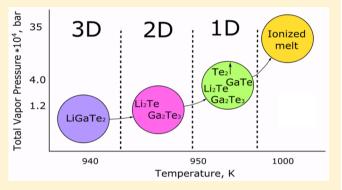
Phase Transitions of Nonlinear Optical LiGaTe₂ Crystals before and after Melting

Inga G. Vasilyeva,**,†60 Ruslan E. Nikolaev,† Pavel G. Krinitsin,‡ and Ludmila I. Isaenko‡

ABSTRACT: Phase transitions of ternary LiGaTe₂ crystals with the chalcopyrite structure were investigated between temperatures 920 and 1300 K using traditional and high-speed thermal analyses together with static tensimetric methods. It was found that solid LiGaTe₂ melts congruently at 940 K without any sublimation. The vapor involving Ga and Te species occurs at 953 K, whereas the Li species are detected only above 1000 K. The lattice stability of solid LiGaTe₂ holds up to the melting point, but the liquid phase begins to form the vapor pressure which increases with temperature due to the dissociation reactions in the melts. The most likely chemical forms of LiGaTe₂ and their structures are suggested on the basis of our own experimental measurements of the



total pressure and composition of the vapor for $LiGaTe_2$ by adding the known information on the chemical bonds and structures of the liquid individual binary Li_2Te and Ga_2Te_3 as constituents of the ternary $LiGaTe_2$. The changes are presented in the scale of temperature and the vapor pressure of the melts. New thermochemical data obtained for $LiGaTe_2$ provide a significant contribution to the field of thermodynamic chemistry and are promising for understanding the precrystallization state of the melts which, in turn, can provide a guideline for optimizing the time—temperature regime of crystallization in order to improve chemical uniformity and optical quality of these crystals.

1. INTRODUCTION

The ternary chalcogenides ABC_2 (A = Li; B = In, Ga; C = S, Se, Te) as tetrahedrally coordinated semiconductors with sphalerite (SP) and chalcopyrite (CH) structure, have a potential for many technological applications, including optical tomography, IR-laser spectrometry, and systems of laser guidance and neutron detection. 1,2 Among these compounds, LiGaTe₂ (LGT) crystal has a unique set of properties. It is transparent, phase-matchable for frequency doubling of CO₂ laser radiation at 10.6 μ m, possess a high birefringence and considerable nonlinear susceptibility equal to 0.094 and $d_{36} = 43 \text{ pm/V}$, respectively.^{3,4} For all these applications, however, large homogeneous single crystals of a high optical quality and strictly stoichiometric composition should be grown. Traditionally, the Bridgman-Stockbarger technique is used to grow crystals, although the compounds have peculiarities associated with enhanced volatility of the chlalcogen and a high chemical activity of the Li-containing vapor and liquid phases. This creates some difficulties in the synthesis of initial charge and crystal growth especially for LGT. Their growth still remains troublesome, even though they are prepared by the same procedure that was effective for growing large optical-quality single crystals of ternary Li-Ga-containing sulfides and selenides. For LGT, only polycrystalline ingots with color variability were obtained, which changed drastically when exposed to air. $^{1,4-6}$ The best results represented by $\sim 3-4$ mm single-crystalline blocks were sufficient to measure linear and nonliner optical properties and to uphold the high practicality of LGT.^{4,7} However, the polycrystalline growth demonstrated that LGT with tetragonal CH structure and space group $\overline{I42}d$ differing from those of the sulfides and selenides has other chemical bonding and hence other thermochemical properties. For LGT, this information is scant and conflicting. 4,5,8,9 This originates both from the low quality of test crystals and inadequate techniques measuring phase transitions of these volatile and aggressive compounds. For crystals, structural and point defects, second phases, light-scattering inclusions invisible for XRD, chemical instability and contamination from the crucible material have a detrimental effect on thermodynamic and thermochemical properties. For LGT, it was shown that the second Te phase and the color variety radically altered melting points and vapor pressure. 4 Therefore, a careful characterization of the LGT crystals should come before the study of their thermal behavior. However, even with well-characterized

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[†]Nikolaev Institute of Inorganic Chemistry, Russian Academy of Science, Siberian Branch, Academician Lavrentyev Avenue, 3, 630090 Novosibirsk, Russia

