CRYSTALLIZATION KINETICS OF GLASSY As_2Se_3

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Abstract

Isothermal crystallization of bulk As_2Se_3 glass was studied in temperature range 270–360°C. Johnson-Mehl-Avrami (JMA) equation describes the crystallization process in the whole temperature range. By means of analysis of JMA equation the temperature dependence of kinetic exponent n was found, its value changes from 3.8 to 1.9 with increasing temperature. The relationship between the value of n and crystal morphology was briefly discussed. Furthermore the value of apparent activation energy E was determined as well as melting enthalpy. Temperature dependence of crystal growth rate was also determined.

Keywords: arsenic triselenide, differential scanning calorimetry, isothermal crystallization kinetics, melting enthalpy

Introduction

Chalcogenide glasses have been studied very intensively for many years. As_2Se_3 glassy system has been studied mainly from the point of view of optical [1, 2] and thermal properties [3]. As_2Se_3 represents one of the best characterized chalcogenide based glass-formers. It can be easily prepared in semiconductor purity and this material is also considerably stable in the glassy state. Good thermal stability and relatively low crystallization rate of glassy As_2Se_3 allow to measure isothermal crystallization and in this way to study a kinetics of crystallization process.

The crystallization kinetics, viscosity and temperature coefficient of expansion of amorphous As_2Se_3 were investigated by Henderson and Ast [5]. The kinetics was characterized under isothermal conditions from 240 to 360°C. Microscopic examination of partially crystallized As_2Se_3 revealed a spherulitic growth of the crystalline phase and the constant isothermal growth rates with respect to time. It was found that below 350°C the individual crystallites grew with a two-dimensional (plate-like) morphology. Above this temperature (at temperatures approaching the melting point, T_M=373°C) the crystal growth morphology change to a rod like structures.

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The activation energy for the crystal growth rate was found to be 1.6 eV by direct observation. The crystallization kinetics was described by the Johnson-Mehl-Avrami (JMA) equation. The constancy of kinetic exponent n for each isotherm was found to be consistent with the fact that the growth morphology, the functional dependence of nucleation rate and growth rate on time do not change throughout the crystallization process. For all powder sizes the value of n was approximately constant and equal to 4.5 for temperatures from 250–300°C. The value of n decreases to 4.0 in temperature range from 300 to 335°C. The value of n greater than 4.0 was interpreted as indicating that the total nucleation rate is an increasing function of time (regardless of the crystallite growth morphology).

In the present work we carried out isothermal DSC measurements of bulk As₂Se₃ in a wide temperature range to obtain more detailed information about crystallization kinetics of this technically interesting material.

Experimental

Bulk amorphous As₂Se₃ was prepared by using conventional method of pure elements direct synthesis. High purity elements (5N) were placed into quartz ampoule. The synthesis was performed in sealed evacuated ampoule in a rocking furnace at 650°C for 24 h. After synthesis the melt was cooled in air.

Isothermal crystallization of bulk samples (about 17 mg) was studied in temperature range 270–360°C by using a differential scanning calorimeter DSC-7 (Perkin Elmer).

The morphology of crystals growing at various temperatures was checked by using optical microscope BX - 60 (Olympus).

Results and discussion

Isothermal crystallization experiments were conducted from 270 to 360°C. The enthalpy of crystallization was found to be $\Delta H_{cryst} = -91.5 \pm 2.7$ J g^{-1}.
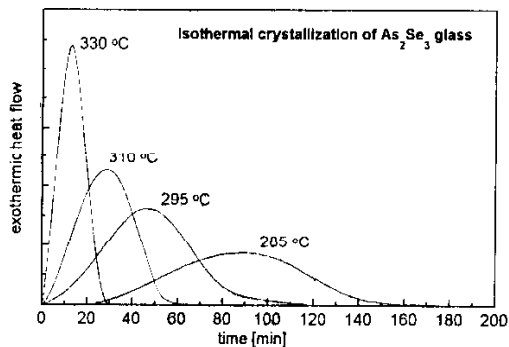

