

High-temperature solid–vapor and liquid–vapor transitions in binary and ternary chalcogenides La_2S_3 , MoS_2 , Mo_2S_3 and LiInSe_2

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Abstract

High heating rate thermo-microscopic analysis, analytical atomic-emission technique with inductively coupled plasma and differential dissolution method have been used to investigate solid–liquid and solid–liquid–vapor transitions of refractory chalcogenides La_2S_3 , MoS_2 , Mo_2S_3 and LiInSe_2 . The techniques were effective in determining the total pressure and vapor phase composition over the compounds in large temperature and pressure ranges. As a result, for compounds that evaporate incongruently, the melting points corresponding to their strict stoichiometry, the decomposition pressure–temperature relations, and other new results of the T – x phase diagrams for the La_3S_4 – La_2S_3 , Mo – MoS_2 , and Li_2Se – LiInSe_2 systems were obtained.

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1. Introduction

Progress in the study of T – x phase diagrams of sulfide systems with refractory compounds decomposing before melting was demonstrated in [1], where the melting points of compounds were measured under conditions reducing or preventing evaporation losses of samples over a heating period due to special apparatuses and procedures. However, the failure of these techniques to measure vapor pressures of decomposing compounds required the development of new methods. A special thermo-microscopic apparatus with rapid heating, high pressures of an inert gas and specific recording systems were proposed in [2]. While the application of the technique to determine the melting points of decomposing compounds was demonstrated in [2,3], other possibilities including precise measurements of vapor pressure still remained to be solved. In the present work, this technique combined with a precise chemical and phase identification of the products (vapor condensate and remainder) quenched from the temperature of any peak in the thermal curves was used. It allowed both melting and evaporation processes to be investigated in detail for refractory La_2S_3 , MoS_2 ,

Mo_2S_3 and LiInSe_2 compounds which are materials of important technical applications. This technique allowed to observe and indicate with high reliability the origin of thermal peaks and to determine quantitatively the pressure and composition of the vapor–solid phases at melting and boiling temperature. High heating rates were not hindrance to the study of equilibrium processes because a few minutes were shown to be sufficient to attain vapor–liquid–solid equilibrium at high-temperatures [1]. As a result, decomposition pressure–temperature relations and melting points corresponding to strict stoichiometry of these compounds evaporating incongruently were obtained as well as some new results for the T – x phase diagrams of the La_3S_4 – La_2S_3 , Mo – MoS_2 , and Li_2Se – LiInSe_2 systems.

2. Experimental

The apparatus for measuring the parameters of melting and evaporation processes is shown in Fig. 1. The specific recording system of the apparatus was sensitive to the detection of all types of transitions (liquid–solid, solid–vapor and liquid–vapor) due to a suitable IR (infra red) photodiode which was mounted on a microscope and measured the emitted thermal radiation of the sample as a function of temperature. The transitions appeared as marked peaks on the thermal radiation curves recorded in the $dU/d\tau$ – T coordinates, where $dU/d\tau$ is the time derivative of sample radiation. A small Mo crucible with about 1 mg of the sample was placed inside a tungsten heater of special geometry in direct contact with a W/W–Re (20%) thermocouple. This assembly was put into a water-cooled chamber filled with helium as a buffer gas. The helium

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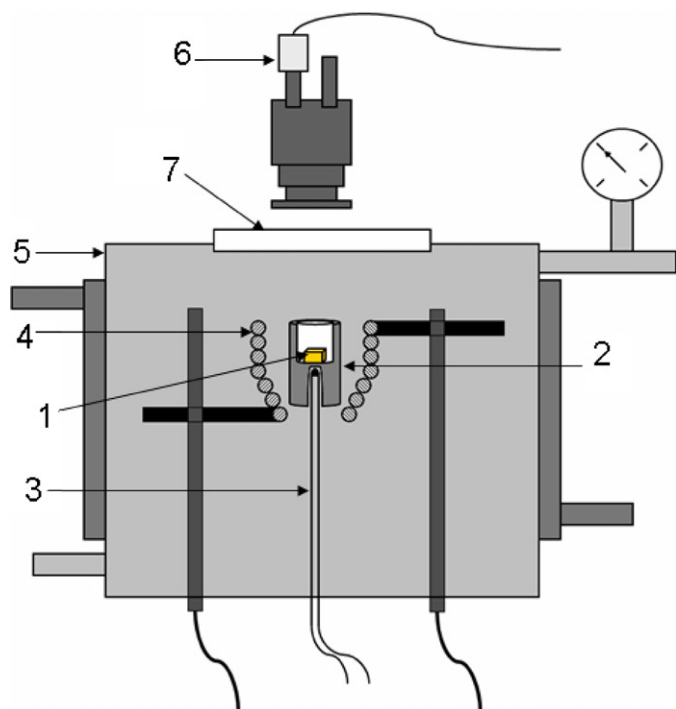