[‡]Institute of Geology and Mineralogy, Russian Academy of Science, Siberian Branch, Academician Koptyug Avenue, 3, 630090 Novosibirsk, Russia

crystals undergoing phase transitions and thermochemical reactions in melts, it will be difficult to determine correctly invariant points of the processes in the absence of special techniques providing real or local equilibrium conditions at a desired temperature. We have succeeded in the development of an experimental approach and technique to measure correctly the melting temperature, quantitative p-T functions, and transitions in melts using a high-speed thermal analysis operated at high, middle, and low buffer-gas pressure and direct tensimetric methods. 11-13 Since the study of thermal behavior of solid and liquid states for LGT has become challenging, we were hopeful of finding the desired thermochemical and thermodynamic data with these techniques. Considering the significant interest in LGT as the unique nonlinear material, in this paper we report a detailed investigation of LGT melting and evaporation which provides reliable data on liquid chemical forms and their arrangement depending on temperature. In turn, the new thermochemical and thermodynamic data can provide a guideline for optimizing the homogeneous crystallization regime and to grow the LGT crystals of optical quality.

2. EXPERIMENTAL SECTION

- 2.1. Synthesis. The synthesis of polycrystalline charge was conducted in a controllable manner in a glass-carbon container from the elementary starting chemicals of 99.99% purity for Li and 99.999% for Ga and Te and with the 16% extra lithium to provide the Li stoichiometry of the charge. The charge was loaded in a crystallization ampule covered by several layers of pyrolytic graphite. The ampule was heated and maintained at about 940 \pm 10 K for several hours, then shifted to the cold zone with a rate of 2-5 mm/day and typical axial temperature gradients of 2-4 °C/mm. This procedure was developed in detail previously. The grown crystals showed the macroscopic lamellar regions of different color from yellow to black, and for further study, yellow crystalline blocks (≤ 1 mm), where possible, were extracted, from the ingots (Figure 1). Usually each block was represented by two, three, or more crystallites.
- **2.2. Characterization.** The chalcopyrite structure of the crystals was verified by powder XRD, and they looked like single-phase with lattice parameters a = 6.330 Å and c = 11.698Å and c/a = 1.85. Their band gap was found to be 2.41 eV, as it was before, which demonstrates a lower density of point



Figure 1. Total view of LGT crystals.

defects. The composition of the yellow crystals was determined by ICP AES for Ga and Te and flame photometry for Li to be $\text{Li}_{0.98(2)}\text{Ga}_{1.00(1)}\text{Te}_{2.02(3)}$ with a nearly actual stoichiometry. However, the crystals showed a quite high residual absorption (scattering) at shorter wavelengths, which is identical with that of the crystals studied in ref 4 (Figure 2). The reason, most probably, is that the colloidal Te inclusions appear on boundaries of small yellow LGT crystallites.

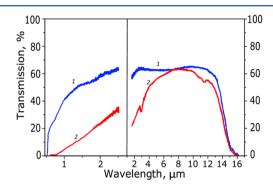


Figure 2. Transmission of the LGT yellow plate (1) and repolished black plate stored for several months in air (2).

The capacity of the inclusions is converted in air to crystalline and slightly oxidized state due to the oxygen catalization, 14 resulting in the formation of thin surface grayblack layers and the degradation of optical quality of the crystals. The chemical nonuniformity (the secondary pure Te phase) and the stoichiometry shift (in terms of color) are crucial factors for the optical quality of the crystals, and their occurrence requires further clarification.

2.3. Techniques and procedures. To characterize the solid and liquid state of LGT, both the melting point (T_{mp}) and the vapor pressure correlating directly with chemical bonding and structure should be measured because all the ABC₂ compounds with the PH and CH structures were found previously to sublimate incongruently.^{5,8} However, there are different sources of errors and inaccuracies which made difficult determination of the thermochemical characteristics with high reliability and accuracy. So, evaporation, chemical composition instability, and contamination from the crucible material as well as overheat of melts are capable to distort the values. $^{4-6,8,14}$ To eliminate the problems, different independent but correlated techniques were used, allowing the correct determination of invariant points of phase transitions. The combination of dynamic polythermal TG-DTA method, quasi-static high-speed thermal analysis (HSTA) capable to create conditions for local equilibrium, and two variants of static tensimetric weight method (or frozen equilibrium) sufficed for the simulation of experiments and a reliable interpretation of the results. Safe measurement of intrinsic vapor pressure of the secondary Te phase and LGT with the same gas species, when they are mixed, was the apparent advantage of the combined methods.

