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PHASE STUDY OF THE SYSTEM Li_2Se–In_2Se_3

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Abstract

The binary system Li_2Se–In_2Se_3 was investigated in the range of 40 to 100 mol% In_2Se_3 by thermoanalytical and X-ray methods. The system is characterized by two eutectic points. Beside the two binary components and the known ternary compound $LiInSe_2$ another ternary compound crystallizes in this binary system at 83.3 mol% In_2Se_3. This compound was identified as $LiIn_5Se_8$. In contrast to (Cu, Ag)$^{I}B_5^{III}C_8^{VI}$ compounds such as $CuIn_5S_8$ [1] it does not crystallize in the spinel structure. $LiIn_5Se_8$ shows a stratified structure. The melting point was determined to be at 810°C. Starting from room temperature up to the melting point no phase transitions were observed.

Keywords: binary system, Li_2Se–In_2Se_3, phase diagram, TA, X-ray, ternary compounds

Introduction

No phase diagram of the ternary system Li–In–Se is known so far. Unlike other A–B–C ternary systems (*A*=Cu, Ag, Li, Na, K; *B*=Ga, In; *C*=S, Se, Te) there are also no information about possible binary systems that could be existent within this system. The only known compound within the ternary system Li–In–Se is $LiInSe_2$ beside the binary compounds. However the knowledge of the phase diagram is a basic prerequisite leading to a successful single crystal growth. The following paper will present the results of the investigations of the binary phase diagram Li_2Se–In_2Se_3. Considering the fact that the lithium-rich material is not stable on air the investigations were focused on the range of 40 to 100 mol% In_2Se_3.

Experimental

In order to synthesize material along the binary section Li_2Se–In_2Se_3 the binary components Li_2Se and In_2Se_3 as well as the elements lithium, indium and selenium were used as starting materials. Li_2Se was prepared by stoichiometric amounts of lithium and selenium placed in a quartz ampoule using the procedure as described by Ader [2]. Stoichiometric amounts of indium and selenium served as starting material in or-

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der to receive In_2Se_3. The resulting binary compounds were characterized by powder diffraction showing that both were single phase.

The mixing proportion of the synthesized compounds in the system $Li_2Se–In_2Se_3$ was varied in steps of 5 mol%. In individual intervals that were important for the determination of the phase diagram the step width had been chosen smaller (up to 1 mol%). All starting materials including the binary compounds were kept in a glove box under argon atmosphere due to the sensitivity of lithium and Li_2Se to oxygen, nitrogen, and moisture.

Lithium attacks quartz glass. In order to prevent the quartz ampoules from being attacked by lithium the synthesis was carried out in a graphite crucible. The crucible was placed in a pyrolized ampoule. The sealed ampoules were heated up to 950°C in a vertical one-zone furnace.

The resulting material was structural characterized by X-ray powder diffraction using CuK_α radiation. Thermoanalytical investigations of the phase diagram were carried out using a DTA 404s (Netzsch Gerätebau GmbH).

Results and discussion

The synthesized samples were characterized by the following facts:

- Material prepared in the range from 40 to <50 mol% In_2Se_3 showed a milky yellow colour. It was not stable on air.
- At 50 mol% In_2Se_3 yellow coloured material has been observed.
- All probes with a composition ≥50 mol% were stable on air.
- In the range from 55 to 70 mol% In_2Se_3 red coloured, compact material was observed. The intensity of the colour raises from light red to dark red with higher percentage of In_2Se_3.
- Material with a composition ≥75 mol% was dark coloured, had a preferred cleavage, and showed a stratified structure.

On the Li_2Se-rich side in the range of 44 to 50 mol% In_2Se_3 only $LiInSe_2$ could be detected by powder diffraction measurements. About an In_2Se_3 content less than 44 mol% another phase was observed which was identified as Li_2Se. This leads to the assumption that on the lithium-rich side no other ternary lithium-rich compounds will be expected to be existent.

Figure 1 shows the variation of the lattice parameters a, b and c of $LiInSe_2$ on the Li_2Se-rich side. All three lattice parameters decrease with increasing Li_2Se content. As depicted the change of the lattice parameters follows Vegard's law.

Powder diffraction measurements of the yellow sample at 50 mol% In_2Se_3 show that the material is single phase $LiInSe_2$.

The homogeneity range of $LiInSe_2$ is on the In_2Se_3-rich side smaller than on the Li_2Se-rich side. With increasing In_2Se_3 content the yellow colour of $LiInSe_2$ changes to red and deep red and finally results in a dark coloured material.