Fig. 1. Schematic diagram of the apparatus used for thermo-microscopic analysis with high heating rates: (1) sample, (2) Mo crucible, (3) W/W–Rh thermocouple, (4) tungsten heater, (5) chamber, (6) IR photo diode, (7) quartz window.

pressure in the chamber was set for any given value in the range 0.01–3 bar. Heating to 2500 K was performed at a constant rate in the range of 1–50 K/s, depending on the material and the task of the investigation. The apparatus was calibrated against the melting points of Au (1337 K), Co (1766 K), Pt (2045 K), Rh (2236 K), Al_2O_3 (2323 K) and the decomposition pressure of GaAs crystals equal to 1.0 ± 0.03 bar at 1883 K (the melting point). The accuracy of the measurements was about 1% for melting points and around 5% for the vapor pressure.

The thermal peaks were identified by microscopic observation of partial melting (solidus point), complete melting (liquidus point) and marked surface change (boiling point). The peak indication was also confirmed by a special quenching experiment: a sample heated to the temperature of the corresponding peak was quenched at a rate of 200 K/s and the chemical and phase compositions of the quenched products (vapor condensed on the window and the residue) were determined by atomic-emission technique with inductively coupled plasma (ICP AES), X-ray diffraction (XRD) or differential dissolution technique (DD).

By varying the heating rates and helium pressure in the chamber, the $T-x$ and $p_{\text{vapor}}-T$ diagrams could be obtained starting with a sample of defined composition such as La_2S_3 , MoS_2 , Mo_2S_3 and LiInSe_2 . Taking the highest heating rates and helium pressures ($P_{\text{He}} \gg P_{\text{vapor}}$), we can force the sample to boil at temperatures past the melting point. The increase of the evaporation rate and the vapor diffusion from the surface to the condenser at and above the boiling point led to the variation of the sample composition. On the contrary, if the melting point peak appeared first in the thermal curves, it signified that the vapor losses were prevented (or reduced) kinetically up to the melting of the sample. The fact that the composition of the samples quenched from the melting point remained really unchanged, was supported by direct chemical analysis. The deviations were always no more than 0.5 mass%. At low helium pressures ($P_{\text{He}} < P_{\text{vapor}}$) and low heating rates, the heterogeneity of the initial phases occurred for the phases existing over little or no stoichiometry range as their composition steadily changed (with a given step) owing to incongruent vaporization within a closed chamber. The composition/temperature values corresponding to these variations reflected, in this case, the form of the solidus–liquidus lines of the $T-x$ diagram.

The boiling point method (isobaric variant), well-known from [4–6], was realized to determine the vapor pressure of the samples. The samples were

linearly heated to the boiling temperature at a given helium pressure. In this case, the boiling peak occurring first in the thermal curves showed that the vapor pressure of the sample was equal to the helium pressure in the chamber ($P_{\text{He}} = P_{\text{vapor}}$). In these experiments, helium pressures varied usually between 0.3 and 2 bar and the partial pressure of the compound tested was considered to be the same as in the absence of helium based on the assumption that the system with helium was ideal (low pressures and no solubility of helium in the condensed phase). Therefore, the dependences of the boiling temperatures on the helium pressure were conceptually identical to the $p_{\text{vapor}}-T$ relation of the initial stoichiometric sample.

