Functional Materials 17, No.4 (2010)

Correlation between Arrhenius equation parameters concerning to Cd(Zn)Te melting and crystallization process

L.P.Shcherbak, O.V.Kopach

Yu.Fedkovich Chernivtsi National University,
2 Kotsyubinskogo St., 58012 Chernivtsi, Ukraine

Received 12 July, 2010

The correlative analysis between the preexponential factor (A) and the activation energy (E_a) as kinetic characteristics of melting and crystallization processes of both pure and doped (with In, Ge, Sn, ZnTe, up to 10 mol.%) cadmium telluride is carried out. A linear dependence has been found between the preexponential factor and the activation energy idetermined from experimental data on the temperature dependences of melt viscosity, the CdTe phase crystallization rate as well as of electrical conductivity. The identity of coefficient a in the $\ln A = aE_a + b$ experimental dependences obtained for all the considered processes is interpreted as an evidence of relation between their enthalpy and entropy.

Проведен корреляционный анализ связи предэкспоненциального множителя (A) и энергии активации (E_a) как кинетических характеристик процессов плавления и кристаллизации чистого и легированного In, Ge, Sn, ZnTe (до 10 мол.%) теллурида кадмия. Установлена линейная зависимость между значениями предэкспоненциального множителя и энергии активации, полученными на основании анализа температурных зависимостей вязкости расплавов, скорости кристаллизации фазы CdTe и электропроводности расплава. Идентичность коэффициента a в полученных экспериментальных зависимостях $\ln A = aE_a + b$ для всех приведенных процессов объясняется связью между энтальпией и энтропией процессов.

1. Introduction

Study of the semiconductor liquid state is of a great fundamental interest and importance for technological applications, since the molten state is a determinative stage in various cases of single crystal growing. For a number of years, numerous literature sources are appeared covering the multistage nature of the melting process for materials with different types of chemical bonding (ionic, covalent, metallic) [1–5]. Diffraction experiments and temperature dependences of thermodynamic functions studies have revealed rapid structural changes within a rather narrow temperature interval in molten GeTe, SeTe, TlSe, GaSe, CdSb, KCl, $Hg_{0.8}Cd_{0.2}Te$, In_2Te_3, etc. [6–14]. According to [14], the melt "structure" depends on the overheating, especially in the case of associated liquid semiconductors with a high ionic contribution to the binding energy (II–VI, IV–VI). Therefore, the structure-sensitive melt properties are of significant interest.

Molten CdTe is difficult object for direct structure investigations by diffraction methods due to high components pressure above the melt. Temperature dependences of electrical conductivity, thermo-e.m.f. and viscosity are among few possibilities to investigate the CdTe phase transitions. The aim of this work is to summarize the available theoretical and experimental data concerning CdTe melting and crystallization processes in various thermodynamic conditions. The influence of slight doping with In or Ge (2 mol. %) and Zn (up to 10 mol %) on the solid-liquid and vice versa CdTe phase transition parameters are taken into account, too.

2. Analytical procedure

As a summarizing approach for various data, the Arrhenius equation was used:

$$k = Ae^{-E_a/RT}, \tag{1}$$

where A is the preexponential factor and R is the gas constant. The units of the pre-exponential factor are identical to those of the rate constant and will vary depending on the reaction order.

The well-known universality of the Arrhenius equation which describes different activation processes stimulates the permanent interest in research of correlations between parameters of this equation for wide range of physicochemical processes. The interrelation between the activation energy (E) and the pre-exponential factor (A) according to the expression

$$\ln A = aE + b \tag{2}$$

referred to as the compensation effect has been reported for heterogeneous catalysis, polarization and oxidation processes, diffusion and self-diffusion in solids, liquid fluidity, for electrical conduction processes in various systems, etc. [15–22].