The traditional longer-time TG-DTA technique was carried out in a crucible with a pyrolytic carbon deposition and with the 3 K/min heating rate to determine precisely the solid-phase transition, $T_{\rm mp}$, and the evaporation weight losses if they exist. HSTA was capable to measure both the melting and boiling points. For measurement of $T_{\rm mp}$, a high buffer-gas pressure in the apparatus and high heating rates were used to prevent kinetically surface evaporation of the LGT crystal located inside of the open Mo crucible where local solid/vapor equilibrium is

realized. 10 The absence of any condensate on the sight-glass of the apparatus supported the fact of conservation of the initial composition up to the melting point. For measurement of the total pressure as a temperature function, a local equilibrium was realized in the open Mo crucible when the vapor pressure under the solid or liquid LGT became equal to the buffer-gas pressure in the apparatus. Temperature of the invariant boiling point at a given pressure (isobaric variant) is determined by the peak on the $dU/d\tau - T$ curves (the time derivative of emissive power versus temperature). The boiling point procedure was very advantageous for finding the dissociation pressure of various liquid and solid phases, involving ternary LiBC2 being sulfides and selenides. 4,10 When recording the heating curves, the temperatures of solid/vapor, solid/liquid, and liquid/vapor transitions were measured, and the amount and composition of the vapor condensates were determined at a temperature of each transition, which served as additional sources for correct interpretation of the melting and evaporation processes.

The total pressure and gross-composition of the vapor being in equilibrium with the solid or liquid phases were characteristics of the solid (liquid)—vapor transitions of LGT studied at different temperatures using the frozen equilibrium procedure in a high quality silica glass reactor with an accurately known volume, Figure 3. ¹⁵

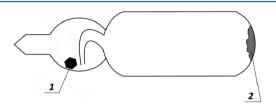


Figure 3. Location of test sample (1) and frozen condensate (2).

The initial charge was that which minimized evaporation losses to 0.5%. The reactor was held at temperatures close to, equal to, or higher than $T_{\rm mp}$ of LGT during 10 min specified as equilibrium, and one end of the ampule was cooled by liquid nitrogen to condense the whole vapor in the same place. Composition and amount of the condensate were determined by ICP AES and flame photometry for Li even if these elements were in the minority (the detection limit of $\leq 10^{-6}$ g). At lower temperatures, only the tellurium phase is sublimated, which allows deducting its amount from the total weight condensate when the LGT and Te phases are evaporated together. The vapor pressure of LGT at each temperature was calculated by the Mendeleev-Klayperon equation, assuming simple evaporation of the determined condensed phase. It was "hypothetical" pressure because reliable data on the vapor composition for the Ga-Te phases, as a rule, were not available. However, even these pressures were essential for understanding the liquid state of LGT.

3. RESULTS AND DISCUSSION

The heating DTA–TG curves were recorded for LGT because the cooling curves commonly showed underestimating values. Temperature of the solid/liquid transition independent of the initial charges was determined to be 943 ± 2 K (Figure 4). It was higher than 913 ± 10 K, which was found previously for inhomogeneous ingots containing the crystalline Te and GaTe phases detectable by XRD. The only endothermic melting peak on the DTA curves demonstrates the absence of the CH–

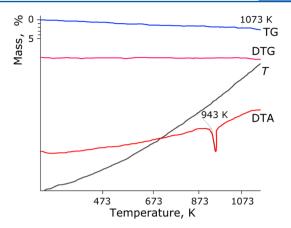


Figure 4. TG-DTA heating curves of LGT recorded with a rate of 3 $\rm K/min$.

PF solid transition for LGT that is in complete accordance with the known general trend observed in the ABC_2 (with A= In, Cu Ag) behavior with the CH structure having lattice parameter ratios c/a < 1.95. The total weight losses ($\sim 1.6\%$) resulted from the sublimation losses ($\sim 0.6\%$) and the volatile melts ($\sim 1.0\%$). Note that this 0.6% belongs to the secondary pure Te phase.

