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EFFECTS OF EVAPORATION AND MELTING ON NONSTOICHIOMETRY AND INHOMOGENEITY OF $LiInSe_2$ CRYSTALS

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Evaporation and compositional changes of the liquids above the melting point of $LiInSe_2$ crystals have been characterized quantitatively by using special techniques of a rapid thermal analysis and differential dissolution. The occurrence of a liquid immiscible region in the Li_2Se-rich side of the Li_2Se–In_2Se_3 diagram and incongruent evaporation with the preferential evaporation of In_2Se_3 rising markedly above boiling point were determined from the peaks on the thermal curves and from precise control over the composition of the vapour and residual solid as a function of temperature. It was shown that both the processes could be the sources of nonstoichiometry and inhomogeneity of the $LiInSe_2$ crystals.

Keywords: *evaporation, evolved gas analysis, $LiInSe_2$, melting , rapid thermal analysis*

Introduction

$LiInSe_2$ is a newly developed and perspective nonlinear optic crystal [1] for which stoichiometry and homogeneity are crucial parameters to its proper functioning in a given application. Several techniques have been used in the past and the deviation from stoichiometry in both the Li_2Se- and In_2Se_3-rich regions for $LiInSe_2$ and some inhomogeneity as light scattering centers in single crystals were claimed in previous publications [2–9]. However, none of these investigations studied the evaporation and changes that accompany the melting of $LiInSe_2$ crystals as possible sources of their nonstroichiometry and inhomogeneity. Meanwhile an incongruent evaporation of the crystals was really observed [2, 8] by the classical TG-DTA technique combined with mass spectrometry, although there were discrepancies between the results concerning the nature of evaporation. Preferential evaporation of In_2Se_3 [8] and that of Li_2Se [2] was observed. Additional information could not clarify the situation since thermodynamic, spectroscopic and structural data on a specific nature of the Li-Se bonds and specific Li positions in the $LiInSe_2$ structure [10–12] were in support of the preferential evaporation of Li_2Se, while the evaporation parameters of Li_2Se and In_2Se_3, as constituent components, were at variance with this conclusion [13, 14].

It is therefore highly desirable to investigate the evaporation process of $LiInSe_2$ by both direct measurements of the vapour pressure and chemical analysis of the evolved gas and of the residual solid to understand the nature of evaporation of $LiInSe_2$ in detail.

In general, measurement of vapour pressures at evaluated temperatures can be carried out relatively easily, but not in the case of the Li-consisting melt and vapour, both of which are highly reactive towards any container material and even Pt, Mo, and W begin to interact with the Li products for prolonged experiments [2, 5, 14]. With the help of this knowledge, a rapid thermal analysis with Mo container and a procedure of ‘boiling points’ in the isobaric version were used [15] as a powerful technique for studying melting and evaporation behaviour of $LiInSe_2$, when other methods had failed. The thermo-microscopic apparatus was able to measure the vapour pressure in the temperature range 600–2200°C at a fixed pressure of helium gas in the camera between 10^{-2} and 3 atm and to record the thermal curves with transformations such as solid-liquid, solid-vapour and liquid-vapour. To determine the composition of the evolved gas a special step-scan thermal procedure was developed where a sample heated to a desired temperature was quenched rapidly with subsequent determination of the Li:In:Se molar ratio in the residual solid and the vapour condensed on quartz window demounted in the chamber. The changes that occurred in the melts heated above melting point were studied by the differential dissolution technique (DD), which is a chemical tool identifying the phases by their composition [16]. The DD analysis was here preferable to XRD since the quenched melts weighing less than 1 mg were expected to be amorphous. The key parameters of evaporation and melting processes for $LiInSe_2$ thus determined were considered in light of their effect upon nonstoichiometry and heterogeneity of the crystals.

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Experimental

The experimental thermomicroscopic apparatus automatically controlled by an electronic device (1) is shown in Fig. 1. It consists of a water-cooled chamber (2) connected to a manometer (3) and to a vacuum pump, and a Mo crucible (4), in which a sample (5) to be tested is placed. A W/W-Re thermocouple (6) is inserted into the bottom of the Mo crucible. The chamber has a window (7) for recording of the emitted radiation variation by a suitable IR photodiode (8) of a sample when heated and for direct observation of the crystal transformations by a microscope (9). A graphite or tungsten heater is (10) with current leads (11) and the gas entry (12) are also shown. Typical parameters of the thermal procedure include a sample mass of about 1 mg, a heating rate of 1000 or 3000°C $\min^{-1}$ and operation under static 0.01–3 atm pressure of the helium gas.