The DD technique as a chemical method of phase analysis was used here for the identification of quenched melts which were amorphous as could be expected. The method was described earlier and demonstrated on many examples [7–10]. A sample is dissolved in a flow of solvent with continuously increasing concentration and temperature. Under these conditions, different phases of a multiphase sample dissolve sequentially but not simultaneously. The elemental composition of the solution is monitored by an ISP AE spectrometer and the dissolution curves of all elements of the sample are recorded. From such kinetic curves, stoichiograms may be calculated which are the time dependences of the molar ratios between each two elements, for example, A:B, B:C and A:C for a three-component ABC sample. The time profile of the stoichiograms is governed by two main rules: stoichiograms remain constant with values equal to the stoichiometric coefficient ratios of the dissolved solid phase if only a single phase is dissolved. The stoichiograms are variable if several phases are dissolved at the same time. A stoichiogram indicates directly whether the mixture is really separated in individual phases, without the necessity of using reference materials for these phases. Therefore, the DD method is a combination of two procedures: separation of phases and measurement of their stoichiometry. 7N HNO_3 with a temperature varying from 20 to 80 °C was used as a solvent to analyze the quenched melts of LiInSe_2 samples.

3. Results and discussion

3.1. $\text{La}-\text{S}$ system

The problem of correct determination of the melting point and the saturated sulfur vapor pressure in the range 0–60 at.% of sulfur arises only for La_2S_3 which decomposes before melting. Due to the above-mentioned technique, the melting point of stoichiometric La_2S_3 was found to be (2133 ± 15) K (Fig. 2, curve 1). The $p_{\text{vapor}}-T$ relation in the temperature range 1853–2013 K (Fig. 2, curves 2–4) could be presented by the following linear equation:

$$\log p_{\text{sulfur}}(\text{bar}) = (6.29 \pm 0.16) - (12660 \pm 310)T^{-1} \quad (1)$$

Both the melting point and the $p_{\text{vapor}}-T$ relation are really correlated with the initial stoichiometry since the composition was found by means of a special high-accurate gas-chromatographic technique [11] to be $\text{La}_2\text{S}_{2.994(3)}$. Following Eq. (1), congruent melting of stoichiometric La_2S_3 takes place under the equilibrium sulfur vapor pressure of 2.26 bar. The melting peaks appearing after the boiling peaks (Fig. 2, curves 2–4) indicated the melting of samples with compositions different from the starting composition of La_2S_3 owing to the increase of the evaporation rate at and above the boiling point of La_2S_3 . The shift towards the less-volatile component resulted in the compositions $\text{La}_2\text{S}_{3.0-x}$ ($x=0.02, 0.04, \text{ and } 0.1$), which together with the melting temperatures being higher than that of the stoichiometric La_2S_3 , reproduce the liquidus curve of the $T-x$ diagram of the $\text{La}_2\text{S}_3-\text{La}_3\text{S}_4$ system. The melting point of La_2S_3 found here as 2133 K was the lowest among those reported previ-

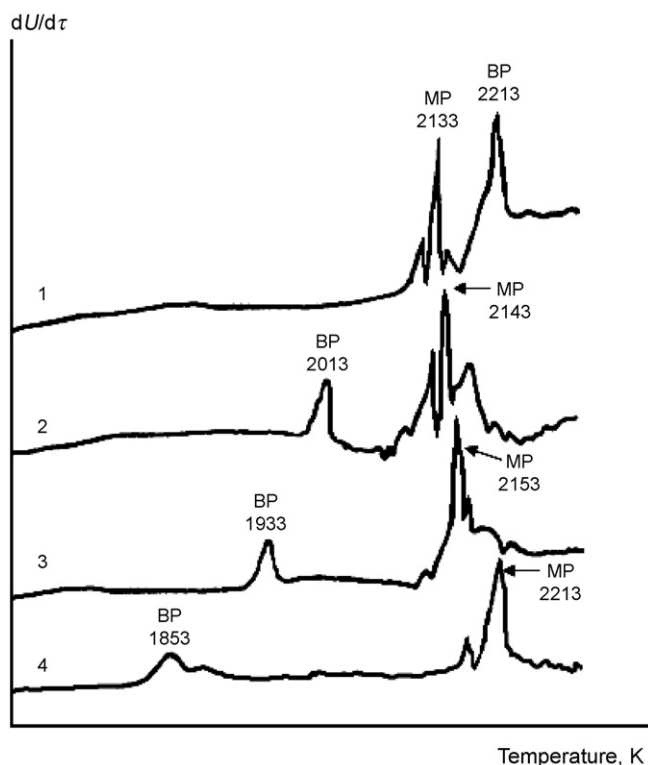


Fig. 2. Profile of heating curves of La₂S₃ recorded at a rate of 17 K/s and different helium pressures: 3 bar (curve 1), 1 bar (curve 2), 0.6 bar (curve 3), 0.3 bar (curve 4). MP and BP symbols are melting and boiling temperatures.

ously. The discrepancy is explained by the uncertainty of the composition/temperature correlations. In previous experiments, evaporation losses of La₂S₃ were not prevented and the end composition was not controlled.

