Structural changes in molten CdTe

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Abstract. Shear viscosity (η) measurements of CdTe and CdTe + 2 at% In melts were performed using a cup viscometer up to 1403 K. The h(T) dependencies obtained during slow heating and cooling ($V_{h/c} =$ $= 10-15$ K/h) show hysteresys near a melting point. According to the $\eta(T)$ dependencies data drastic changes the melts structure occurred at 1376 K both during the heating and cooling of the melts.

1. Introduction

In recent years, many efforts have been made to investigate a melt structure and its correlation with growth properties for different substances. Investigations of density, viscosity, electrical resistivity, adiabatic compressibility and other structural-sensitive properties of molten semiconductors lead to the conclusion that a postmelting effect exists both in elements (Ge,Si) and complex (A^3B^5, A^4B^6 etc.) objects [1]. It was shown that nonisothermal gradual phase transition from solid to liquid occurs in certain temperature range above a melting point (T_m) through some steps of crystal-like structural units (clusters) transformation. Therefore, a liquid remains two-structural one in a certain temperature range above T_m. Nevertheless, it is not clear *a priory* whether or not the structural transformation occurs isothermally as first order transition or diffusely, as a second order one. For example, rapid structural changes in molten Si, Te-Se, Ge-Te and Cd-Sb as well as in other systems were revealed by diffraction methods or by heat capacity temperature dependencies [2,3], but their nature remains unknown.

It seems to be of interest to study a transformation of cadmium telluride melt structure with temperature. Previously, thermodynamic analysis of molten CdTe structure was usually performed in the framework of associated solutions model, assuming as the structural units atoms Cd and Te and associates Cd-Te only. According to [4], a mole fraction of associated species Cd-Te near T_m is estimated to be 0.908. Comparing both the calculated and experimental (based on calorimetric study) values of thermodynamic parameters of CdTe fusion, the author of [5] concluded that full entropy was not realized at T_m(CdTe). This prediction

was illustrated later by DTA method in [6-9] where small additional endothermic effects (AEE) were obtained at 1373, 1379, 1393 and 1413 K at certain thermodynamic conditions, i.e. the postmelting effect in the CdTe melts was revealed. It was proposed in [8,9] that the CdTe melt in the vicinity of T_m up to $T_m + 10$ K can be considered as a solution of crystal-like clusters in the liquid. Upon heating, the clusters undergo thermal dissolution, which may be due to either dissolution from the surface or a fragmentation on smaller species. The most correct treating of the structure transformation in molten CdTe needs direct diffraction experiments at various temperatures. But due to chemical aggressivity of this object, the only neutron diffraction study at 1373 K was performed up to now by Gaspard et al. [10,11]. Surprise of researchers was connected with the fact that the main parameters of crystal (bond distances, valence angle, coordination number) are kept in the liquid. Each atom was surrounded by a distorted tetrahedron of atoms of other species. It was concluded that this liquid structure is analogous to the Connel-Temkin model of alternate amorphous semiconductors that is rather unexpected in liquid semiconductors.

On the other hand, the data of Gaspard et al. agree with electrical properties of the CdTe melt. According to [8, 9,12], CdTe kept semiconductor properties up to T_m +100K, at least. Ioffe [13] had explained such type of phase transition of semiconductors by affirmation that covalent bonds are retained above T_m, and a short-range order of crystalline phase is preserved despite the loss of a long-range order.

Based on results of a direct structural investigation [10, 11], an *ab initio* molecular dynamic simulation of CdTe at three different temperatures (800 K – as super-cooled state, 1370 – near T_m and 3000 K – as super-

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heated state) has been performed in [14, 15]. It was found that near T_m atoms of tellurium form infinite branched chains. Short and simplified chains are still presented in the supercooled phase. As the temperature increases, the chains break, become shorter and transform into close-packed clusters even in the superheated state.

In order to examine this theoretical model a temperature dependence of viscosity as one of the most structural sensitive properties of a liquid has been studied. As published previously in [12,16], the kinematic viscosity of CdTe decreases gradually with a temperature increase, but a slope of the temperature dependencies near T_m differs twice in both references. In the present work, the dynamic viscosity of CdTe and CdTe + 2 at % In during heating and cooling at quasi-equilibrium conditions with heating/cooling rates of $V_{h/c} = 0.33 – 0.42$ K/min from T_m to 1403 K was measured.