The special calibration of the apparatus with melting of Cu, Ag, Si and with evaporation of the GaAs and GaP crystals were performed to provide deviation of measured values of about 1% for melting points and around 5% for the vapour pressure.

The step-scan procedure was performed with a fresh portion (~1 mg) of the same bulk crystal. The sample heated up to a temperature usually on 10°C higher than that of each peak on the thermal curves was quenched to room temperature at the rate 200°C s^{-1}. Amounts of Li, In and Se in the vapour condensate and in the appropriate residual solid were determined by ICP AES after dissolution of the products in the concentrated HNO_3.

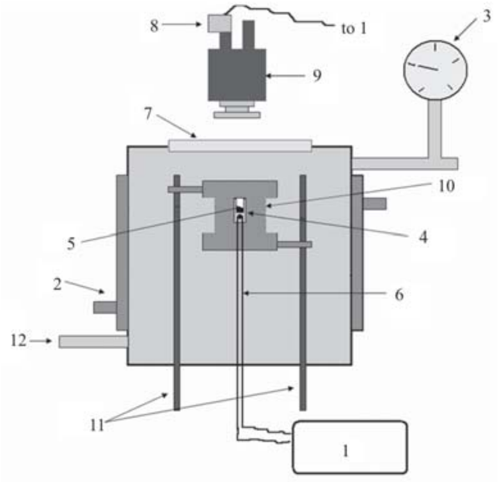


Fig. 1 Apparatus for the study of melting and evaporation of $LiInSe_2$ crystals

In the case of DD analysis HNO_3 (1:1) was taken as a solvent with temperature varying from 20 to 80°C. The DD procedure allowed chemical changes of the liquids above the melting point of the $LiInSe_2$ to be examined and some characteristics of the liquid metastable state to be assumed. Principles of DD technique identifying chemically phases and its application to characterize amorphous samples have been provided elsewhere [16–18]. The main principles of the technique are given shortly here. Dissolution of an individual and chemical homogeneous phase will be manifested by a horizontal linearity of the Li/In ratio during the whole dissolution process. Any local or extended deviation from this linearity along the time scale will be contributed in the calculating error of the averaged magnitude of the molar ratio and will be an evidence of a spatial chemical inhomogeneity of the sample.

A large (30 mm long and 15 mm in diameter) $LiInSe_2$ crystal was prepared according to the recipe described by Isaenko *et al.* [9]. The crystal identified by the XRD as single-phase was red in colour with the density consistent with an In_2Se_3-rich crystal. The chemical analysis showed composition as $LiIn_{1.02}Se_2$ or $0.49Li_2Se{:}0.51In_2Se_3$, i.e. as a solid solution with the excess of In_2Se_3.

Results and discussion

The typical thermal curves recorded with ~1 mg crystals for a heating rate of 1000°C $\min^{-1}$ and for various helium pressures are shown in Fig. 2. The first and second peaks on the curves (at 896 and 938°C, respectively) were pressure-independent, while temperatures of the next two peaks varied with the helium pressure. Temperatures of the peaks are compared with those on the TG-DTA curves recorded for $LiInSe_2$ in vacuum for a heating rate of 10°C $\min^{-1}$ in [2, 8].

One can see that the heating rate in these experiments differed in magnitude substantially but the temperatures of the pressure-independent peaks differed

Table 1 Comparison of the peak temperatures measured by various techniques, (°C)

Technique	Peak 1	Peak 2	Peak 3	Peak 4
Classical DTA-TG [2]	810	899–950 broad peak	1050	1150–1200 broad peak
Classical DTA-TG [8]	850	904–1000 broad peak	1020	1100
Rapid therm. anal. (this study)		899 and 940	1038	1124, 1147, 1173*