At an In_2Se_3 content of 52 mol% and higher an additional phase was found to be present. The reflexes could not be charged to In_2Se_3. The existence of the new com-

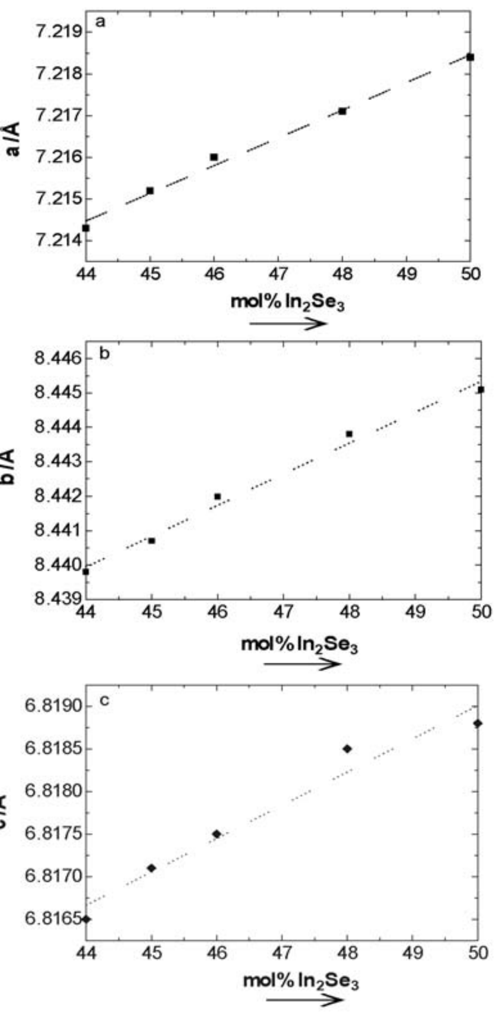

Fig. 1 Variation of the lattice parameters of $LiInSe_2$ with changing In_2Se_3 content on the Li_2Se rich side; a – lattice constant; b – lattice constant; c – lattice constant

pound $LiIn_5Se_8$ at 83.3 mol% In_2Se_3 could be proofed. That means that in analogy to other $A^{I}_2C^{VI}-B^{III}_2C^{VI}_3$ systems another ternary compound of the type $A^{I}B^{III}_5C^{VI}_8$ is existent [1, 3]. $LiIn_5Se_8$ crystallizes in the space group P3 with the lattice parameters a=4.06 Å and c=19.878 Å. It shows a stratified structure. No phase transitions could be observed between room temperature and melting point. A more detailed characterization of the compound will be given in [4].

In the range between 85 and 98 mol% In_2Se_3 both phases $LiIn_5Se_8$ and In_2Se_3 could be detected. The homogeneity range of In_2Se_3 was observed between 100 and 98 mol% In_2Se_3.

Thermoanalytical investigations showed that the melting point decreases starting from $LiInSe_2$ up to an In_2Se_3 content of 72 mol%. At 72 mol% In_2Se_3 a eutectic point was found at 794°C. For concentrations higher than 72 mol% the melt point increases slightly up to 810°C. This melting temperature almost remains constant for 72 mol% $In_2Se_3 < x < 87$ mol% In_2Se_3. At 87 mol% In_2Se_3 a second eutectic point could be detected at 790°C. Starting from this eutectic point the melting point increases up to 100 mol% In_2Se_3.

Combining the results of the thermoanalytical measurements with the results of the powder diffraction investigations the following binary phase diagram of $Li_2Se–In_2Se_3$ in the range of 40 to 100 mol% In_2Se_3 results as depicted in Fig. 2.

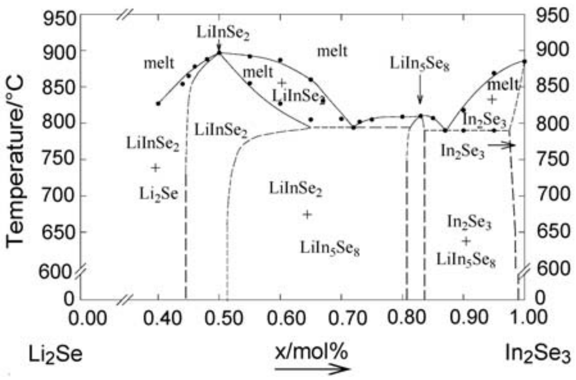

Fig. 2 Phase diagram of the binary system $Li_2Se–In_2Se_3$; RT=room temperature

Beside the known ternary compound $LiInSe_2$ a second ternary compound $LiIn_5Se_8$ could be proofed to be existent in the binary system $Li_2Se–In_2Se_3$. No phase transitions could be observed between room temperature and melting point for $LiIn_5Se_8$. The compound $LiInSe_2$ shows on the Li_2Se-rich side a larger homogeneity range as on the In_2Se_3-rich side. The same phenomenon was observed for $LiIn_5Se_8$. The binary system $Li_2Se–In_2Se_3$ is also mainly characterised by two eutectic subsystems.

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