2. Experimental

The shear viscosity was measured using the computer controlled cup viscometer similar to [17]. CdTe samples of stoichiometric composition and 1.10^{20} cm^{-3} Te excess and CdTe + 2 at % In were prepared from pure elements (6N grade) in evacuated and sealed quartz cups. The melts were homogenized at T_m+ 30 K during 12 hours and cooled with a furnace. Then the polycrystal charges were heated in the viscometer from room temperatures up to 1403 K following by the melt cooling with intermediate holding up to solidification. Doped by 2 at % In CdTe specimen was heated repeatedly from T_{room} up to 1403 K with the holding at 1403 K during 60 min. The heating/cooling rates $V_{h/c}$ were varied from 0.33 K/min to 0.5 K/min.

3. Results and discussion

The data of the CdTe shear viscosity (η) changes on heating and cooling combined with holding at 1388 K (30 min) and 1378 K (30 min) with $V_{h/c} = 0.33$ K/min are presented in Fig. 1. Kinetics of the CdTe melting process is illustrated by Fig. 1a. The viscosity growth above $T_m = 1363$ K up to $T_{crit.} = 1376$ K reflects the raise of the liquid phase volume fraction in this two-structural system. Taking into account that $T_{crit.}$ is close to the temperature of first observed in [7-9] AEE, one can conclude about the completion of the crystal-like clusters dissolution process near 1376 K. However, reached at 1376 K the viscosity value retains almost constant during the next heating up to 1379 K only, following by occurrence a peak on the $\eta(T)$ dependence in a rather narrow temperature range. So, the melt shows typical for homogeneous, Newtonian liquids features above 1387 ± 1K on the heating and from 1403 up to 1376 K on cooling. The observed on the heating peak did not reproduced during the melt cooling from 1403 K, in spite of the melt holding at 1388 K during 30 min. Obviously, the high-temperature melt structure is conserved in the course of cooling up to T_{crit}, were the holding near $T_{crit.}$ caused the noticeable reduction of the melt viscosity. It means
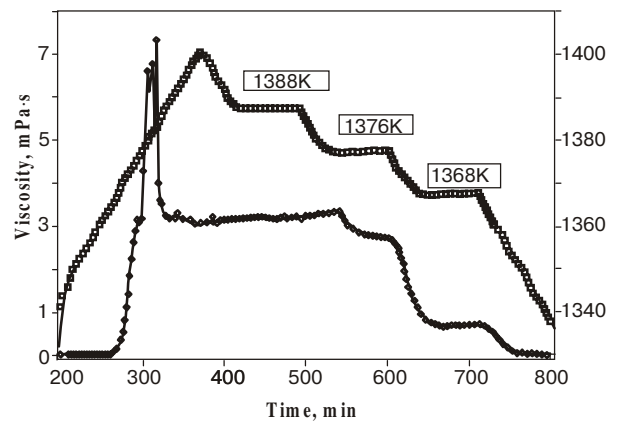

Fig. 1. Temperature dependence of stoichiometric CdTe melt dynamic viscosity. The heating/cooling rate $V_{h/c} = 0.33$ K/min.

that structural changes in molten CdTe are not symmetric on heating and cooling at given experimental conditions, except the temperature range near $T_{crit.}$ demonstrating the hysteresis near T_m and above $T_{crit.}$.

Stability of the melt structure both above 1388 ± 1 K up to 1403 ± 1 K and below 1403 ± 1 K up to 1378 ± 1 K is illustrated more clearly by Fig. 1b. One can see that typical for Newtonian liquids viscosity growth with a temperature decreasing is observed in restricted temperature range up to $T_{crit.}$ only, following by the viscosity reduction.

The viscosity changes on heating and cooling (at $V_{h/c} = 0.42$ K/min) of the charge with slight Te excess in comparison with previous case is demonstrated in Fig. 2 a,b. As one can see, a λ-like view of $\eta(T)$ dependence on heating and critical point where the melt structure changes is reproducible in general. The holding of the cooled melt at $T_{hold} = 1378$ K, i.e. the temperature of essential viscosity rise during the melt heating (also does not cause any changes of the melt structure during 30 min, at least. Comparing Figs 1b and 2b, one can see that the viscosity of both melts is the same upon cooling, in spite of some difference in composition. The role of the Te excess is
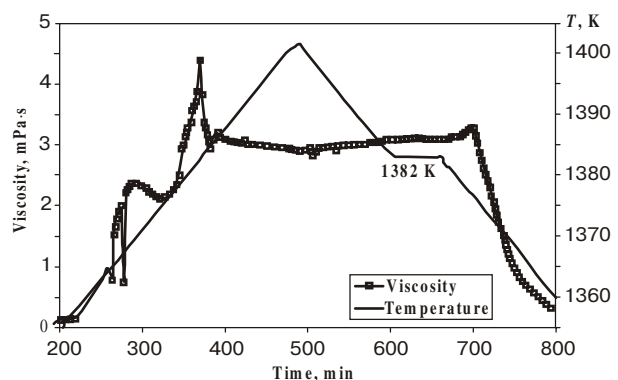

Fig. 2. Temperature dependence of CdTe + 1.10^{19}at/cm^3 Te melt dynamic viscosity. The heating/cooling rate $V_{h/c} = 0.4$ K/min.

more visible in the fact of the CdTe melting point reduction. Besides, the Te liquid phase presence in solid CdTe accelerates the clusters dissolving in the melt in comparison with the case of the stoichiometric CdTe, however $T_{\text{crit.}}$ remains the same.

