_2 and PbI_2 were heated at 470 K in a vacuum before use. LiI was dehydrated by reaction with 2,2-dimethoxypropane [1]. MnI_2 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 $\text{Cu K}\alpha_1$ 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 $\text{LiI-M}^{\text{II}}\text{I}_2$ ($\text{M}^{\text{II}} = \text{Mn, Cd, Pb}$)

LiI and CdI_2 form deficient NaCl-type solid solutions at elevated temperatures. Opposite to the results reported in [5] these mixed crystals cannot be

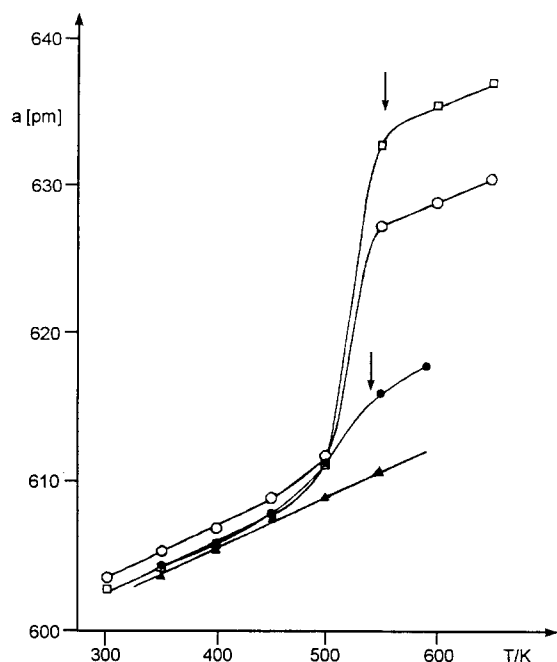


Fig. 1. Unit-cell dimensions of deficient NaCl-type $\text{Li}_{1-x}\text{Cd}_{0.5x}\text{I}$ (full signs) and $\text{Li}_{1-x}\text{Pb}_{0.5x}\text{I}$ solid solutions (empty signs) (high-temperature X-ray measurements): (▲) $x=0$; (○) $x=0.2$; (●) (□) $x=0.33$; (arrows) monophase solid solutions.

quenched to ambient temperature. On cooling down they decompose forming LiI and CdI_2 with only small mutual solubility at room temperature. For samples of the composition Li_2CdI_4 , a monophase solid solution is obtained above 538 K. On heating, the gradual incorporation of CdI_2 in NaCl-type LiI is revealed from the increase of the cubic lattice constant (see fig. 1). Contrary to LiI and CdI_2 , the mutual solid solubility of LiI and MnI_2 is negligible at any temperature below the melting temperature of LiI at 722 K.

The system $\text{LiI}-\text{PbI}_2$ is similar to that of $\text{LiI}-\text{CdI}_2$.

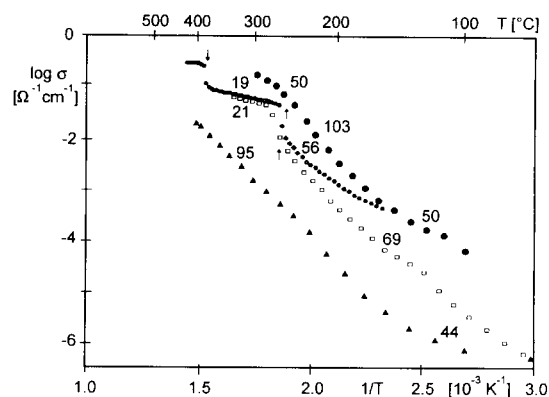


Fig. 2. Arrhenius plots of the electric conductivity ($\log \sigma$ versus $1/T$) of LiI [1] (▲), Li_2CdI_4 (●), Li_4PbI_6 (○), and Li_2PbI_4 (□) (all NaCl-type solid solutions); activation energies of conduction in kJ mol^{-1} ; arrows, formation and melting of the solid solutions.

At ambient temperature mutual solubility is negligible. LiI coexists with CdI_2 -type PbI_2 polytypes [13]. On heating initially, i.e. at 508 K, the PbI_2 polytype present is changed to that of 12H type. Above 545 K, $\text{Li}_{1-x}\text{Pb}_{0.5x}\text{I}$ 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 $\text{Li}_{1-x}\text{M}_{0.5x}\text{I}$ ($M=\text{Cd}, \text{Pb}$) solid solutions

The electric conductivities (Arrhenius plots) of NaCl-type solid solutions with the composition Li_2CdI_4 , and Li_2PbI_4 and Li_4PbI_6 are shown in fig. 2, respectively. Numerical data are given in table 1.

Table 1

Specific electric conductivities ($\Omega^{-1} \text{cm}^{-1}$) of deficient NaCl-type Li_2CdI_4 , Li_2PbI_4 and Li_4PbI_6 solid solutions at elevated temperatures (K) (see fig. 2).

	Temperature			
	470 K	510 K	570 K	585 K
Li_2CdI_4	3×10^{-3}	5×10^{-2}	1×10^{-1}	—
Li_2PbI_4	3×10^{-5}	5.3×10^{-4}	3×10^{-2}	3.5×10^{-2}
Li_4PbI_6	1.7×10^{-4}	1×10^{-3}	7×10^{-2}	9×10^{-2}

Table 2

Electric conductivities ($\Omega^{-1} \text{ cm}^{-1}$) of ternary lithium halides $Li_2M^{II}X_4$ at 570 K [6,8,14,15].

	Li_2MgX_4	Li_2MnX_4	Li_2ZnX_4	Li_2CdX_4
$Li_2M^{II}Cl_4$	3.5×10^{-2}	3.5×10^{-2}	8×10^{-4}	6.0×10^{-2}
$Li_2M^{II}Br_4$	1.6×10^{-2}	2.2×10^{-2}	5×10^{-4}	5.0×10^{-2}
$Li_2M^{II}I_4$	–	–	$3.5 \times 10^{-3a)}$	1×10^{-1}

a) 520 K.

The ionic conductivities of the ternary iodides (Li_2CdI_4 , Li_4PbI_6) 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 (Li_2PbI_4 and Li_4PbI_6) 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 $Li_2M^{II}X_4$, 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 Li_4PbI_6 to Li_2PbI_4 (see fig. 2) despite the in-

crease of the unit-cell volumes (see fig. 1). The size of the vacancies in Li_4PbI_6 is probably more appropriate for Li^+ ion mobility than those in Li_2PbI_4 .

Acknowledgement

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

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