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Thermal properties and viscous flow behavior of As_2Se_3 glass

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ABSTRACT

Thermal deformation of the As_2Se_3 bulk samples polished to optical quality has been investigated in the undercooled liquid region using thermomechanical analyzer (TMA). During the non-isothermal measurements the change of sample height has been monitored under compression at different heating rates (1–5 °C/min). The coefficient of linear thermal expansion, glass transition temperature and two characteristic extrapolated temperatures T_0, as beginning of sample deformation caused by viscous flow, and T_f, as temperature at which the deformation is stopped by crystal growth and the sample reaches the final height h_f, were obtained from TMA measurements. It was found that the value of activation energy obtained from the shift of characteristic temperature T_f with heating rate using the Kissinger method is very close to activation energy of crystal growth obtained by direct monitoring using microscopic methods. The influences of applied force, sample dimensions and heating rate on the overall TMA crystallization curve are discussed. For the first time, theoretical simulations of crystal growth were used to correlate the course of the TMA curve with the direct microscopic observation of the crystallization process.

1. Introduction

Glass transition, crystallization and melting temperatures, along with the coefficient of thermal expansion are the typical thermal quantities associated with glass. Amorphous chalcogenide glass-forming materials exhibit variety of interesting properties used in a wide range of industrial applications. The understanding of their thermal properties and especially of their crystallization behavior is important for the characterization and possible usage of these materials. Kinetics of crystallization can be examined using two approaches. The first one is the macroscopic approach, which is based on monitoring of the specific macroscopic quantity related to the overall crystallization process proceeding in the studied system (e.g. thermoanalytical behavior, intensities of XRD diffraction lines, or electrical conductivity). The thermoanalytical techniques such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) [1–3] belong among the most frequently used indirect methods. The second experimental approach used to investigate crystallization kinetics in glasses is the direct observation of the growing crystals by optical, infrared, or electron microscopy [4–8]. This approach is based on the difference in optical contrast between the amorphous and crystalline phases.

Recently, it has been reported [9–11] that Thermomechanical analysis (TMA) can be used for obtaining kinetic information. This method is particularly advantageous in cases when crystallization heat evolution is below the detection limit of the DTA/DSC instrument (the crystallization is either very slow or only a minor component of the studied material crystallizes). The study of crystallization using TMA is based on the viscous flow behavior of glass-forming undercooled melts. During the non-isothermal measurements, the change of the sample height is monitored in dependence on temperature. With increasing temperature the viscosity of the material decreases and this leads to flattening of the sample associated with a decrease of its height and increase of its width. Due to the formation and growth of crystals the sample deformation is slowed down and subsequently it is stopped. In this paper such a method of measurement is applied in the study of non-isothermal crystallization of single compound chalcogenide glass As_2Se_3 that has been previously studied mainly by the conventional methods.

Most famous study dealing with crystallization behavior of glassy As_2Se_3 is that by Henderson and Ast [5]; the following techniques were employed: DSC, direct observation by optical and electron microscopy, measurements of viscosity and of the coefficient of thermal expansion. The crystallization kinetics was described by Johnson–Mehl–Avrami equation. Studies of

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isothermal DSC crystallization and nucleation can be found in Refs. [12–15]. Several works [16–18] deal also with non-isothermal DSC data, however, these experiments were performed using only very low heating rates (<3 °C/min) due to the relatively low crystallization rate of As_2Se_3 that restricts the use of non-isothermal method.

2. Experimental

The As_2Se_3 glass was prepared by synthesis from pure elements using the melt-quenching method. The adequate amounts of elements (4 g total weight) were weighted into a clean quartz ampoule (inner diameter 4 mm, length 80 mm). The ampoule was then evacuated to a pressure of 10^{-3} Pa for 30 min, sealed and then placed in a rotary furnace. The ampoule was heated well above the melting point of the particular elements, to a temperature of 750 °C, where the melt was homogenized for 20 h. The amorphous character of the prepared glass was confirmed by X-ray diffraction analysis (XRD, AXS diffractometer D8 Advance, Bruker, CuK_α).

Experiments were performed with thermomechanical analyzer TMA-CX03R (R.M.I. Company). This instrument measures sample height changes relative to a quartz sample holder with a differential capacitance displacement detector. The detector is controlled through an electronic system which ensures linearity with deviation better than 0.1% (full scale), high sensitivity (0.01 μm resolution), low noise (typically 0.02 μm without signal filtering), very good resolution, and baseline flatness over broad temperature and time scale (<0.002 μm/°C and 0.008 μm/h, respectively). More detailed specification of this instrument is described elsewhere [19]. The instrument was calibrated by height standards and by melting temperatures of Ga, In, Pb, Zn and Al standards. Precision of temperature measurement was ±0.2 °C. The force was calibrated by placing a known weight on the system.