Both the melting point and the $p_{\text{vapor}}-T$ relation determined here are the key parameters providing strict stoichiometry of La₂S₃ during its high-temperature preparations as large-sized crystals and ceramics. Only stoichiometric La₂S₃ in the range 0.5–16 μ shows transparency high enough making the material a good candidate for IR optic atmospheric windows.

3.2. MoS₂-Mo system

The Mo-S system was subjected to repeated investigation [1], but still remains not completely established. New results were obtained by our technique in the range of Mo-MoS₂ starting with only two samples of stoichiometric Mo₂S₃ and MoS₂. Two kinds of thermal curves at high (17 and 50 K/s) and low (1 and 5 K/s) heating rates were recorded for MoS₂ and Mo₂S₃ (Fig. 3a). At high rates, solid MoS₂ began to decompose at 1853 K under $p_{\text{vapor}} = 1$ bar to Mo₂S₃ and sulfur gas. Since this reaction proceeded very rapidly, only one half of MoS₂ decomposed resulting in the MoS₂ + Mo₂S₃ mixture (1:1) with eutectic and liquidus temperatures of 1953 and 2053 K, respectively (Fig. 3a, curve 1). At low rates, the evaporation losses increased markedly and MoS₂ was converted into the Mo₂S₃ + Mo mixtures composed of variable amounts of these phases identified chemically and structurally (Fig. 3a, curve 3). All the mixtures showed an eutectic temperature of 1893 K and liquidus points

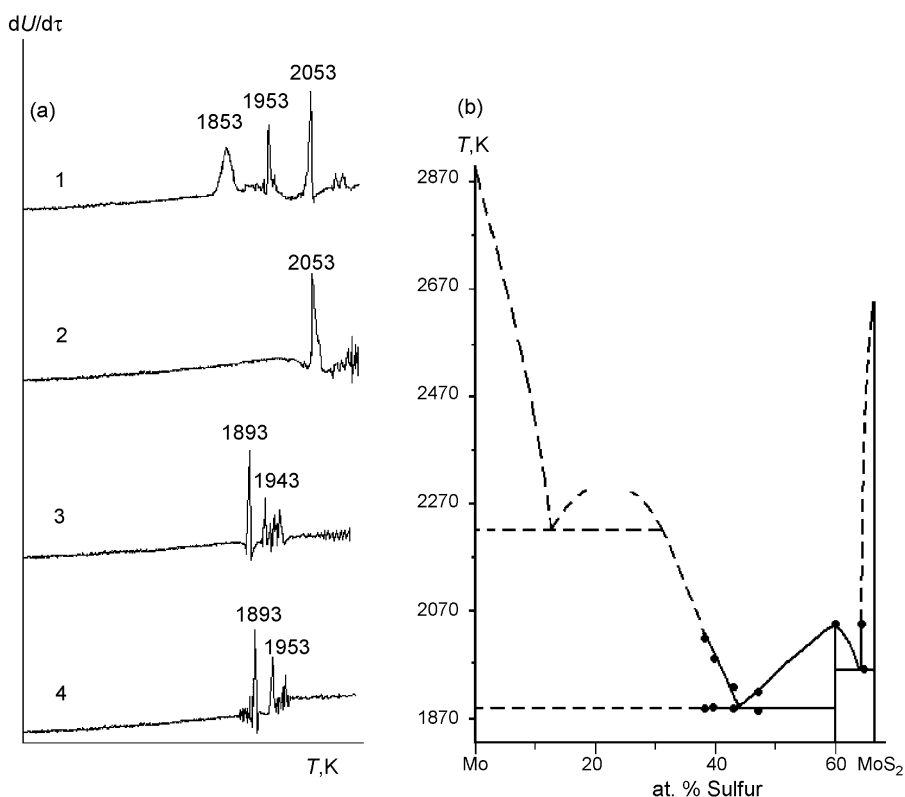


Fig. 3. (a) Profile of heating curves of MoS₂ and Mo₂S₃ recorded at a helium pressure of 1 bar and different heating rates: MoS₂ (17 K/s, curve 1), Mo₂S₃ (30 K/s, curve 2), MoS₂ (1 K/s, curve 3), Mo₂S₃ (5 K/s, curve 4) and (b) the $T-x$ diagram of the Mo-MoS₂ system.

