Chalcogenide Letters Vol. 2, No. 12, December 2005, p. 121 - 124

GLASS-FORMATION AND CRYSTALLIZATION IN THE SYSTEM Ge-Te

D. I. Bletskan

Uzhgorod University, Uzhgorod, Ukraine

The results on glass formation in the binary system Ge-Te are reviewed. The crystallization of Ge-Te glasses is analysed.

The glasses in the system Ge-Te have been obtained for the first time by quenching the molten alloy on cold copper plate in a chamber filled by pure argon, using the splat-cooling method [1]. In this case the cooling rate of the melt reaches $\sim 10^5$ K/s. The extension of the glass formation domain in the system Ge-Te was established in [1]. The domain is situated in the composition range 10 - 25 at. % Ge. A domain of glass formation of similar extension has been reported for quenched samples ($\sim 10^3$ K/s), by spraying the molten alloy on a rotating wheel covered by silicon oil [2, 3].

The quenching regime in the domain of alloys with high tellurium content has a significant influence on the extent of the glass formation domain. In the quenching regime in iced-water, by casting the melt as a thin layer on the ampoule walls, there were obtained glassy Ge_xTe_{1-x} compositions with $x = 0.15 – 0.20$ [4]. By using the method of quenching the alloys in iced water [5, 6] and liquid nitrogen [7], the glass formation domain extended from 10(12) up to 25 at. % Ge and from 15 up to 28 at.% Ge, respectively. The influence of the cooling rate of the melt on the position of the boundary of the glass formation domain in the system Ge-Te has been investigated in detail by Cornet and Psarev et al. [8-10]. In this system the glass with the composition $Ge_{18}Te_{82}$ is formed on the basis of the eutectic situated on the side of tellurium. The presence of this eutectic allows for the decrease of the crystallization ability of the non-stoichiometric alloys of the eutectic and close to eutectic compositions. For the increase of the cooling rate of the alloys up to 180 K/s the boundaries of glass formation domain extend, in this case, from 10 to 23 at.% Ge [8, 9], and the glass temperature of the glassy compositions formed in these conditions, reaches the values from 373 to 433 K.

The application of the spinning method for the preparation of the glasses in the system Ge-Te gave the possibility to extend the glass formation domain from 0 to 29 at. % Ge [11]. Above the limits of the glass formation domain the rapidly quenched alloys consists in a mixture of glass and crystallites. With this method the samples are obtained as bands of width 5-6 mm and thickness of 20-40 μm, The length of these bands is limited only by the charge of the quartz ampoule with molten alloy.

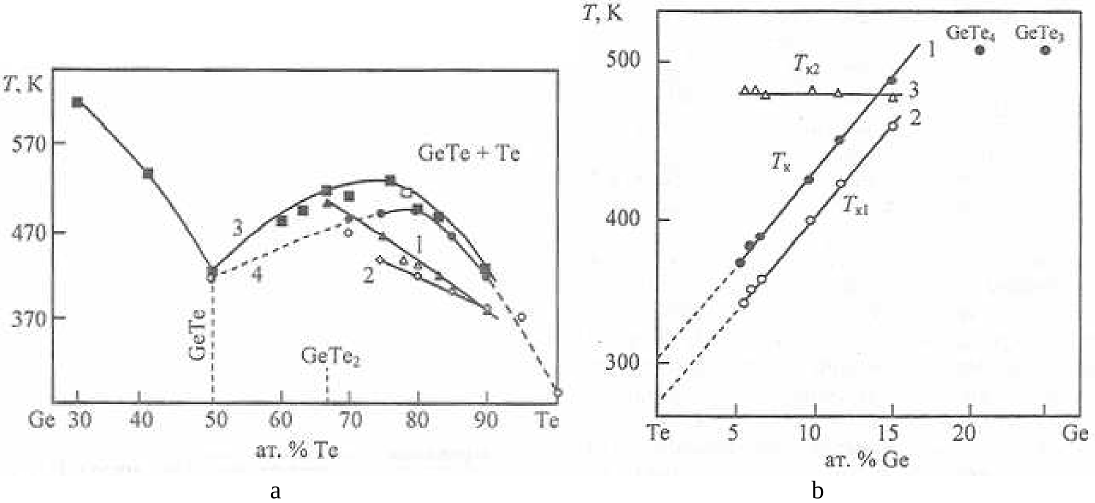
Using the magnetron method (sputtering) and the flash method of deposition one obtains amorphous films in the composition interval 5 – 100 at. % Ge [3, 12].