*Temperatures measured at 0.1, 0.2 and 0.3 atm of helium in chamber

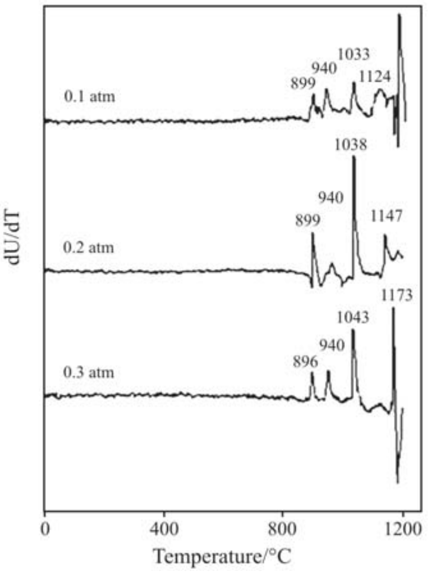


Fig. 2 Typical thermal curves recorded with the rate of 1000°C min^{-1}

only slightly from each other. In [2, 8] the peaks at 810 and 850°C have been interpreted as the start of evaporation and at 899 and 904°C as melting points of $LiInSe_2$ [2, 8]. All the peaks above melting point were not identified before.

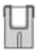
In order to check the origin of the peaks besides visual observations the authors measured the compositional changes of both the vapour and the residual solid quenched from desired temperature. These results are summarized in Table 2.

It follows from Table 2 that the initial red $0.49Li_2Se\cdot0.51In_2Se_3$ crystals heated up to 840°C losses the excess In_2Se_3 and turns out into the stoichiometric crystal of a yellow colour, although the thermal method itself in this case was insensitive to that determination. That the vapour consisted only from In and Se species at 850°C was also established by the mass-spectroscopic study [8].

The peak at 899°C corresponds to the melting point of $LiInSe_2$ that was confirmed by direct observation through the chamber window. It is important thus to mention that the peak at 899°C is indicative of congruent melting of the stoichiometric $LiInSe_2$ crystal. Hence it follows that all peaks above this temperature reflect transformations in the liquid melt. The peak at 940°C may be an indication of the occurrence of a liquid immiscible region for the samples on the Li_2Se-rich side. The peak at 1050°C then is a conversion of the inhomogeneous melt again into a homogeneous one. A series of experiments at helium pressures between 0.01 and 2.5 atm were performed to find precisely temperatures of the monotectic horizontal and the liquidus line. Finally, the phase diagram of the Li_2Se–In_2Se_3 system thus determined in the Li_2Se-rich side is shown in Fig. 3a along with the diagram studied before at temperatures below 900°C in Fig. 3b [7]. One can see that the high-temperature diagram indicates the formation of a solid solution in the Li_2Se-rich region within more narrow limits (about 1 mol% of Li_2Se) than is shown it the low-temperature diagram.

To support the high-temperature phase diagram obtained by the thermal results, the DD analysis was performed on three samples. It was the initial solid crystal and two melts quenched from 1050 (above the monotectic line) and 1150°C (above the liquidus line) the compositions of which were found to be $0.51Li_2Se:0.49In_2Se_3$ and $0.52Li_2Se:0.48In_2Se_3$, respectively. Figure 4 shows compositional changes of the samples by profiles of the dissolution kinetic curves of Li (1), In (2), and Se (3) elements and the molar Li:In ratio (4) as a function of dissolution time. Figure 4 corresponds to dissolution of a single-phase sample in which the kinetic curves of the elements behave absolutely synchronically, the Li:In ratio equal to 0.97±0.10 reflects real non-stoichiometry of the initial crystals with the In excess, this agrees well

Table 2 Characteristics of samples quenched from desired temperatures

Temperature of quenching/°C	840	905	950	1050	1150	>1150
Degradation in shape and colour	yellow	dark grey	grey	grey	light grey	light grey
						
Quantity of vapour condensate/%						
at 0.1 atm	nd	0.7	0.5	0.6	4.3	50
at 0.2 atm	nd	0.8	0.7	0.6	4.0	16
Molar Li:In:Se ratio in vapor						
at 0.1 atm		1:23:38	1:2:12	1:12:12*	1:16:14	1:29:33
at 0.2 atm		1:19:21	1:2:8	1:7:8	1:19:11	1:38:36
Composition of solids at 0.2 atm	$0.50Li_2Se:$ $0.50In_2Se_3$	$0.50Li_2Se:$ $0.50In_2Se_3$	$0.51Li_2Se:$ $0.49In_2Se_3$	$0.52Li_2Se:$ $0.48In_2Se_3$	$0.60Li_2Se:$ $0.40In_2Se_3$	$0.65Li_2Se:$ $0.35In_2Se_3$

nd = not detectable,
[*] The Li:In:Se intensity ratio determined by mass-spectrometry was 1:15:13 [8]

