Crystallization processes in Ge$_2$Sb$_2$Se$_4$Te glass

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A B S T R A C T

Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis were used to study crystallization in Ge$_2$Sb$_2$Se$_4$Te glass under non-isothermal conditions as a function of the particle size. The crystallization kinetics was described in terms of the autocatalytic Šesták–Berggren model. An extensive discussion of all aspects of a full-scale kinetic study of a crystallization process was undertaken. Dominance of the crystallization process originating from mechanically induced strains and heterogeneities was confirmed. Substitution of Se by Te was found to enhance the manifestation of the bulk crystallization mechanisms (at the expense of surface crystallization). The XRD analysis showed significant dependence of the crystalline structural parameters on the crystallization conditions (initial particle size of the glassy grains and applied heating rate). Based on this information, a new microstructural crystallization mechanism, indistinguishable by DSC, was proposed.

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1. Introduction

Chalcogenide glasses are currently among the most attractive high-tech materials. Owing to their unique photosensitivity, wide infrared transparency window, finely tunable material properties, and the large difference between the optical and electrical properties of their amorphous and crystalline states, chalcogenide glasses have been utilized in many important applications. In particular, the Ge–Sb–Se, Ge–Sb–Se–Te and Ge–Sb–Te families have scored significant success as phase-change materials. Ultrafast crystallization of these materials has found use in optical recordings (DVDs and Blu-Ray discs) and in the construction of electrically switched memories (PCRAMs) [1,2]. From the latter point of view, it is interesting to consider the relatively unexplored quaternary Ge-Sb-Se-Te glassy system, as it may not only offer new application possibilities, but also enhance some of the properties of these already utilized high-tech materials (e.g., improve the thermal stability of Ge–Sb–Te glasses). Several studies regarding their glass-forming ability [3], structural arrangements [4–6], glass-transition behavior [7], microhardness [8], as well as molar volume and elastic properties [9,10] have previously been published. However, surprisingly, no data on the crystallization or kinetics of these materials can seemingly be found.

Clearly, the quality of the prepared glasses (or their thin layers) and their stability are key factors for their utilization in high-tech applications. In this regard, it is mainly the crystallization process that can be limiting for the applicability of newly developed glasses. Crystallization has to be either avoided in order to obtain perfect and stable glass with the finest optical or electrical properties or, on the contrary, the crystallization process in the glassy matrix must, in fact, be the fundamental basis of the technology, which is the case for data-storage media. Nevertheless, in either case, it is important to know the mechanisms of the nucleation and crystallization processes.

A detailed study of the crystallization behavior of Ge$_2$Sb$_2$Se$_4$Te glass (i.e., the Se↔Te substitution analogue of the famous GST-225 PCM material) will be the main aim of this work. In particular, based on differential scanning calorimetry (DSC) data, a full kinetic analysis of the crystallization process will be performed. The study will be performed as a function of the particle size (powders of varying coarseness will be measured) in order to reveal the involved crystallization mechanisms. Furthermore, X-ray diffraction (XRD) analysis will be performed on samples crystallized under different conditions, so that further insight into the crystal growth mechanisms is acquired.

2. Experimental

The Ge$_2$Sb$_2$Se$_4$Te glass was prepared from pure elements (5N, Sigma–Aldrich) by the classical melt-quenching technique. Elements were accurately weighed into a fused silica ampoule,

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degassed, sealed, and the batched ampoule was held, first, in a rocking furnace for 6 h at 650 °C, then it was heated to 950 °C and annealed for 24 h, and lastly, the ampoule was slowly cooled to 650 °C, at which it was maintained for 1 h. The ampoule containing the melt was quenched in water in order to prepare the glass. The amorphous nature of the glass was checked by XRD and the homogeneity was verified from the position of the relaxation peak, which was measured under defined conditions for samples taken randomly from the bulk glass. The glass was ground, and the prepared powder was divided according to particle size into the following ranges: 0–20, 20–50, 50–125, 125–180, 180–250, 250–300, and 300–500 μm. Bulk samples were prepared by cracking a thin sheet of as-prepared bulk glass.

Crystallization of the as-prepared powder fractions was studied by a conventional DSC 822^e (Mettler, Toledo) that was equipped with a cooling accessory. Dry nitrogen was used as the purge gas at a rate of 20 cm^3 min^{-1}. Calibration of the DSC was performed using In and Zn. A thin layer of the powder was spread on the bottom of aluminum pans in order to improve thermal contact; the masses of the powder samples varied between 8–10 mg. The temperature program was, first, a short 5 min stabilization isotherm at 200 °C, which was followed by a heating step at various heating rates (1–3, 5, 7, 10, 15, 20, and 30 K min^{-1}) up to 380 °C. Each measurement was reproduced in order to reveal any experimental errors. A spline-type baseline was used to imitate and subtract the thermokinetic background [11]. A typical DSC curve (measured to the melting point) is shown in Fig. 1.