In glasses and glass-crystals of the system Ge-Te have been revealed structural fragments of the metastable compound $GeTe_2$, which is lacking on the phase diagram of the stable equilibrium phases in the system Ge-Te [13, 14]. The presence of the compound $GeTe_2$ having the lattice isomorphous to the β-cristobalite, SiO_2, was demonstrated by X-ray diffraction in the annealed samples, at 473 K, of the amorphous films of analogous composition [15]. When the temperature increases up to 523 K, $GeTe_2$ decomposes in GeTe and Te. The macro-phase of the compound $GeTe_2$ does not permit its stability when prepared in usual conditions. Funtikov [13] obtained glass-crystal of composition $GeTe_3$, where the above compound, $GeTe_2$, is stable, being finely dispersed in the glassy matrix.

The bulk glasses and amorphous thin films of composition Ge_xTe_{1-x} exhibit poor stability and large crystallization ability during heating. The crystallization processes of the glassy alloys Ge_xTe_{1-x} were studied by DTA, XRD, electron microscopy and electron diffraction (SAED) by many authors [5, 10, 11, 16-20]. On the example of the glassy alloy $Ge_{0.15}Te_{0.85}$ it was studied the influence of the heating rate (β) on the magnitude of the softening temperature (T_g), crystallization temperature (T_k), melting temperature (T_{melt}) and on the parameter $K_g = (T_k-T_g)/(T_{melt}-T_k)$ [19, 20]. It was established the increase of T_g and T_k with the increase of the heating rate, the change of the crystallization from the glassy phase, the shift of the maximum of the heat release, corresponding to these stages on the side of higher temperatures. Thus, during the modification from 1.25 to 80 K/ min. the parameters T_g and T_k changed by 27 and 42 K, but the melting temperature remained constant [19]. The glasses prepared by cooling with the rate that significantly overcomes β, are characterized by more abrupt dependence of T_g and T_k on β, than the glass prepared by slow cooling of the melt. For the comparison of the ability of the materials to form glasses, it was proposed in [19] to use the normalization parameter K_g, determined for β=1. It is necessary to observe that although the parameter K_g is accepted for qualitative estimations, it does not have a defined physical content.

The investigation of the thermal crystallization process of the $Ge_{0.15}Te_{0.85}$ glass by electron microscopy has shown [18] that there exists many common things between crystallization from glass and from the liquid state. The process of transition from glassy state to the crystalline state is intermediary between crystallization from liquid state and the process of incoherent separation from saturated solid solution. For this, the energy of elastic deformations that appear during the transition from glassy phase in the crystalline phase, calculated for one atom gram Δga, is basically determined from the density ρ_c and ρ_k of these phases according to the law $\Delta ga \sim \ln(\rho_c/\rho_k)$.

The study of the aging process of the glassy alloy $Ge_{-0.15}Te_{0.85}$ at temperatures somewhat lower than 451 K (minimum, down to 411 K) has shown that on its surface crystallizes pure Te [21]. The activation energy of the growth process of Te is 193 kJ/mol, which corresponds to the energy of self-diffusion in tellurium perpendicular to the hexagonal plane. Simultaneously, the formation of germanium rich phases and of the chemical compound GeTe prevent the free growth of the Te crystals, and as a result the thickness of its films on the surface does not overcome 5 μm.



a b

Fig. 1. a – Concetration dependence of the glass temperature (1,2) and crystallization temperature (3,4) of the glassy and amorphous Ge-Te alloys 1,3 [2] 2,4 [5]; b – Dependences of crystallization temperature on composition for the Ge-Te alloys ν heating, k/min 10(1) and 1(2,3).