Table 1
Melting and evaporation parameters for MoS₂ and Mo₂S₃

Parameter	Earlier works	This work ^a
$P_{\text{part}} = f(T)$ for MoS ₂	The flow method followed by only Mo analysis in vapor [14]: 10^{-5} – 10^{-4} bar at 1523–1738 K	Boiling points method: 1.0 ± 0.1 bar at (1853 ± 15) K for solid MoS ₂
MP of Mo ₂ S ₃	<1973 K, 2013 K, >2273 K [1]	(2053 ± 10) K
Melting behavior of Mo ₂ S ₃	Incongruent melting, disproportion or dissociation [1]	Congruent melting under equilibrium sulfur vapor pressure
Eutectic temperature of MoS ₂ + Mo ₂ S ₃ mixtures	No data	(2226 ± 15) K
Eutectic temperature of Mo + Mo ₂ S ₃ mixtures	1563 K, (1773 ± 100) K, ~ 1733 K, (1883 ± 15) K [1]	(1888 ± 15) K

^a Partial and full melting of samples and the appearance of solid Mo in the melts were also revealed microscopically.

between 1923 and 2053 K depending on the total composition of the mixture (Fig. 3b). Contrary to MoS₂, Mo₂S₃ heated at a rate of 30 K/s melted congruently without marked loss of sulfur (Fig. 3a, curve 2) which was not attained in previous experiments [1]. Heating at low rates varied the composition Mo₂S₃ to a Mo₂S₃ + Mo mixture as verified by XRD and chemical examination of the quenched products. The different mixtures showed eutectic temperature of 1893 K and liquidus temperatures between 1900 and 1980 K, as in the case of mixtures formed by decomposition of MoS₂ (Fig. 3a, curve 4). All the results are summarized in the T - x phase diagram shown in Fig. 3b, where the dashed lines relate to data taken from [1]. In Table 1, our results are compared with literature data for the MoS₂-Mo system. They demonstrate clearly the effect of evaporation on stoichiometry and the heterogeneity of heated samples of Mo₂S₃ and MoS₂ which is important for a correct representation of the T - x diagram.

3.3. Li₂Se-LiInSe₂ system

LiInSe₂ was included in this study as an object for which all transitions appeared in the thermal curves above the melting point. Since both its vapor and melt were very aggressive toward any container material, the high heating rate technique was useful to study the melting and evaporation processes due to the lower time of melt-crucible contact. A typical thermal curve (profile depended only slightly on helium pressure and heating rate) is depicted in Fig. 4a. The origin of the peaks lying after the melting peak at 1169 K was clarified by the quenching procedure and chemical/phase identification of the quenched products. This experiment showed the preferential transition of the In₂Se₃ component into the vapor phase and indicated the incongruent evaporation of LiInSe₂ melts. The shift of the initial composition to the Li₂Se side led to the occurrence of the liquid immiscibility characterized by a monotectic temperature of 1213 ± 10 K. The peak at 1316 K (at 1323 K on another curve not shown here) occurred when the inhomogeneous melt turned back into the homogeneous state (Fig. 4b). The boiling peaks being the last in the thermal curve appeared at temperatures between 1397 and 1446 K when the helium pressure in the chamber changed from 0.1 to 0.3 bar. If the results are presented as $\log p_{\text{vapor}} - 1/T$ and the line is extrapolated to the melting point of LiInSe₂ at 1169 K, the pressure of saturated vapor over the melt would be about 10^{-5} bar.