Figure 5 shows HSTA apparatus and the heating curves recorded up to 1050 K with a rate of 1000 K/min using different buffer-gas pressures to measure temperatures of solid/liquid and liquid/vapor transitions.

In this short-time experiment, the melting point of LGT independent of the buffer-gas pressure was found to be 940 ± 5 K. This value agrees well with that determined by the longer duration TG-DTA, and they both demonstrate the congruent character of the LGT melting. Neither Ga nor Li but only the Te species were detected in the vapor condensate at this temperature.

Isobaric experiments measuring the p-T dependences were carried out under buffer gas pressures varying between 7 and 0.1 bar, and no boiling peaks were detected on heating curves (Figure 5). Since the pressure below 0.1 bar is measured here with the experimental error greater than we would like, visual observation for the LGT behavior in temperature range from 25 to 1050 K with chemical analysis of the condensates became the subject of study. The first surface change occurred at 850 K together with the Te condensate; at 955 K, the vapor condensate consists of the Te and Ga species, whereas Li appears in the vapor only at 1000 K. Above this temperature, the melt drastically reduced in size due to the full LGT evaporation followed by solidification into a gray-white residue. It was identified as TeO₂ according to small peaks at 1000 K, which is its melting point, Figure 5 (below). This oxide is derived from the boundary surface layers on the initial LGT

The weight method was most promising for quantitative measurement of the $p\!-\!T$ functions. The average from three measurement values on the element amounts in condensates and the solid remains found at different temperatures are given in third and fifth columns of Table 1. The reactor from a high-quality silica glass, the short-duration experiment, and the lack of any postmelting degradation of the reactor walls ensured the absence of a detectable interaction of the vapor and melt with the silica glass. Besides, the acceptable composition balance between the weight loss of initial charges and analytical results

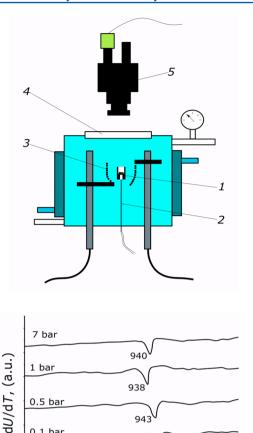


Figure 5. Apparatus (top): 1, Mo crucible with crystal; 2, Pt/Rd thermocouple; 3, W heater; 4, sight-glass; 5, photodiode; thermal curves of LGT at different buffer-gas pressures (bottom).

Temperature, K

900

945

950

1000

0.1 bar

850

of the condensates indicates that the results are nondistorted and reliable.

Data of Table 1 show that at 920 K only the secondary pure Te phase in amounts of 0.4% (0.6% was found in TG experiment) is evaporated producing the vapor pressure in 10^{-3} bar that is less than expected equilibrium pressure of the elemental Te equal to 1.5×10^{-2} bar. Being unsaturated, this vapor was capable with temperature only to thermal dilatation that showed in the fourth column of Table 1. No Li and Ga gaseous species were detected under the solid LGT. At other temperatures, the crystals are melted, wetting slightly the reactor walls and forming a vapor from the Te and Ga-Te species. The total amount of Te species in the condensates was reduced by the Te amount in the Te phase which was determined in advance. The atomic Te/Ga ratio in the total

condensate increases strongly with temperature and intrinsic pressures calculated for both these phases are given in the fourth column of Table 1.

To separate the Te and Ga-Te species in condensates, experiments in long ampules with temperature-gradient profile were performed, where the vapor condensates were located in different places (Figure 6).

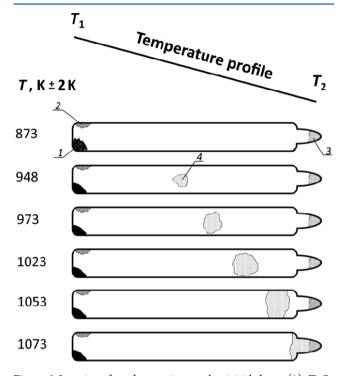


Figure 6. Location of condensates in ampules: initial charge (1); TeO₂ (2); Te (3); Ga-Te (4).