The character of the crystallization of the glasses Ge_xTe_{1-x} depends on composition, heating rate, rate of quenching from the melt and on the history of the processing. On the figure 1 a are shown the dependencies on concentration of the T_g (curves 1, 2) sand T_k (curve 3) of the glassy and amorphous phases of the binary system Ge-Te. With the increase of the tellurium content the glass formation decreases monotonously and T_k reaches a maximum at 80 at. % Te [5]. More detailed study of the crystallization process of the amorphous and glassy Ge_xTe_{1-x} alloy has shown that the character of their crystallization depends on the heating rate. By heating with ~10 K/min the crystallization takes place in one stage, that is characterized by one peak on the DTA curve, whose temperature T_k in dependence on the concentration of the alloys is described by a linear dependence 1 (fig. 1 b). The crystallization temperature for the compositions $GeTe_4$ and $GeTe_3$ does not superpose on this dependence. During heating with ~ 1 K/min the transformation process is a two-stage process with two peaks on the DTA curves, corresponding to the temperature T_{k1} and T_{k2}. Tk1 is linearly dependent on the composition of the alloys, and T_{k2} does not depend on the composition of the alloys in the limit of the experimental error (Fig. 1 b).

The crystallization of the pre-eutectic, eutectic and post-eutectic glassy alloys Ge_xTe_{1-x} are multi-stage processes and have in every case their own characteristic peculiarities. The first stage of crystallization of the post-eutectic glassy alloys is characterized by the separation of the monoclinic tellurium (whose formation is related to the dissolution of germanium in it), which transforms in hexagonal one only in the last stages of transformations that accompany the separation of germanium (at 623 K) and the formation of the compound GeTe. During crystallization of the glasses of the eutectic and pre-eutectic composition, in the first stage is formed firstly the hexagonal tellurium and, thereafter, the eutectic Te+GeTe [10]. The morphology of the formed crystalline phases depends on the concentration of the germanium in the alloy. The formation of the dendrite structure in the growth process of the crystalline phase was explained by Oleszak et al. [17] by the enrichment of the amorphous matrix with Te atoms and the approaching of their composition to the eutectic one.

The character of crystallization of the amorphous films Ge_xTe_{1-x} ($0.1<x<1$), obtained by discrete evaporation, also depends on the composition [12]. For the compositions with $x>2/3$ one observes one-stage transformation at 635 K with the formation of Ge and GeTe crystals having the structure of the high temperature modification with the NaCl-type lattice. For the compositions with $x<1/3$ one observes one-stage crystallization accompanied by the formation of a mixture of crystalline Te and rhombohedral GeTe at 443 K. In the intermediary domain of Ge concentration ($1/3<x<2/3$) there were observed two stages of crystallization. In the first stage, at 443 K, are separated GeTe crystals with rhombohedral lattice. In the second stage, at 653 K, takes place the separation of germanium crystals and the transformation of the GeTe lattice from rhombohedral to cubical one (NaCl type).

References

[1] H. L. Luo, P. Duwez, Metastable amorphous phases in tellurium –base alloys, Appl. Phys. Lett., **2**(1), 21-23 (1963).

[2] D. J. Sarach, J. P. De Neufville, W. L. Haworth, Studies of amorphous Ge-Se-Te alloys (I) Preparation and calorimetric observations, J. Non-Cryst. Solids, **22**(2), 245-267 (1976).

[3] J. P. De Neufville, Chemical aspects of glass formation in telluride system, J. Non-Cryst. Solids, 8-10, 85-105 (1972).