3. Results and discussion

The peculiarities of CdTe nucleation and crystallization processes during the cooling of CdTe and related (CdTe–Ge; In; ZnTe) melts from 1400 K were studied by dynamic viscosity monitoring in [23, 24]. Besides, the crystallization rate (V_s) of CdTe melts and CdTe phase in the CdTe–Ge (In, Sn) systems at the dopant concentrations up to 10 mol.% was evaluated by differential thermal analysis (DTA) in [25]. In addition, results of electrical conductivity $\sigma(T)$ measurements in CdTe both doped with In, Ge, Sn [23] and undoped [26, 27] as well as in $Cd_{1-x}Zn_xTe$ melts [28] were considered to check their correspondence to the Arrhenius equation. It was estimated that the dynamic viscosity temperature dependence of the melts under cooling can be described by the Arrhenius equation

$$\eta = \eta_0 \exp - E_{a,visc.}/RT, \tag{3}$$

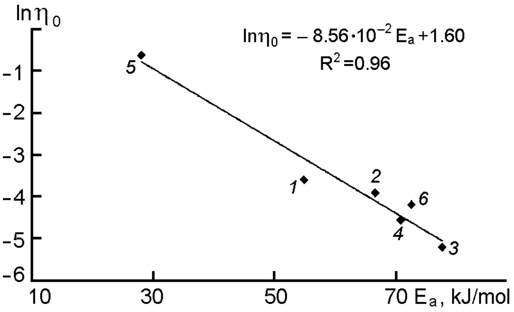

Fig. 1. Correlation between Arrhenius equation parameters (preexponential factor η_0 and viscous fluid activation energy $E_{a,visc.}$) for CdTe based melts: CdTe–Te (*1*), CdTe–Cd (*2*), CdTe + 2 mol.% Ge (*3*), CdTe + 2 mol.% In (*4*), CdTe + 2 mol.% ZnTe (*5*), CdTe + 10 mol.% ZnTe (*6*) [23, 24].

where η_0 is preexponential factor; $E_{a,visc.}$, the viscous fluid activation energy. The parameters η_0 and $E_{a,visc.}$ in this equation for the CdTe melts with different deviation from stoichiometry, CdTe + 2 mol.% Ge (In) melts and CdTe + 4 (or 10) mol.% ZnTe show an interrelation (Fig. 1) which is described by the equation

$$\ln\eta_0 = -8.56 \cdot 10^{-2} E_a + 1.60. \tag{4}$$

The linearity of the relation between the parameters of the melt viscosity temperature dependence suggests that increase in the process activation energy which is connected with vacancy formation for a viscous flow particle replacement is connected with preexponential factor decrease. A similar correlations between the logarithm of preexponential factor $V_{s,0}$ and activation energy $E_{a,s}$ in equations describing the temperature dependences of crystallization rate for CdTe and CdTe + 1–10 mol.% (In, Sn, Ge) melts was obtained from [25] (Fig. 2). The parameters of these equations for undoped and doped CdTe melts show a linear dependence with the angular coefficient very close to that obtained in Eq. (4):

$$\ln V_{s,0} = -(8.58 \pm 0.18) \cdot 10^{-2} E_{a,s} + \\ + (-6.15 \div 1.00). \tag{5}$$

The obtained empirical dependences confirmed a general conclusion of a theoretical analysis in [16] about the close relation between the preexponential factor and the activation energy $E_{a,s}$ of nucleation process in the condensed phase according to the equation

