

Thermographical monitoring of structure transformations in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ melts

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Thermal effects in the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0; 0.04; 0.1$) melts at lowering under temperature gradient at a speed of 1 to 10 mm/h and at isothermal holding at certain temperatures have been monitored using the derivative thermal analysis method. The multistage character of the nucleation and the crystallization centers formation in the investigated melts has been discuss. That conclusion has been drawn basing on the presence of discrete temperature intervals where temperature oscillations occur in the cooling melt in the certain thermodynamics conditions.

Методом производного термического анализа проведен мониторинг тепловых эффектов в расплавах $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0; 0.04; 0.1$) при опускании в градиенте температур со скоростью 1–10 мм/ч и во время изотермической выдержки при определенных температурах. Обсуждается многостадийный характер формирования зародышей и центров кристаллизации в исследованных расплавах. Вывод о последнем основан на существовании дискретных интервалов температур, в которых при определенных термодинамических условиях охлаждения расплава происходят осцилляции температуры.

Single crystals of CdZnTe solid solution are now used in various semiconductor devices. There is increasing interest in using CdZnTe crystals as X-ray and γ -radiation detectors operated at room temperature. The advantage of CdZnTe based detectors is defined mainly by the high resistance and lower noise level in comparison with traditional materials [1]. Moreover, due to the strengthening effect of Zn isovalent dopant in the CdTe lattice, CdZnTe crystals increasingly replace the CdTe binary compound as a substrate for CdHgTe epitaxial layers used in optoelectronic devices [2]. The effective application possibility of CdZnTe high-resistance crystals in communication facilities has been recently elucidated in [3]. In most cases, the practical application of the mentioned solid solutions, bulk homogeneous crystals are required. This results in special requirements for their production technology. The most productive method to grow such crystals is the directional melt crystallization. Therefore, the investigation of kinetic regularities of the new condensed phase formation depend-

ing on thermodynamic conditions at the melt cooling is of substantial interest. However, such studies are complicated due to physical and chemical properties of the system containing metal components with high vapor pressure. The state of CdZnTe melts is very scarcely described in literature and direct structure investigations are absent due to complications with the use of diffraction apparatus because of possible contact thereof with chemically aggressive tellurides.

Recently, the $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ transition process from liquid to solid phase *in situ* was monitored by of eddy current sensor techniques [4] and by laser ultrasound [5]. The research results of the melt overcooling interrelation with its overheating [4] indicate that the increase of melt overheating stimulates rise of its overcooling. The overcooling by about 20 K already causes the spontaneous crystallization. Indirect data on the melt composition influence on the kinetics of solid solution phase transformation to the liquid state are obtained also in [6] by the melt viscosity monitoring during heating. It was concluded that the viscosity

oscillations inherent in CdTe melts during isothermal holding at 1403 K (which are likely due to periodical alterations of the melt structure) became markedly weaker in Zn-containing melts. It was discovered that substitution of 4 % Cd atoms by Zn causes a substantial change in the melting process character in comparison both with binary compound and with $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$.

The purpose of this paper was to investigate thermal processes characteristics accompanying nucleation and crystallization in the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0; 0.04; 0.1$) melts using derivative thermal analysis (DrTA) method.

The samples for DrTA were synthesized without recharging in a graphitized quartz ampoule evacuated down to 10^{-3} Pa. The total mass of high-clean (6N grade) components was 300 g. The ampoule lowering speed in temperature gradient was regulated within the range of 1 to 10 mm/h. The thermal effects in the melt accompanying structural transformations at ampoule lowering or at isothermal holding were monitored *in situ* using a computer. During the experiments, the scanning frequency of the controlling thermocouple was from 1 to 10 s^{-1} . The signals of controlling Pt/PtRh thermocouple (measured at ± 0.5 K accuracy) were processed by calculating the derivative $dT/d\tau$ of temperature (T) with respect to time (τ). During the experiments, the controlling thermocouple was fixed at the center of the quartz ampoule flat bottom, the ampoule internal diameter being 50 mm. The furnace temperature stabilization accuracy within the isothermal holding zone was estimated to be ± 0.5 K.