All the vapor condensates were identified chemically and by different colors; white, pale gray, and almost black correspond, respectively, to TeO₂, any Te/Ga phases with the ratio varying between 1.5 and 0.9 inside extended coating, and the elemental Te. At 948 K, the Ga-Te condensate was closely spaced to the hot zone, whereas the total Te condensate was in the cold zone; at above 1000 K, the Ga-Te condensate shifted more and more to the cold zone due to the increase of the Ga-Te species

In Figure 7, the Te/Ga ratios and the $\log p-1/T$ dependence at temperatures ranging from 940 to 1040 K are plotted. One can see that ternary LGT species are unrecognized in the vapor and the melts are evaporated incongruently, which happens due to chemical transitions.

Although melting is the most familiar physical phenomenon, chemical changes in the LGT melts remain unknown, and

Table 1. Characteristics of LGT Evaporation Process

		atomic ratio, vapor			total pressure (bar)		atomic ratio, residue		
T (K)	mass loss % ^a	Li	Ga	Te	LGT	Te	Li	Ga	Te
920 solid	0.4	no	no	(2.0)	no	1.20×10^{-3}	1.02	0.99	1.97
955 melt	0.6	no	1.5	7.6	1.2×10^{-4}	1.24×10^{-3}	1.03	0.98	1.99
990 melt	0.9	no	5	50	4.0×10^{-4}	1.28×10^{-3}	1.02	0.99	1.99
1040 melt	1.7	< 0.1	16	340	3.5×10^{-3}	1.39×10^{-3}	1.00	0.99	1.97

^aError in $<5 \times 10^{-6}$ g

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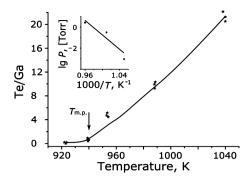


Figure 7. Te/Ga atomic ratio versus temperature; in the inset: $\lg p-1/T$ dependence for the liquid LGT.

results in Figure 7 can be valuable in the field. Two facts, congruent melting of LGT and too low total pressure (here below zero) at $T_{\rm mp}$, point out that a structural change in the melt is also small, and only minor modifications of the dispositions of all, or most, ions of LGT occur. Therefore, $T_{\rm mp}$ is identified as the temperature at which a single regular initial structure of LGT can coexist in the melt. This interpretation is in complete accordance with the known general trend for $A^{\rm T}B^{\rm III}C^{\rm YI}_{\ \ 2}$ chalcopyrite compounds to melt with conservation of the short-range order and the chemical bonds inside large macromolecular units. Between 940 and 950 K, a small change is expected also, although the fact of overcooling in 15—30 K for the melts heated up to such temperatures should be attributed to the dissociation process. $^{5-7}$

In an attempt to identify this process, we focused on a high structural stability of the solid LGT revealed in our experiments. For LGT, melting goes without evaporation, whereas the Li-Ga sulfides and selenides sublimate before melting with the vapor from B_2C_3 species.^{4,14,19} The stability of two structural CH and SP types of the LiBC2 family was also considered previously using (i) diffraction measurements, (ii) analysis of the lattice vibrational properties, and (iii) the principles of the close anion packing 4,5,7,8,17 The CH lattice was found to be more stable than the SP lattice, especially in the case of LGT where sizes of both the Li⁺ and Ga³⁺ cations were well suited for the tetrahedral interstice size in order to form almost ideal LiTe, and GaTe, tetrahedrons. For the LiGaS₂ (LiGaSe₂) with orthorhombic structure, the tetrahedral interstice size is smaller than that of the Li¹⁺ ion, which results in a distortion of the LiS₄ (LiSe₄) and GaS₄ (GaSe₄) tetrahedrons with the tendency of the Li coordination change and changes of the Ga-S (Ga-Se) binding energy.

Our attention was directed to the polyhedral LGT structure, which allows assuming its possible reconstructions with temperature, Figure 8. The structure is a three-dimensional framework built from the LiTe₄ and GaTe₄ tetrahedrons differing in chemical bonding and interatomic distances. The nature of Li—Te and Ga—Te bonding in the tetrahedrons follows from the interatomic force constants estimated in refs 5,7 and from calculation of electron density within the density functional theory. The covalent character of the Ga—Te bonding dominates, and Li—Te bonding possesses a strong ionicity. The mutual arrangement of the LiTe₄ and GaTe₄ tetrahedrons demonstrates two clearly defined molecular fragments that are shielded only slightly. The same structural feature is also observed for LiInTe₂. We suggest that the structural feature can promote the melt dissociation into binary liquid Li₂Te and Ga₂Te₃ forms over this temperature interval,