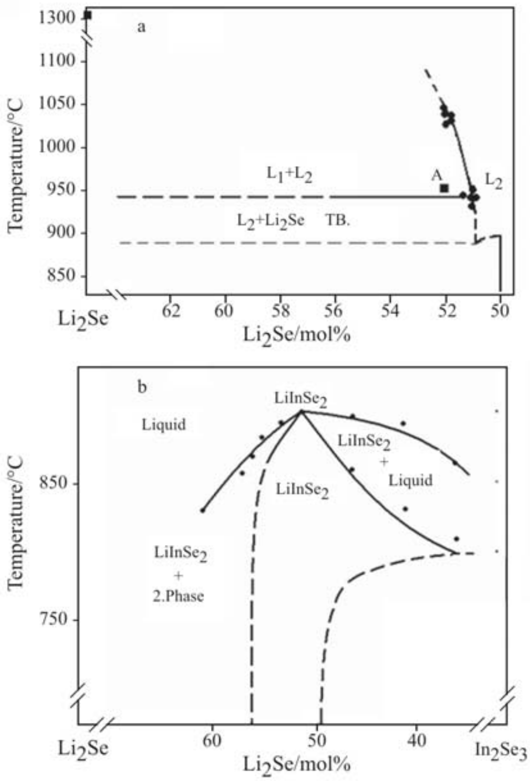


Fig. 3 The phase diagram of the Li_2Se – $LiInSe_2$ system on the Li_2Se side a – this study, b – from [7]

with results of the total chemical analysis. A fluctuating character of the Li:In line reflecting by the error value such as ±0.1 indicates a slight spatial inhomogeneity of the initial real crystal. Figure 4b shows the dissolution of a heterogeneous sample. The small peak starting at 0.5 min is dissolution of a binary Li–Se species while another species is three-component with the averaged Li:In value equal 1.2±0.2. The amount ratio of the Li–Se and Li–In–Se species agrees with the location of the A point on the phase diagram, Fig. 3a. Figure 4c shows the dissolution again only of the three-component species with the variable Li:In ratio between 1.27 in the beginning and ~1.0 in the end of the line.

Based on the results, we assumed that the melt quenched from 950°C is heterogeneous due to the occurrence of two liquids with compositions close to Li_2Se and $Li_{1.1}InSe_2$. Li_2Se being an ionic salt is supposed to dissociate into ions. The Se ions while in any polymeric form differ significantly by the nature from the three-component species and this contrast should be manifested itself by a mutual insolubility of the liquids and the occurrence of an immiscible region. The observed variable composition of the three-component species in both the melts may be explained by the existence of various types of ionic or molecular clusters. This explanation is based on a melt models proposed in [19–21] with their wide applicability to different systems and on the experimental results that the chemical individual of $A^{III}B^{YI}$ compounds due to a high thermal stability is valid even after overheating the liquid on 300°C [22]. Although the results of the overhead-quench processes studied here by the DD analysis were adequate to identify the liquid immiscible region in the Li_2Se-In_2Se_3 system, more extensive work is needed to better understand the structural features of the liquid state of the $LiInSe_2$ overheated melts.