The monitoring of cooling process in the melts of investigated A^2B^6 compounds using the derivative $dT/d\tau$ made it possible to discover the presence of critical temperatures and melt compositions at which periodic thermal oscillations take place. Fig. 1 illustrates the sharp jump of the CdTe melt temperature at the relatively rapid (10 mm/h) ampoule lowering speed in temperature gradient. According to those data, a short-time melt temperature growth happened at 1379 K, that exceeds considerably the maximum value of this compound melting temperature $T_m = 1365$ K accepted in literature [7]. It should be noted that the temperature of this exothermal effect in the melt under cooling coincides with the temperature of one of the additional endothermic effects (AEEs) fixed by differential thermal analysis (DTA) in CdTe melt under

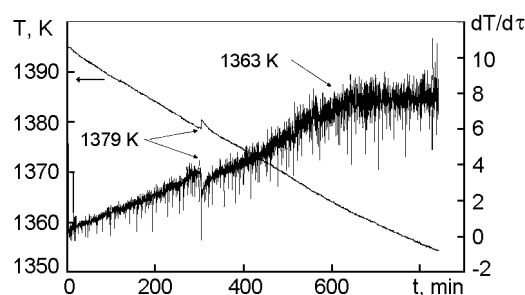


Fig. 1. Temperature oscillations in CdTe melt during the directional crystallization from 1395 K down at the lowering speed 10 mm/h.

heating in certain thermodynamics conditions [8]. In addition to this temperature reflecting the certain melt state, other AEEs at other critical temperatures: 1373 ± 1 ; 1393 ± 1 ; 1403 ± 1 K were revealed by DTA during CdTe melting [8, 9] that could be interpreted as a result of non-equilibrium states of the melt being heated.

To attain a state of investigated melt closer to equilibrium, an isothermal holding was carried out at 1403 K at which substantial CdTe melt viscosity oscillations were observed in [6]. Fig. 2 evidences the oscillations both of $dT/d\tau$ value and absolute melt temperature during that isothermal holding. At the same time, a stepwise temperature decreasing of subsequent isothermal holdings (at 1394 and 1391 K) did not cause similar oscillations, even at longer duration of the holdings. This confirms the conclusion on a specific melt state at $T_{AEE} = 1403$ K that was revealed in [10]. The appearance of similar alternating thermal effects at further melt cooling (at $T = 1375 \pm 1$ K, see Fig. 2) confirms the conclusion about the melt specific state at another critical temperature known from DTA data, namely, $T_{AEE} = 1373 \pm 1$ K [6, 8–10]. However, the exothermal effect of crystallization expected at $T_m = 1365$ K (usually cited in literature) was not observed in our experiment. The obtained experimental results can be treated as an illustration to conclusion based on calculations [11] on oscillating nature of nucleation process in molten tetrahedral semiconductors with covalent type bonds. According to [11], small "crystallites" are continuously formed and destroyed in the melt transforming their structure between cubic and hexagonal configurations. Obviously, such a competition occurs in the CdTe melt during heating at certain tem-

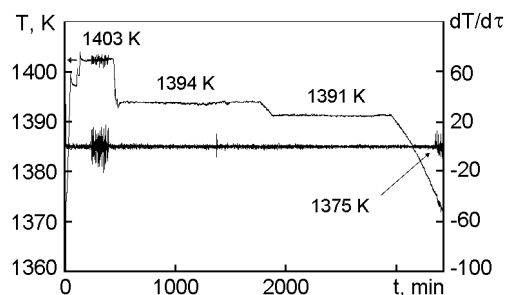


Fig. 2. Temperature oscillations in CdTe melt during the directional crystallization from 1395 K down at lowering speed 6 mm/h and intermediate isothermal holding.

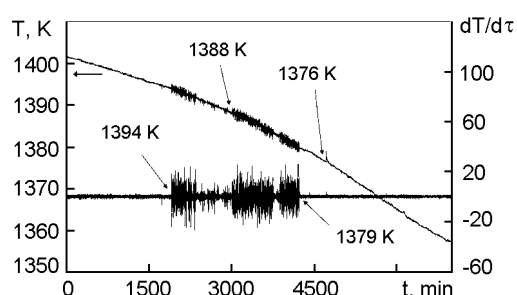


Fig. 3. Temperature oscillations in $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ melt during the directional crystallization from 1402 K down at lowering speed 1 mm/h.

perature(s) only depending on thermodynamic conditions in the system.