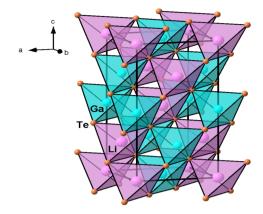


Figure 8. Polyhedral chalcopyrite structure of LiGaTe₂.

especially if one takes into account thermal decomposition of the solid $LiBC_2$ compounds just into the same binary compounds.⁵ Other available data indicate that these solid binary compounds passed into melts without the structural changes.^{20,22} Therefore, one can assume that both forms pass into the melt into the molecular state. This is the second step of the melt dissociation.

The behavior of the liquid Li_2Te and Ga_2Te_3 forms in the melts can be clarified by considering the liquidus lines of the Ga_2Te_3 and Li_2Te compounds in the binary Li–Te and Ga–Te phase diagrams. 21,22

Obvious irrational forms of the liquidus lines demonstrate a great tendency to dissociation of the Ga_2Te_3 and Li_2Te melts, though at different temperatures equal to 1065 and 1477 K, respectively. Therefore, when both the forms occur in the melts, Ga_2Te_3 begins to dissociate before Li_2Te , which is more realistic based on our experiment where the Ga–Te gaseous species occurred at 955 K, whereas Li species were not observed up to 1000 K.

Summarizing the experiments, we believe that above 950 K, the liquid Ga_2Te_3 forms undergo chemical transitions and three independent equilibriums, thermal decay of Ga_2Te_3 , simple and dissociating evaporation of Ga_2Te_3 are most adequate processes in the melts:

$$Ga_{2}Te_{3} (liquid) \rightarrow 2GaTe (liquid) + 1/2Te_{2} (vapor)$$

$$(1)$$

$$GaTe (liquid) \rightarrow GaTe (vapor)$$
 (2)

$$Ga_2Te_3$$
 (liquid) $\rightarrow 2GaTe$ (vapor) + 1/2 Te_2 (vapor) (3)

According to thermodynamic database, the dimer Te species are the major portion of vapor over temperature range from 480 to 1265 K because total content of other polymeric species such as Te_5 , Te_6 , and Te_7 is less than 2% and monomer species occur in vapor only above 1200 K.

As a result, we can conclude that the arguments given above, which satisfy all the experimental facts, are enough to describe chemical transitions in melts above 950 K by the processes (1-3) among which the process (1) is basic.

The following experimental results support the validity of these reactions.

1. In the Ga–Te system, GaTe rather than Ga_2Te is the only stable subtelluride in solid, liquid and vapor states. ^{16,20,22} It justifies both reactions 1 and 3.

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- 2. The Te/Ga ratio found between 1.5 and 0.9 in the individual Ga—Te condensates supports reactions 2 and 3, whereas the Te/Ga ratio varying from 5 to 20 in total condensates is evidence for reactions 1 and 3.
- 3. The linearity of the experimental $\lg p-1/T$ dependence (inset, Figure 7) indicates the monovariant character of the evaporation process as a whole. One can see that each of the equilibrium processes is really monovariant by itself. The dissociation process (3) is also monovariant because stoichiometry is observed in the vapor. ¹⁵
- 4. Ga₂Te₃ and GaTe are stable and immiscible forms in solid and liquid. The conclusion is based on linearity of the solid phases and the eutectic type of their particular Ga₂Te₃-GaTe diagrams according to Figure 9. Exper-

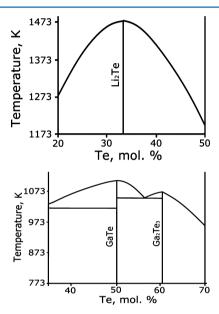


Figure 9. Liquidus lines of the binary Li-Te and Ga-Te phase diagrams.

imental singular-type isothermal dependences of such properties as viscosity, density, and conduction studied in detail in ref 23 demonstrate clearly their stability and immiscibility in a wide temperature range of the melts.