The structure of the chosen crystalline samples was studied by XRD analysis. Samples were ground in agate mortar in a suspension with cyclohexane. The suspension was then placed on top of Mylar foil in a transmission sample holder. After evaporation of the solvent, a thin layer of the as-prepared sample was covered with a second Mylar foil. Diffraction patterns were collected using a PANalytical X'Pert PRO diffractometer that was equipped with a conventional X-ray tube (CuKα 40 kV, 30 mA, line focus) and was used in transmission mode. An elliptical focusing mirror, a divergence slit of 0.5°, an anti-scatter slit of 0.5°, and a Soller slit of 0.02 rad were used in the primary beam. A fast linear position-sensitive detector PIXcel with an anti-scatter shield and a Soller slit of 0.02 rad were used in the diffracted beam. All patterns were collected in the range of 2θ = 3–88° with a step of 0.013° at 600 s/step, producing a scan time of about 4.5 h. Qualitative analysis was performed with the HighScorePlus software package (PANalytical, The Netherlands, version 3.0e) and JCPDS PDF-2 databases [12,13]. All line-profile-fitting procedures were performed in the HighScorePlus software package.

3. Results and discussion

In the following text, the crystallization behavior of the Ge$_2$Sb$_2$Se$_4$Te glass is described. Firstly, full-scale kinetic analysis was performed, and, in particular, the basic DSC kinetic equation (Eq. (1)) [14] is enumerated:

$$\Phi = \Delta H \times A \times e^{-E/RT} \times f(\alpha) \tag{1}$$

where Φ is the measured heat flow, ΔH is the crystallization enthalpy, A is the pre-exponential factor, E is the apparent activation energy of the process, R is the universal gas constant, T is temperature, and $f(\alpha)$ is an expression of a kinetic model with α being the conversion. Determination of E, ΔH, and the dominating crystallization mechanism are included in Section 3.1, whereas determination of the kinetic model and a detailed description of the involved microstructural crystal growth mechanisms are introduced in Section 3.2. Finally, the XRD analysis of the particle-size-differentiated Ge$_2$Sb$_2$Se$_4$Te crystalline powders, and the correlation of these results with the DSC data is presented in Section 3.3.

3.1. Primary kinetic analysis of DSC data

In the first step of the kinetic analysis, the apparent E value for the crystallization process was determined using the original Kissinger [15,16] and isoconversion Friedman [17] equations. In Fig. 2, the Kissinger plot is shown for all studied particle size ranges. The Kissinger equation is expressed as:

$$\ln\left(\frac{q^+}{T_p^2}\right) = \frac{E}{RT_p} + \text{const.} \tag{2}$$

E is determined from the slope of the displayed dependence of the temperature corresponding to the maximum of the crystallization peak (T_p) on the heating rate (q^+). As can be seen in Fig. 2, the linearity of the dependencies is high, suggesting the absence of major data-distortion effects (e.g., thermal gradients in the sample or in the measuring DSC cell). In addition, linear Kissinger dependencies throughout the whole set of particle size ranges also indicate uniformity of the dominant crystallization
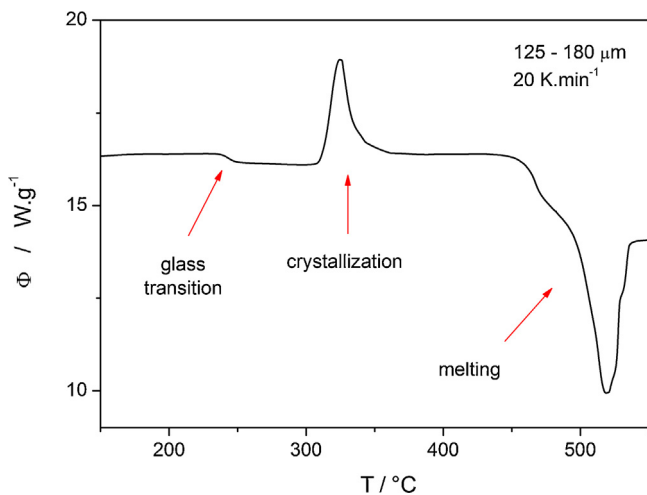

Fig. 1. Example DSC curve (measured up to the melting point) obtained for samples with a particle size of 125–180 μm at a heating rate of 20 K min^{-1}.
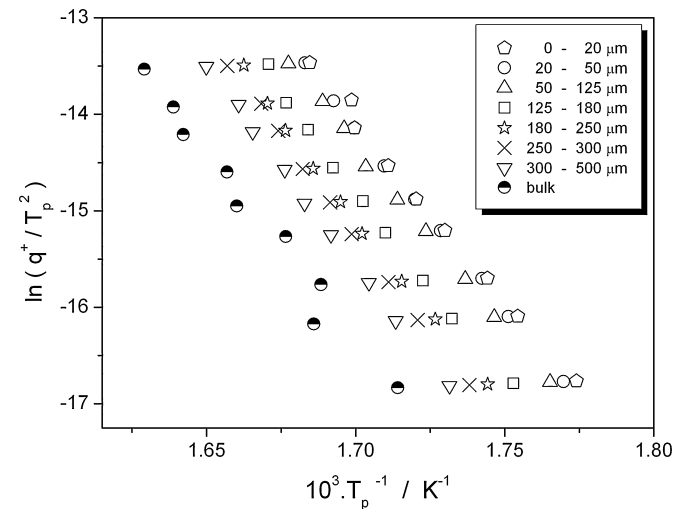

Fig. 2. Kissinger plot for a set of particle size ranges measured for the Ge$_2$Sb$_2$Se$_4$Te glass.