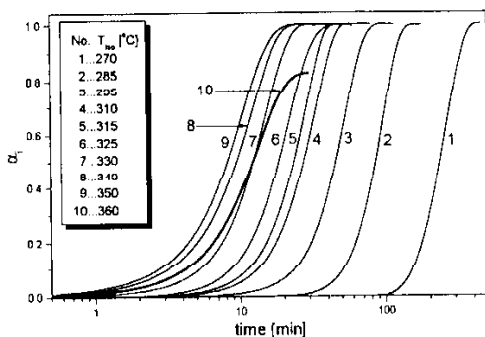**Fig. 1** Some of experimentally obtained isothermal DSC traces of glassy As₂Se₃

Fig. 2 Time dependence of degree of crystallization obtained by integration of experimental data. Curve 10 (360°C) is pertinent to equilibrium of crystal growth and melting. See also Fig. 3 for maximum crystallization rate temperature dependence

Experimental isotherms (Fig. 1) were integrated and the time dependence of degree of crystallization α_i was obtained, Fig. 2. Temperature dependence of maximum crystallization rate is shown in Fig. 3. The crystallization rate increases to the temperature 350°C. Close to the melting temperature the equilibrium between crystal growth and melting occurs significantly, Fig. 2, curve No. 10, and crystallization rate falls down rapidly, as one can assume, Fig. 3.
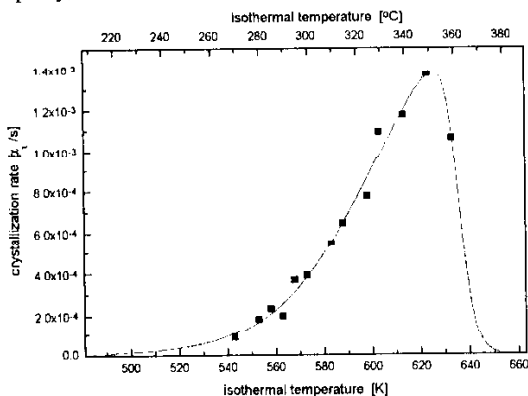

Fig. 3 Temperature dependence of isothermal crystallization rate (points) obtained from computer fit of degree of crystallization time dependence

All data were analyzed in terms of JMA equation:

$$\alpha_i = 1 - \exp(-(kt)^n), \tag{1}$$

where t is time, k is rate constant having an Arrhenian temperature dependence ($k = A\exp(-E/kT)$), E is an apparent activation energy of crystallization and n is a ki-

netics exponent reflecting the growth morphology and nucleation time dependence [5]. Other constants have conventional denotation. JMA equation is the same as general equation describing kinetic of new phase growth as well as for the phase changes [6] and thus according to our opinion its application is correct. Demonstration of JMA fit for two different isotherms are shown in Fig. 4.
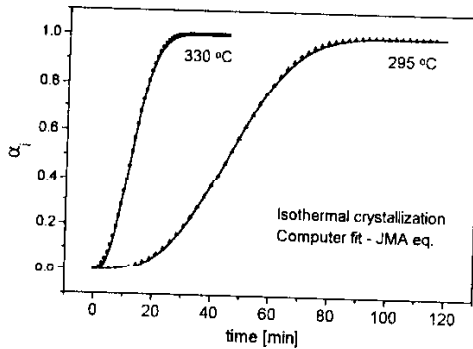

Fig. 4 Experimentally obtained degree of crystallization time dependence (points) and its computer fit (lines), Johnson-Mehl-Avrami equation was used