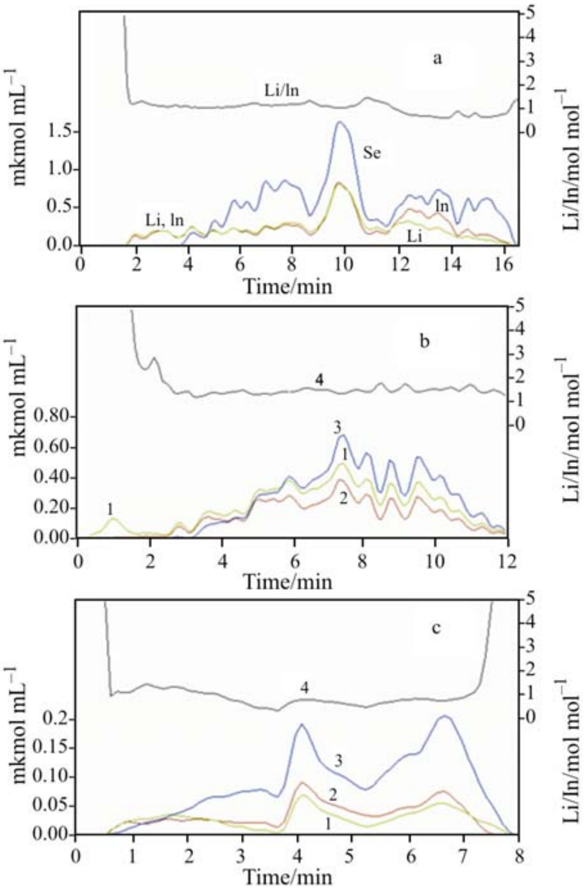


Fig. 4 Kinetic curves of elements dissolution and the molar Li/In ratio for a – the initial solid crystal, b – melts quenched from 950°C and c – from 1050°C

Three evidences are there to indicate the peaks in the range 1050–1200°C to the boiling points of the melts. First, these peak temperatures depend on the helium pressure in chamber and vary for the $0.52Li_2Se\cdot 0.48In_2Se_3$ sample as 1124, 1147 and 1174°C at 0.1, 0.2 and 0.3 atm, respectively. Extrapolation of these values as the lg$P$–1/T dependence allowed the equilibrium pressure of $LiInSe_2$ at melting point to be estimated at the level of about 0.05 torr. Second, it is these temperatures at which diffusion of the vapour equilibrium with the solid gave way to a flow resulting to sharp increasing of the evaporation rate and the vapour condensate amount. Third, because of the preferable evaporation of the In_2Se_3 component (incongruent process), upon heating composition of melt shifts to the Li_2Se-rich side. This change correlates well with a wetting phenomenon shown in Table 2. The higher the concentration of Li_2Se in the melt, the greater is the wetting which is an indicator of starting interaction of the melt enriched by Li with the Mo crucible. So, data in Table 2 is clearly shown the incongruent evaporation of the initial sample due to the preferential passage of In_2Se_3 into the vapour within the whole temperature range. The reliability of conclusion on the incongruent evaporation of $LiInSe_2$ is supported by quantitative compositional measurements of both the vapour and the residual solid that agrees well with results of the mass-spectroscopic study published previously by Hönle and Kühn [8], but not with those reported by Weise [2].

The pressure values found here at and above the melting point are small enough to be a source of the crystal inhomogeneity during the growth process in closed ampoules. However, growing $LiInSe_2$ single crystals is usually carried out with the Li_2Se excess and after 3–4 h of holding the melts at temperatures 920, 930 or 950°C [2–4, 9]. Our study shows clearly that at these conditions incongruent evaporation and the thermal dissociation in the melts take place that may vary radically the physico-chemical properties of the melts and may have appreciable effect on crystallization process. In this case the relation between the rate of diffusive transfer of various size species in the melt and the crystallization rate will determine the level of the crystal inhomogeneity. The higher the crystallization rate the higher is a probability for metastable and small-sized precipitates to occur. Therefore, the high-temperature diagram seems to explain better why crystals grown at above-mentioned conditions show light scattering centres, milk opacity and instability on air observed experimentally [2–4, 9]. The heterogeneity due to metastable Li-products occurs in the crystals well before than the low-temperature diagram shows. Only choosing properly the starting composition, crystallization temperature and the growing rate, the quality may be improved so that no Li-product inclusions may occur.

Conclusions

Novel techniques were developed for studying evaporation and compositional features of overheated and quenched melts of the $LiInSe_2$ crystals. Our study showed clearly incongruent evaporation and occurrence of a wide liquid immiscible region on the Li_2Se-rich side at temperatures above the melting point. Using the results on deviations from stoichiometry in the Li-rich crystals, which were smaller than values reported before, the main mechanism for the formation of inhomogeneities in $LiInSe_2$ crystals was considered.

The authors plan to use these techniques to make a systematic study of the processes for $LiMX_2$ compounds (M=In, Ga; X=S, Se), which clearly occur during the growth of these single crystals of a high optical quality.

Acknowledgements

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