[4] V. P. Panus, Glassy alloys with high tellurium content in the system As-Ge-Te (russ.), Vestnik Leningrad. Univ., Ser. Fiz. Him., **22**(4) 135-139 (1969).

[5] T. Takamori, R. Roy, G. J. McCarthy, Structure of memory-switching glasses. I. Crystallization temperature and its control in Ge-Te glasses, Mater. Res. Bulletin, **5**(7), 529-540 (1970).

[6] A. A. Andreev, M. S. Ablova, V. P. Podhaliuzin, Z. V. Maclova, B. T. Meleh, Properties of the glasses A^{III}-Te, A^{IV}-Te in strong electrical field, Fiz. i Him. Stekla, **5**(3) 375-378 (1979).

[7] J. A. Savage, Glass formation and DSC data in the Ge-Te and As-Te memory glass systems, J. Non-Cryst. Solids, **11**(2), 121-130 (1972).

[8] J. Cornet, The eutectic law for binary Te-based systems, Mejd. Konf. Po amorf. i Jidk. Polupr., Leningrad, Nauka, 1976, stran. 72-77.

[9] J. Cornet, Préparation, charactérization et propriétés des verres Ge-Te. Application au stockage optique de l’information, Ann. Chim. (France) **10**(4-5) 239-251 (1975).

[10] V. I. Psarev, A. L. Ivanov, T. Yu. Vtorkina, M. Yu. Fedorov, Conditions of preparation and crystallization of the amorphous alloys of the system Ge-Te (russ.), Izv. Akad. Nauk SSSR, Neorg. Mater. **18**(6), 942-945 (1982).

[11] R. D. Vengrenovich, M. O. Stasik, I. A. Lopatniuk, S. D. Tcachev, S. V. Podolianchuk, Formation of the structure and crystallization of the chemically ordered amorphous alloys

Ge-Te, Fiz. i Him. Stekla, **20**(2) 163-170 (1994).
[12] T. Okabe, M. Nakagawa, Crystallization behavior and local order of amorphous Ge-Te films, J. Non-Cryst. Solids, **88**(2-3), 182-195 (1986).
[13] V. A. Funtikov, On the problem of building of glasses and physico-chemical analyses of glassy systems, Fiz. i Him. Stekla, **22**(3), 279-285 (1996).
[14] V. A. Funtikov, Influence of the chemical and phase equilibrium on the medium range order and the physico-chemical properties of the chalcogenide glasses, Fiz. i Him. Stekla, **27**(5) 651-663 (2001).
[15] H. Fukumoto, K. Tsunetomo, T. Imura, Y. Osaka, Structural changes of amorphous $GeTe_2$ films by annealing (Formation of metastable crystalline GeTe films), J. Phys. Soc. Japan, **56**(1) 158-162 (1979).
[16] S. Asokan, G. Parthasarathy, E. S. R. Gopal, Crystallization studies on bulk Ge-Te glasses, Int. J. Rapid. Solid., **2**(4), 257-271 (1987).
[17] D. Oleszak, B. Dobrowski, H. Matyja, Crystallization studies on Te-Ge amorphous alloys, J. Mater. Sci. Lett., **8**(10) 1131-1134 (1989).
[18] M. Kaczorowski, Morphological aspects of crystallization of chalcogenide glasses obtained by rapid cooling from the liquid state, J. Mater. Sci., **17**(10), 3045-3051 (1982).
[19] M. Lasocka, Normalizeed value of K_g parameter of glass formation ability, J. Mater. Sci. **11**(9) 1770-1771 (1976).
[20] E. Ia. Malinocika, A. M. Durachenko, Calorimetric study of the transformation by heating of Te-Ge amorphous alloys obtained by quenching from liquid, Cosmic technology and advanced materials, Moscow, Nauka Publ. House, 1982, pp. 159-163.
[21] Y. Nishi, M. Kawakami, K. Mikagi, Isothermal crystallization on the surface of Te - 15 at. % Ge alloy glass, J. Mater. Sci., **22**, 554-556 (1987).