Using non-linear regression the values of parameters k and n of JMA equation were obtained. Based on the thermal dependence of the rate constant k the value of apparent energy E was determined, Fig. 5. The value of E is 1.58 eV (pre-exponential factor $A=1\cdot10^6$ s⁻¹) at temperatures below approximately 570 K (297°C) and above this temperature the E value decreases to 0.99 eV ($A=7\cdot10^6$ s⁻¹). Because the mechanism of crystallization process can be temperature dependent, two different mechanisms with different values of E can be assumed. Nucleation together with crystal growth are dominating at lower temperature region while entirely crystal growth is crucial at higher temperatures.
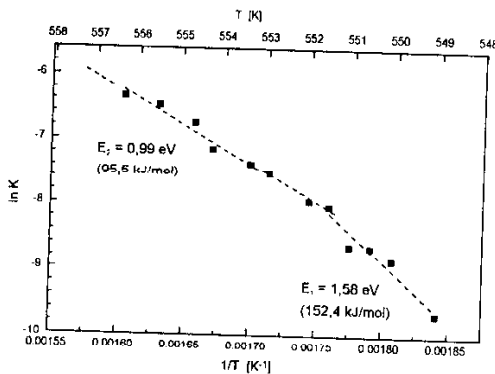

Fig. 5 Activation energy of crystallization process obtained from computer fit of experimental

Furthermore the kinetic exponent n exhibits temperature dependence and its value decreases from 3.8 to 1.9 over the whole studied temperature interval. The temperature dependence of the kinetic exponent can clearly be divided into four parts, marked A-D in Fig. 6.
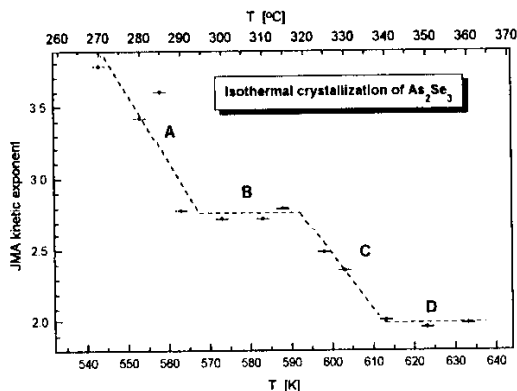

Fig. 6 Temperature dependence of JMA kinetic exponent n obtained from computer fit of experimental data

In the part A the kinetic exponent n decreases from the value ~3.8 to 2.75. With respect to the higher value of apparent activation energy (E=1.58 eV) we suppose that the nucleation and the crystal growth take place at the same time as we mentioned above. This conclusion is in accordance with values of n for various crystallization processes predicted by Mora [7].

In the part B the n value (~2.75) is practically constant. In accordance with experimentally obtained value of n and lower value of apparent activation energy E=0.99 eV only the crystal growth is probably the dominating process. Optical microscopy measurement confirmed that consistent with the value of n the crystals growing under these thermal conditions are three-dimensional. This agrees well with [7] again.

In the third temperature region (C) the kinetic exponent n decreases from 2.75 to 1.9 and the E value remains constant (E=0.99 eV). The crystal growth process is probably the same as in previous case but dimensionality of crystals changes. Two dimensional plate-like crystals come up together with three-dimensional ones as confirmed by optical microscopy.

The last region (D) approaches at the end the melting point of As₂Se₃ crystals. The plate-like crystal growth morphology predominates, which is in accordance with experimentally found kinetic exponent value (n~1.9).

In comparison with Henderson and Ast [5] our results differ especially in the magnitude of kinetic exponent values. They found n changed from value 4.5 in the low temperature region to n=4 (at 335°C) and the value of n was interpreted regardless of the crystallite growth morphology. In contrast, the value of n calculated in our

work reflects the growth morphology of crystals (n~2 in case of two-dimensional growth and n~2.75 in case of three-dimensional one). The values of n>3 found by isothermal measurement in the low temperature region can be explained by mixing nucleation and crystal growth [7].

Temperature dependence of kinetic exponent n experimentally taken is in strong contradiction with the assumption of constant n used in numerical analysis of non-isothermal data [8–10]. We are afraid that the result obtained by analysis of non-isothermal data can be incorrect at least in some cases. Especially in those cases when non-isothermal crystallization can be observed over a wide thermal interval. It is well known from many experiments that only Šesták-Bergren accommodation function (having no physical meaning) can be used to the description of experimental data in these cases.

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