Repeated investigations of thermal processes at $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ melt heat treatment and cooling were accompanied by noticeable temperature oscillations neither at cooling of the melt nor during the isothermal holding. However, an increase of Zn content to 10 mole % caused a series of critical phenomena similar to those observed in the binary compound melt. Similar to the CdTe case, during a series of $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ melt isothermal holdings in the temperature interval of 1393 to 1405 K, the specific critical conditions which have been revealed accompanied by the melt temperature instability (oscillations). The appearance of melt temperature fluctuations at the ampoule lowering at 1 mm/h speed after isothermal holding at 1401.5 K is shown in Fig. 3. Once the melt temperature of 1394 ± 0.5 K was reached, it caused prolonged oscillations in the temperature interval of 1394 to 1379 K, i.e. between the values close to the critical parameters of $T_{AEE} = 1379 \pm 1$ and 1393 ± 1 K known from DTA data [6, 8–10]. Consequently, the oscillations are related both to melt composition and to the kinetic peculiarities of change in thermodynamic parameters of the investigated system. The most probable cause of this phenomenon is the melt structure transformations in certain discrete temperature intervals.

The phenomenon of temperature instability in both metal [12–15] and semiconductor [15] melts is known for a long time, being referred to more frequently as "overstable temperature fluctuations" [13–15]. Usually, their nature is considered within the frame of ideas of the cluster melt theory. The inhomogeneity (fluctuations of composition) of the melt, even in the case of elemental metal, is a common property of a condensed

system, providing its accordance to the principle of the energy minimum [17]. The cluster size is obviously a function of temperature: in the hotter part of melt, it is smaller and vice versa. In the presence of a temperature gradient, there is a continuous heat exchange between clusters, which results in their fluctuating disintegration and association. This heat absorption and release is recorded by the thermocouple as thermal fluctuations. The amplitude of melt thermal fluctuations depends on the extent of simultaneous enlargement or diminishing of the clusters.

CdTe as well as its solid solutions containing zinc belong to tetrahedral semiconductors retaining the coordinating number four even in the molten state [18]. The strength and stability of covalent constituent of chemical bonds in the CdTe crystal lattice provide that not only spatial clusters consisting of hundreds of atoms [19] but also products of their gradual dissolution with temperature growth remain conserved above the melting point as chain or cyclic structures based on Te–Te bonds [20]. As it shown in [20] by the molecular dynamic simulation method, a very substantial overheating is needed for complete homogenization (atomization) of such melts. The above-described monitoring results of thermal effects at melt cooling yield a concept of the non-monotonous, multi-stage nature of the new condensed phase which formed in an inhomogeneous liquid medium. Obviously, formation of covalent bonds between tellurium atoms in the melt being cooled and, later on, of ionic bonds with cadmium atoms takes place in different discrete temperature intervals depending on the melt thermal pre-history. The coincidence or closeness of the critical temperature values visualized either as temperature extremes

in dependences of physical and chemical properties [6, 8–10] or as boundaries of discrete temperature intervals of structure transformations (Figs. 1–3) testifies to the dominant role of geometrical factor in formation of chemical bonds of a certain type.

The multistage character of nucleation in the investigated A^2B^6 melts is caused probably not only by the mixed character of chemical bonds including covalent and ionic constituents [20], the contribution of each of those changing in the course of the system cooling. Probably, in the case of CdTe, the nucleation in the melt occurs through the formation of blocks having both hexagonal (wurtzite), and cubic (zinc blende) modifications, that hexagonal modification being predominant at higher temperatures [11]. Obviously, it is just the competition of both nucleation paths that causes the observed temperature oscillations.

Thus, the melting and crystallization of CdTe and CdZnTe occur not isothermally but in certain discrete temperature intervals. The range of the latter is defined both by the melt composition and its "thermal pre-history". An important factor controlling the nucleation process is provided also by kinetic features of the local thermodynamics equilibrium established between layers of different ordering.

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Моніторинг структурних перетворень у розплавах $Cd_{1-x}Zn_xTe$

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Методом похідного термічного аналізу проведено моніторинг теплових ефектів у розплавах $Cd_{1-x}Zn_xTe$ ($x = 0; 0,04; 0,1$) при опусканні у градієнті температур та під час ізотермічної витримки при певних температурах. Обговорюється багатостадійний характер формування зародків та центрів кристалізації у досліджених розплавах. Такий висновок зроблено на підставі існування дискретних інтервалів температур, в яких при певних термодинамічних умовах охолодження розплаву відбуваються осциляції температури.