To support the thermal experiment that revealed the coexistence of two liquids in the Li₂Se-rich range, a DD analysis was performed for melts quenched from temperatures slightly higher than the melting, monotectic and liquidus points, respectively (Fig. 5). The changes in composition follow immediately from the profiles of both the dissolution curves of Li, In, Se elements and the molar Li/In ratio. The single-phase three-component species dissolved as shown in Fig. 5a and c: here the kinetic

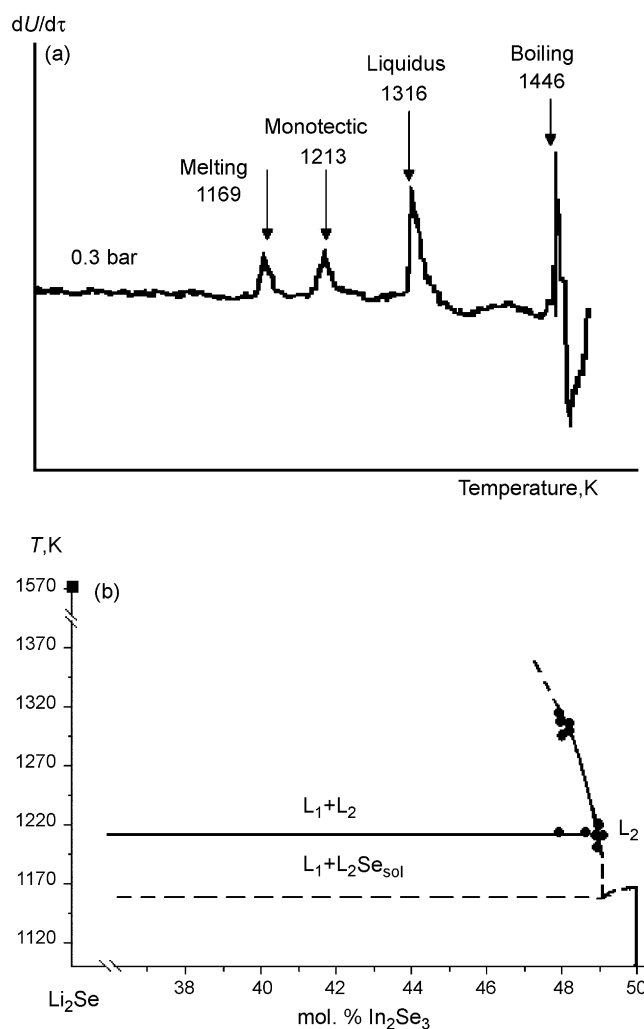


Fig. 4. (a) Profile of heating curves of LiInSe₂ recorded at a rate of 17 K/s and helium pressure 0.3 bar and (b) The T - x diagram of the Li₂Se-LiInSe₂ system.

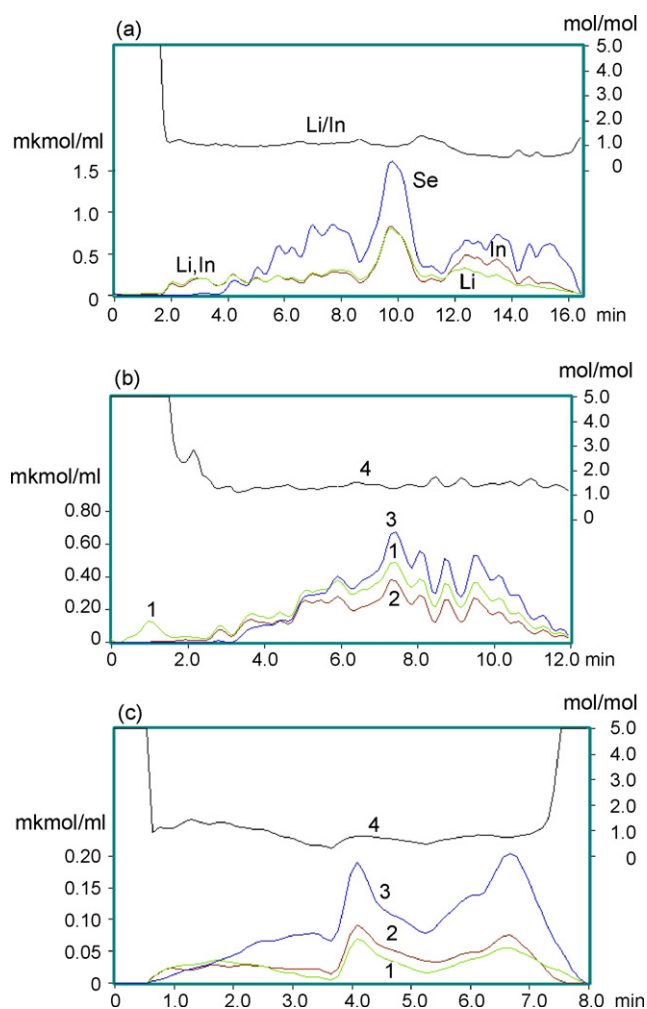


Fig. 5. Kinetic curves of Li (1), In (2), Se (3) dissolution and molar Li/In ratios (4) as functions of dissolution time for LiInSe₂ melts quenched from melting (a), monotectic (b), and (c) boiling temperature.

