CRystallization kINetics of GlASSy As$_2$Se$_3$

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Abstract

Isothermal crystallization of bulk As$_2$Se$_3$ 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$_2$Se$_3$ glassy system has been studied mainly from the point of view of optical [1, 2] and thermal properties [3]. As$_2$Se$_3$ 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$_2$Se$_3$ 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$_2$Se$_3$ 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$_2$Se$_3$ 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 (IMA) 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 As$_2$Se$_3$ in a wide temperature range to obtain more detailed information about crystallization kinetics of this technically interesting material.

**Experimental**

Bulk amorphous As$_2$Se$_3$ 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 $\Delta H_{\text{cryst}} = -91.5 \pm 2.7 \text{ J g}^{-1}$.

![Isothermal crystallization of As$_2$Se$_3$ glass](image)

*Fig. 1 Some of experimentally obtained isothermal DSC traces of glassy As$_2$Se$_3$*

*J. Therm. Anal. Cal., 56, 1999*