Linear thermal expansion was measured using TMA during intrinsic cycles where the rectangular sample of As_2Se_3 glass ($4 \times 4 \times 7$ mm) was first heated to a temperature 230 °C, which is above T_g, to erase any previous thermal history. In the second step, the sample was cooled to 100 °C at the defined cooling rate β^- (1, 3 and 5 °C min^{-1}). In the third step, the sample was immediately reheated to 230 °C at the same rate at which it was previously cooled. The change of the sample height was measured.

Sample deformation at non-isothermal conditions was studied by parallel plate method. This method is based on measuring the height of the cylindrical glass sample which is squeezed between two parallel alumina plates loaded by force F. The viscosity can be determined from the variation of sample height h with time using following equation [20]:

$$\eta = \frac{2\pi F h^5}{3V(dh/dt)(2\pi h^3 + V)} \tag{1}$$

where F is an applied force, h is a measured sample height, V is the sample volume, and dh/dt is the deformation rate. The parallel plate method is typically used for measurement of viscosity in a broad range from 10^4 to 10^{10} Pa s. For some systems, the viscosity measurement is complicated due to the crystallization of undercooled melt in this region [5,25]. It was found that the measurement response for crystallization is quite reproducible and could be used to monitor crystal growth kinetics [9–11].

The TMA experiments were performed in the temperature range from 30 °C to 374 °C (below melting point) at heating rates 1, 2, 3, 4 and 5 °C/min. The loading forces of 5.6, 12.6 and 32.6 mN were applied. The amorphous samples used for TMA measurement were of a cylindrical shape with a diameter of 4 mm and height of 0.5, 1 and 2 mm or with a diameter of 3 mm and height of 1 mm. The cylinder bases were polished to optical quality.

From the experimental data, the following parameters were calculated:

a) normalized sample height = $(h - h_f)/(h_0 - h_f)$
b) relative displacement = $(h - h_0)/h_0$
c) aspect ratio = h_0/D_0
d) true height strain = $\ln(h_0/h)$
e) true stress = F/A, where $A = m/\rho h$

where h_0 is initial sample height, h_f is final sample height, D_0 is initial sample diameter, F is applied force, A is cross-sectional area, m is sample weight, and ρ is density.

The microscopy measurements were performed by using an optical microscope Olympus BX 51 with microscopic camera DP 72. The elaboration of digital images and evaluation of crystal length were done using software QuickPHOTO Industrial 2.3 (Promicra Ltd.).

The simulation of crystal growth and the kinetic analysis were done using software OriTas [21]. The process of crystal growth simulation requires following data inputs:

- dependence of viscosity on temperature, which is given by VFT equation [22]:

$$\log \eta = -5.886 + \frac{2995.182}{T - 275.02} \tag{2}$$

- dependence of crystal growth rate on temperature. In case of 2D surface nucleation growth, the growth rate of As_2Se_3 crystals can be expressed as follows [23]:

$$u = \frac{9.74 \cdot 10^{-5}}{\eta^{0.653}} \exp\left(-\frac{1.69 \cdot 10^4}{T \cdot (647.55 - T)}\right) \tag{3}$$

Parameters of the growth rate equation were determined from the microscopic measurement of As_2Se_3 crystals after non-isothermal heat treatments. The crystal growth rate was measured from temperature 230 °C up to melting point 374.4 °C. The applicability of this equation was verified using Henderson and Ast data [5].

- average distance of the nuclei on surface, which was found to be 65 ± 5 μm [23].
- dependence of sample height on temperature (measured in this work)

Regarding the technical details of the simulation procedure, random distribution of nuclei on the surface (while retaining the above-mentioned condition of average distance between the nuclei) was used; variance of applied growth rates was ±15%; considered temperature range was from 20 °C to the melting point; time step for the simulation was 1 s; and volume was kept constant during the height change. For the subsequent calculation of the degree of conversion, the sample was divided through a network of points with a given point density (distance between the network nods was $5 \cdot 10^{-6}$ m). Then the degree of conversion corresponds to the ratio of points, into which the crystals extend, and the total number of points.