Unfortunately, data on evaporation of Ga₂Te₃ and GaTe are scant and conflicting. The complex composition of the vapor from the Ga₂Te₃, to be Ga₂Te, Te₂, GaTe, GaTe₂, and Ga₂Te₂ species was found under Ga₂Te₃ at 1038 K.¹⁶ Only two volatile GaTe and Te2 species were found in ref 22 with total vapor pressure determined quantitatively as $\sim 1.3.10^{-6}$ bar at 955 K. GaTe is evaporated to form GaTe, GaTe₂, and Ga₂Te₂ species. 16 Its total pressure is unknown, and we estimated its by comparison method using the pressures of In₂Te₃ and InTe phases (analogies to Ga tellurides) as $\sim 10^{-8}$. One can see that both decay products Ga₂Te₃ and GaTe in eq 1 contribute a little to the total pressure which was measured experimentally to be equal to 3.5×10^{-3} bar at 955 K for the LGT melt. Since the chemical forms of eq 1 differ strongly in volatility, the total vapor pressure under the melts will be determined in the first approximation, by the pressure of the more volatile component that is tellurium. This fundamental finding allows monitoring the melt composition by fixing its temperature and the Te pressure in the setup for crystal growing.

Having available and trustworthy literature data, 20,23 we tried to characterize structurally the chemical liquid forms identified above. According to these references, the initial threecomponent macromolecular 3D units formed at the melting point are transformed then into a two-dimensional layered structure composed of the Te-Ga-Ga-Te packets with covalent bonds inside and weak bonds between layers. These 2D units are stable at intensive thermal motion of the liquid at 955 K and structurally close to the layered solid phase GaTe. Above this temperature, the main changes go over long linear chains of the 1D-structure with covalent bonds. The chains are able to dissociate, producing short chains, and finally, they are transformed into ions, electrons, and holes due to covalent bond breakage. Temperature above 1000 K is adequate to break the Li-Te bonds of Li₂Te. Additionally, our finding is supported by the mass-spectra measured for LGT⁴ and for its structural analogue LiIn $\hat{T}e_2$. 14 It seems that the ionized state is actual for Li₂Te melts above 1000 K, although the Ga₂Te₃ and GaTe chemical forms remain to be stable up to a temperature of 1400 K.²⁰ Note that the melt viscosity varies in a manner similar to the structural variation: it increases sharply at the melting point and then decreases very smoothly with temperature. 20,22

Chemical inhomogeneity of the LGT melts identified in our experiments is responsible for polycrystalline and heterophasic crystallization because the grown crystals trap the dissociation products located on the crystallization front. Attempts initiated in recent works^{6,7} to avoid the melt dissociation by minimal overshoot of melts resulted again in the formation of 4-5 mm single-crystal blocks. It means that the tellurium addition, producing an appropriate partial pressure in the growth zone and suppressing the melt volatility, is a key and fundamental parameter to provide homogeneous crystallization and strong stoichiometry of the LGT crystals. The exact determined $T_{\rm mp}$ will be very important for monitoring the temperature interval of the crystallization whereas the melt temperature and the Te pressure will control the degree of chemical inhomogeneity of melts. As one final point, the physical-chemical data obtained here open up new possibilities for optimizing the processes responsible for chemical and physical kinetics on the phase boundary of melts and growing the LGT crystals of a high quality.

4. CONCLUSIONS

Different experimental techniques sensitive to detection of the phase transitions of LiGaTe₂ before and after melting have been developed. The melting of LGT was detected at 943 \pm 2 K without any solid-phase transitions and without sublimation that emphasizes the lattice stability of the chalcopyrite structure. Melts of LGT were found to be volatile and their hypothetic vapor pressures determined by the Te gas species only were measured at temperatures between 943 and 1040 K. On the basis of the increase of the Te/Ga ratio in the vapor, dissociation reactions, stable liquid chemical forms, and their structures were presented in coordinates of temperature and the vapor pressure of the melts. It was shown that the tellurium addition, which produces an appropriate pressure in the growth zone and suppresses the melt volatility, is a key parameter for homogeneous crystallization and strong stoichiometry of LGT crystals. Controlling the melt temperature and the Te pressure under the melts, it is possible to find the best combination of the composition, structure, and viscosity of melts, and thus, it is an attractive way to grow high-quality LGT crystals.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kamarz@niic.nsc.ru.

ORCID ®

Inga G. Vasilyeva: 0000-0003-4045-9820

Notes

The authors declare no competing financial interest.

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