curves of all the elements go synchronically and the Li/In ratio is almost constant and close to unity similar to stoichiometric LiInSe₂. Dissolution of two phases is demonstrated in Fig. 5b: the small peak appearing at 0.5 min corresponds to dissolution of a binary Li–Se species. Another three-component species with synchronic kinetic curves dissolves later and its averaged Li/In ratio is also close to unity. This means that two liquids with compositions Li₂Se and close to LiInSe₂ are present in melts quenched from the monotectic temperature. This finding agrees well with the form of solidus–liquidus lines obtained in the thermal experiment and shown in Fig. 4b. A more detailed study of the behavior of overheated LiInSe₂ melts will be published later. However, it is clear even now that the incongruent evaporation of LiInSe₂ and the immiscibility region detected

here may lead to the occurrence of non-stoichiometry and undesirable Li₂Se precipitates which are the scattering centers of LiInSe₂ crystals grown from the overheated melts [12]. This seems not to fulfill the basic requirements providing practical applications of LiInSe₂ as a promising nonlinear optic material [13].

4. Conclusions

A rapid heating thermal technique combined with analytical methods was applied to La₂S₃, Mo₂S₃, MoS₂ and LiInSe₂ which were evaporated incongruently to study the details of the melting and evaporation processes. The unique ability of the technique to measure high vapor pressures (up to 3 bar) at high-temperatures (up to 2500 K), to determine correctly the high melting points of decomposing compounds while preserving their initial stoichiometry, and to study transitions in overheated melts is demonstrated. The rapid heating technique combined with quenching experiments followed by analyses of the quenched products is a very promising method for investigating solid–liquid–vapor and liquid–liquid–vapor equilibria of compounds with a rather high own vapor pressure. This motivates further development of the technique for application to other materials.

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References

- [1] G. Moh, *Top. Curr. Chem.* 76 (1978) 108–125.
- [2] Ya. Gibner, I. Vasilyeva, *J. Therm. Anal.* 53 (1998) 151–160.
- [3] I. Vasilyeva, E. Belyaeva, Ja. Gibner, *J. Therm. Anal.* 52 (1998) 403–412.
- [4] T. Sato, H. Kaneko, *Technol. Repts. Tohoku Univ.* 16 (1952) 18–33.
- [5] D.T. Ulrich, *Naturwiss-phil. FFH, Diss.* Braunschweig, 1954.
- [6] V. Glasov, A. Pashinkin, A. Malkova, M. Pasternak, *Neorg. Mater.* 15 (1979) 408–411.
- [7] V. Malakhov, *J. Mol. Catal. A* 158 (2000) 143–148.
- [8] I. Vasilyeva, A. Vlasov, V. Malakhov, M. Predtechensky, *Thin Solid Films* 292 (1997) 85–90.
- [9] I. Vasilyeva, *J. Alloy Compd.* 323/324 (2001) 34–38.
- [10] A. Prokofiev, I. Vasilyeva, V. Ikorskii, V. Malakhov, I. Asanov, W. Assmus, *J. Solid State Chem.* 177 (2004) 3131–3139.
- [11] L. Chuchalina, I. Vasilyeva, A. Kamarzin, V. Sokolov, *Zh. Analyt. Khimii, (Russ.)* 33 (1978) 190–192.
- [12] L. Isaenko, I. Vasilyeva, A. Merkulov, A. Yelissev, S. Lobanov, *J. Cryst. Growth* 275 (2005) 217–223.
- [13] D. Nikogosyan, *Newly Developed and Perspective Crystals*, Springer Sciences/Business Media, Inc., Printed in USA, 2005, p. 267.
- [14] R. Isakova, *Izv. Acad. Nauk Kaz. SSR (Russ.)* 3 (1961) 3–7.