The essential elevation of the heating melt viscosity above the cooling one at the temperature range from 1376 ± ± 1 K to 1388 ± 1 K witnesses about certain intensive chan-ges of the melt structure in the course of heating. The latter resulted in growth of internal friction forces, which compensate and exceeds the action of temperature rise leading to a rise of atom mobility. Taking into account the calculated by Godlevsky et al. [14,15] CdTe melt structure model, it should be supposed that the Te branched chains formation is the reason of the λ-like view of η (T) dependence of the heating melt, but this process occurs in a rather narrow temperature range. Obviously, the intensive destruction of the chains above the temperature of the top of the peak resulted in creation of some smaller structure units. Taking into account that $\eta(T)$ dependencies of the heating and cooling melt coincide in 1388-1403 K range, one can conclude that a packing of this structure units is the same in whole investigated temperature range up to $T_{\text{crit.}}$.

It must be noted that «anomalous» temperature dependence of viscosity which pass through a maximum at T_m + (60÷100) K, was obtained in case of other compounds with semiconductor-semiconductor type of the melting, e.g. Ga_2Te_3 and In_2Te_3 by Tsuchiya et al. [18,19]. The authors [18,19] had regarded these melts as superposition of two structures: a loose low-temperature structure which retain the main parameters of solid state, and more densely packed high temperature structure presumably of a linear type (chains and molecules). Really, according to X-ray investigation in [20], a tetrahedral coordination of covalently bonded nearest neighbors remains in molten In_2Te_3. It was regarded that tetrahedra are the main structure units up to T_m + 30 K, at least, but their packing differs from that in the crystal.

The influence of 2 at % In on the CdTe viscosity dependence on the temperature was observed during two consecutive heating/cooling processes with $V_{h/c}$ = 0.5 K/min (see Fig. 3). The choice of the investigated dopant was connected with some reasons. Thermodynamic analysis of the quasi-binary CdTe – In system liquidus had revealed close to ideal behavior of the melt components. Besides, it was shown in [8] that the CdTe melt kept its semiconductor nature up to 1473 K despite the presence of the metallic impurity. Therefore, the short- range order of zinc-blend structure does not change essentially in this two-phase melt. According to [8], the CdTe + 2 at % In melt temperature dependence $\sigma(T)$ had revealed the remarkable changes of the $\sigma(T)$ slope at the temperatures 1373, 1393 and 1413 K, which are close to position of the AEEs in the pure CdTe melt. The most sharp growth of the electrical conductivity of CdTe + 2 at % In melt was observed from 1373 to 1393 K.

As one can see in Fig. 3, similarly to pure CdTe, the doped by In CdTe melt has the hysteresis of the cooling
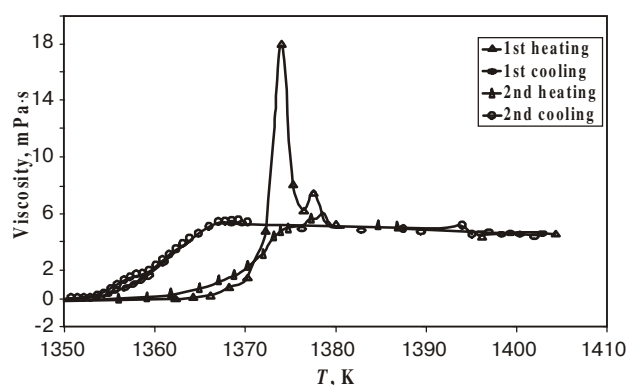

Fig. 3. Temperature dependence of dynamic viscosity for the CdTe + 2 at % In melt ($V_{h/c}$ = 0.5 K/min).