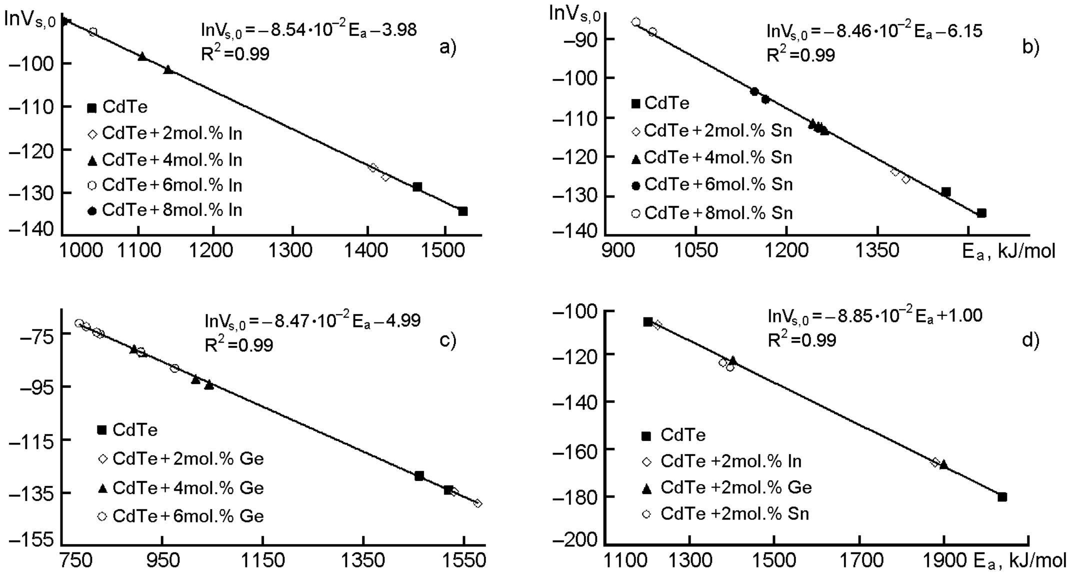

Fig. 2. Correlation between Arrhenius equation parameters for temperature dependences of CdTe crystallization rate in CdTe based melts (preexponential factor and activation energy of the melt crystallization process) [25].

$$V_s = V_{s,0}\exp(-\Delta G^*/RT), \qquad (6)$$

where the $V_{s,0}$ characterizes the frequency of molecule transfer from an initial phase to new one; ΔG^* is the potential barrier which prohibits the formation of critical size nucleus.

The reason for the proximity of angular coefficient values in Eqs. (4) and (5) which describe processes different in their essence in the melt being cooled within the same temperature range can be due to proportionality between their energy and entropy parameters. In both cases (vacancy formation for a viscous flow and critical nucleus formation processes), more energy-intensive processes are characterized by smaller entropy changes, which indicates the presence aggregations of atoms in the liquid more complex than binary ones. Thus, the observed entropy reduction accompanied with the energy barrier increase during formation of a more complex new phase can be treated as an evidence for the compensation effect in this specific system, namely, in the tetrahedral semiconductor melt.

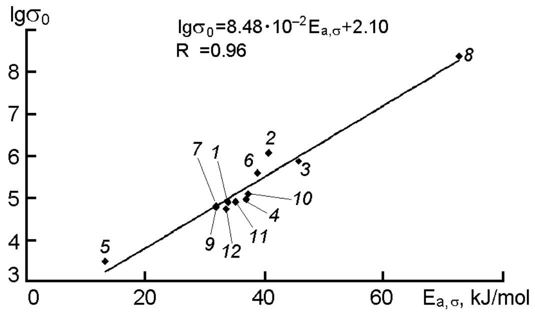

Fig. 3. Correlation between Arrhenius equation parameters (pre-exponential factor σ_0 and electroconductivity activation energy $E_{a,\sigma.}$) of the CdTe based melts: CdTe — heating (*1*) [23]; CdTe + 2 mol% In — heating (*2*) [23]; CdTe + 2 mol% Ge — heating (*3*) [23]; CdTe + 6 mol% Ge — heating (*4*) [23]; CdTe + 2 mol% Sn — heating (*5*) [23]; CdTe + 6 mol% Sn — heating (*6*) [23]; CdTe — heating (*7*) [26]; CdTe — cooling (*8*) [26]; CdTe — heating (*9*) [2]; CdTe — heating (*10*) [2]; $Cd_{0.955}Zn_{0.045}Te$ — heating (*11*); [27]; $Cd_{0.92}Zn_{0.08}Te$ — heating (*12*) [27].

The compensation effect is confirmed also by the parameters of electrical conductivity temperature dependence $\sigma(T)$ for the CdTe-related melts investigated in various thermodynamic and kinetic conditions by different experimental methods [23, 26–28]. The correlation between the activation energy $E_{a,\sigma}$ and preexponential factor σ_0 can be described satisfactory as

$$\lg\sigma_0 = 8.48 \cdot 10^{-2}E_{a,\sigma} + 2.10. \qquad (7)$$

Fig. 3 demonstrates a good agreement between the obtained angular coefficient and ones derived from Eqs. 4 and 5. It is to note that Fig. 3 combined the data obtained both during the melt heating and cooling (point *7* and *8*, respectively, obtained in the same experiment [26]). However, elimination of point *8* does not change the angular coefficient. Thus, it must be concluded about universality of the compensation effect during both transformations of the condensed phases.

4. Conclusions

Eight CdTe-based systems were considered for possibility of the compensating effect in various physical-chemical characteristics of CdTe phase transitions between condensed phases. It has been shown that logarithm of the preexponential factor in the Arrhenius equations of the viscosity, crystallization rate and electrical conductivity temperature dependences for the pure and doped (Indium, Stannum, Germanium, Zinc, Stibium) molten CdTe has depends linearly on the process activation energy. From the obtained mathematical expressions, close values of angular coefficient are estimated. The data are interpreted as an evidence of presence more complex than binary structure units in the CdTe melts with high interatomic binding energy. The increase of cluster dissociation activation energy is accompanied by small changes of the system entropy.

