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KINETICS OF THE RECRYSTALLIZATION OF Sb_2S_3 IN THE GLASSY $(GeS_2)_{0,3}(Sb_2S_3)_{0,7}$

Nataša Ryšavá[x], Ladislav Tichý, Čestmír Barta
Institute of Physics, Czechoslovac Academy of Sciences, Prague, Czechoslovakia

ABSTRACT

Recrystallization of antimony (III) sulphide in the glassy Ge-Sb-S system was studied under non-isothermal conditions. Using the phenomenological Johnson-Mehl-Avrami equation both the kinetics exponent n and an apparent energy E_a were determined. Both values are characterising in the first approximation the kinetics of crystallization.

INTRODUCTION

In recent years attempts have been made at the study of recrystallization of different types of glasses /1-5/, using differential thermal analyses (DTA) or differential scanning calorimetry (DSC). Starting from the phenomenological J-M-A equation /6/

$$x(t) = 1 - \exp(-Kt^n), \qquad (1)$$

where x is the fraction of the transformation after time t, K is rate constant, and n reflects nucleation rate and/or growth morphology, attention is paid to the determination of both the n and apparent activation energy (E_a)

$$K = K_0 \exp(-E_a/K_BT). \qquad (2)$$

K_0 is preexponential term (often taken as a constant), T is absolute temperature and K_B is Boltzmann constant. Both values of E_a and n are thus parameters characterizing, in the first approximation, the kinetics of the crystallization. For the study of phase transformation both the isothermal and nonisothermal DTA or DSC methods have been used. On the contrary to the isothermal method the advantage of the non-isothermal method is /6/ (i) rapidity of experiments, (ii) possibility to extend the temperature region of the study.

In this paper we present preliminary results of the study of crystallization kinetics of Sb_2S_3 in glassy $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ using non-isothermal DTA.

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EXPERIMENTAL

Glassy $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ was prepared by a method described elsewhere /8/. No fractions of crystalline inclusions were found by X-ray diffraction. The homogenity of the studied glassy sample was verified by IR microscopy and using TOPO and COMPO analyses. The DTA was made using DuPont Thermal analyser 990 (in DTA mode), by heating rates (Φ) Φ = 1K/min; 2 K/min; 5 K/min; 10 K/min and 20 K/min. Bulk glasses were used only. During the measurements the sample chamber was continuously purged by 50 cc/min of dry Ar. Two characteristic thermal phenomena are clear in the studied temperature region. The first one corresponds to the softening of glassy sample, the second one -exo-corresponds to the recrystallization. Verification of the softening was made by penetration method.

The identification of the crystalline phase was made by X-ray diffraction in two samples of the same composition annealed to two different temperatures. From the diffraction patterns it is clear that the recrystallized substance is most probably Sb_2S_3.

RESULTS AND DISCUSSION

The values of both the softening temperature (T_g) and temperature of the peak of recrystallization (T_p) are summarized in table 1.

(K min^{-1}) / T_i(K)	1	2	5	10	20
T_g	499	503	508.5	514	517
T_p	614	621	642	657	671

It is evident from this table that both values of T_g and T_p are depending on the heating rates. This fact reflects the kinetic nature of both the softening and crystallization, respectively. It was shown e.g. in /6,7/ that applicability of J-M-A rate equation for the study of kinetics of crystallization using non-isothermal DTA requires the validity of a series of assumptions. However, as a cursory check of the applicability of J-M-A can be taken the validity of x_p 60-63% /6/, where x_p is a fraction transformed at the peak in the transformation rate. It means that at

$d(dx/dt)/dt = 0$ the x_p is $\sim 60 - 63\%$, independent on the Φ used. In our case the x_p vary between 59 - 61% for values of Φ used and we suppose that the above mentioned condition is fulfilled. As shown in /4/ solving rels. (1,2) for $d^2x/dt^2 = 0$ it is valid (for $n > 1$)

$$\frac{d\left[\ln(\Phi/T_p)\right]}{d(1/T_p)} = -\frac{E_a}{nK_B} \qquad (3)$$

In Fig. 3 (right hand side) are shown our experimental data (full points) fitted by rel.3. The estimated value of $E_a/n = 1.72$ eV. The determination of the kinetic exponent n in eq.(1) can be made e.g. using method proposed in /9/ and recently discussed in /6/. In the case of single scan it can be written /6/

$$\frac{d\left[\ln\ln(1-x_T)^{-1}\right]}{d(1/T)} = -\frac{E_a}{K_B} \qquad (4)$$

where x_T is a fraction transformed at temperature T. On the left hand side of Fig.3 are shown our experimental data (open circles for $\Phi = 20$ K/min, half filled circles for $\Phi = 10$ K/min) fitted by (4). The estimated values of E_a are ~ 3.36 eV, and thus consequently the kinetic exponent n is $\doteq 1.95$.

Finally, the dependence of the T_g on heating rate is shown in Fig.4. Such a type of $\ln\Phi$ vs. T_g^{-1} dependence is often observed in case of different noncrystalline materials and reflects the kinetic nature of the softening. The value of activation energy, $\Delta E_a = K_B\, d(\ln\Phi)/d(1/T_g)$ for the overall relaxation time controlling the structural transformation in the vicinity of T_g, is $\Delta E_a = 2.37$ eV. We conclude that kinetics of the recrystallization of Sb_2S_3 in glassy $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ can be described using J-M-A phenomenological rate equation with apparent activation energy $E_a = 3.36$ eV and kinetic exponent $n \sim 2$. Further work, i.e. a study of recrystallization of Sb_2S_3 in $(GeS_2)_x(Sb_2S_3)_{1-x}$ glasses, is in progress.

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