and heating curves both near the melting point and in the vicinity of the peaks on the heating curve. The first peak caused by essential growth of the melt viscosity at 1373 K following by its rapid decreasing. The second, smaller, peak is observed near 1378 K. The reached above 1380 K viscosity value, and, consequently, the melt structure became stable as long as the melt is heated up to 1400 K and then cooled almost to T_m. Taking into account a similarity of the $\eta(T)$ dependencies of CdTe and CdTe +. In melts, it should be assumed that the first peak in Fig. 3 is caused by Te-chains formation (according to the theoretical model of l-CdTe transformation by Godlevsky et al [14,15]). But break of Te chains during the heating in presence of In atoms occurs in such way that some smaller structural units with the same coordination number, valence angle and inter-atomic distances, form. Hexagonal Te rings are the most probable candidates for this process. The dissociation of the rings on shorter chains, probably, is eliminated by the second peak at 1379 K shown in Fig. 3. Note, that the presence of In led to increase of the melt viscosity value (e.g., from approximately 3 mPa·s in pure CdTe to 5 mPa·s at 1400 K). According to this version it should be thought that a second order phase transition of the sphalerit – wurtzit type takes place in CdTe and CdTe + + In melts in the vicinity of the peak between 1376 and 1388 K. To maintain this hypothesis, one can add the sharp growth of the CdTe + 2 at % melt electrical conductivity from 1373 K up to 1393 K, caused, probably, by reorganization of the structural units accompanied with an increase of the broken bonds and configuration entropy changes.

The relaxation of the melt structure during the cooling, obviously, needs much more time in comparison with the process of the crystal structure break by the temperature growth. Using the cooling curves as characteristic of the reached at high temperatures the melts equilibrium state, one can estimate the activation energies of viscous flow E_a by the Arrhenius type equation

$$\eta(T) = \eta_o \exp(-E_a / RT) \qquad (1)$$

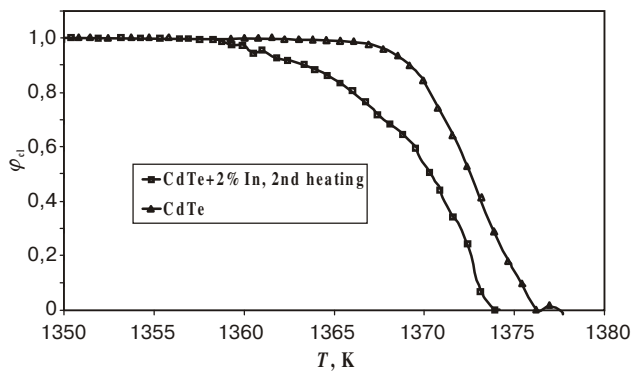where R is the universal gas constant.

Fig. 4. Volume fraction of clusters in stoichiometric CdTe and CdTe + 2 at % In melts *vs* temperature.

The approximation of the viscosity dependencies on temperature by (1) in the temperature ranges 1400 K – T_{crit} for CdTe melts (see Figs 1 and 2) and 1400 K – T_m for CdTe + 2 at % In melt (Fig. 3) led us to E_a values 51 ± ± 3 kJ/mole and 66 ± 1 kJ/mole for pure and doped melts, accordingly. It is known that E_a value is connected with the forces needed for creation of a free volume for replacement of the melt structure unit. E_a values obtained using Eq. (1) are close to the typical ones, observed for chemical reactions. Therefore, they show that viscous flow of the investigated melts needs the rupture (and creation) of chemical bonds, retaining in the melts.

The obtained heating curves can be used for an illustration of the crystal-like clusters in content in the melts reduction with the temperature growth. Assuming that the full solving of clusters in the melt occurs when the viscosity value reaches the equilibrium one, we estimate a volume fraction of the clusters dependence on temperature (Fig. 4). As one can see, the presence of the second phase in CdTe + In melt intensifies the process of the clusters dissolving, which had finished near 1373 K in both cases. Therefore, the minimal sizes of created in both melts clusters are close. However, their composition and structure need more detailed investigation.

Conclusions

The dynamic viscosity measurement vs. temperature $\eta(T)$ is a reasonable tool for studying CdTe melt structure changes. The obtained $\eta(T)$ dependencies on the heating agreed with assumption about postmelting, i.e. nonisothermal CdTe melting process, ranged up to $T_m + 10 = 1373$ K. The appea-rance of the peak on the $\eta(T)$ dependence between 1376 K and 1388 K illuminates certain drastic CdTe melt structure changes, which can be explained both as Te branched chains creation following by their destruction and/or by changes of the tetrahedral structural units type of packing. Similarity of CdTe and CdTe + 2 at % In melts $\eta(T)$ dependencies led to conclusion about similarity of a structurization type for both melts within the same temperature range. According to the viscosity measurements data, the most prominent melt structure rearrange-ment on heating occurs nearby 1388 ± 1 K. The viscous flow energy activation of coo-led, more equilibrium, CdTe and CdTe + 2 at % In melts was estimated as equal to 51 ± ± 3 and 66 ± 1 kJ/mole, accordingly.

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