References

1. B.Chalmers, Principles of Solidification, John Wiley, New York (1965).
2. V.M.Glazov, S.N.Chizhevskaya, N.N.Glagoleva, Liquid Semiconductors, Plenum Press, New York (1969).
3. A.R.Ubbelohde, The Molten State of Matter, Wiley, London (1978).
4. G.Marcus, Introduction to Liquid State Chemistry, Jonn Wiley, Chichester (1977).
5. W.Hayes, *Contemp.Phys.*, **27**, 519 (1986).
6. L.A.Bityutskaya, E.S.Mashkina, *Pis'ma v Zh. Teor. Fiz.*, **21**, 8 (1995).
7. V.Glazov, *Inorgan.Mater.*, **32**, 1125 (1996).
8. Y.Tsuchiya, S.Takeda, S.Tamaki, E.F.W.Seymour, *J.Phys.C.:Solid State Phys.*, **15**, 2561 (1982).
9. Y.Tsuchiya, *J.Phys.C.:Solid State Phys.*, **21**, 5473 (1988).
10. Y.Tsuchiya, *J.Phys.Soc.Jap.*, **64**, 159 (1995).
11. Y.Tsuchiya, *J.Chem.Phys.*, **94**, 998 (1997).
12. S.B.Lague, A.C.Barnes, A.D.Archer, W.S.Howells, *J.Non-Cryst.Solids*, **207**, 89 (1996).
13. C.Li, R.N.Scripa, H.Ban et al., *J.Non-Cryst. Solids*, **351**, 1179 (2005).
14. P.Rudolph, H.J.Koh., T.Fukuda, *J.Cryst.Growth*, **166**, 578 (1996).
15. M.C.Wilson, A.K.Galwey, *Nature*, **243**, 402 (1973).
16. A.V.Nikolaev, V.A.Logvinenko, V.M.Gorbachev, *J.Therm.Anal.Calorimetry*, **6**, 473 (1974).
17. Deepali Sarkar, Kapur Mal Jain, Tridibendra Narayan Misra, *Bull.Chem.Soc.Japan*, **59**, 1561 (1986).
18. G.C.Montanari, A.Motori, *J.Phys.D:Appl.Phys.*, **28**, 1433 (1995).
19. K.Y.Suh, Hong H.Le, *J.Appl.Phys.*, **81**, 7067 (1997).
20. Y.L.Khait, R.Beserman, R.Shaw, K.Detmer, *Phys.Rev.*, **B 50**, 14893 (1994).
21. Y.L.Khait, R.Weil, *J.Appl.Phys.*, **78**, 6504 (1995).
22. E.Neagu, R.Neagu, *Thermochim.Acta*, **395**, 183 (2003).
23. Yu.Plevachuk, V.Sklyarchuk, Ch.Dong et al., *J.Phys.:Condens. Matter.*, **14**, 5711 (2002).
24. L.Shcherbak, P.Feychuk, O.Kopach et al., *J. Alloys Comp.*, **349**, 145 (2003).
25. L.Shcherbak, P.Feychuk, Yu.Plevachuk et al., *J.Alloys Comp.*, **371**, 186 (2004).
26. E.Belas, R.Grill, J.Franc et al., *J.Electron. Mater.*, **32**, 752 (2003).
27. H.N.G.Wadley, B.W.Choi, *J.Cryst. Growth*, **172**, 323 (1997).

Кореляція між параметрами рівнянь Арреніуса, які характеризують процеси плавлення та кристалізації Cd(Zn)Te

Л.П.Щербак, О.В.Копач

Проведено кореляційний аналіз зв'язку між передекспоненційним множником (A) та енергією активації (E_a) як кінетичних характеристик процесів плавлення та кристалізації як чистого, так і легованого In,Ge, Sn, ZnTe (до 10 мол.%) кадмій телуриду. Встановлено лінійну залежність між значеннями передекспоненційного множника та енергії активації, отриманими на основі аналізу температурних залежностей в'язкості розплавів, швидкості кристалізації фази CdTe та електропровідності розплаву. Тотожність коефіцієнта a в отриманих експериментальних залежностях $\ln A = aE_a + b$ для всіх згаданих процесів пояснюється зв'язком між ентальпією та ентропією процесів.