Available online at www.sciencedirect.com
ScienceDirect
Journal of Non-Crystalline Solids 353 (2007) 4702–4706
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Thermal analysis of RbI crystallization in the $GeSe_2$–Sb_2Se_3–RbI system

L. Calvez [a], H.L. Ma [b], J. Lucas [b], P. Glouannec [c], X.H. Zhang [b,*]

[a] *Arizona Material Laboratory, 4715 East Fort Lowell Road, 85712 Tucson, United States*
[b] *Laboratory of Glasses and Ceramics, UMR-CNRS 6226, Université de Rennes1, 35042 Rennes, France*
[c] *Laboratoire d'Etudes Thermiques, Energétique, Environnement, Université de Bretagne Sud, Lorient, France*

Received 6 December 2006; received in revised form 26 June 2007
Available online 8 August 2007

Abstract

The crystallization of glasses in the $GeSe_2$–Sb_2Se_3–RbI system has been studied by using differential scanning calorimeter. Thermodynamic study has permitted to determine the best nucleation time and temperature for the $60GeSe_2$–$30Sb_2Se_3$–10RbI glass composition. RbI crystals with controllable size were reproducibly and homogeneously generated in the glassy matrix with appropriate annealing times and temperatures. Mechanical properties and resistance to thermal shocks of glasses and transparent glass–ceramics were investigated.

PACS: C145; C290; G160; M120

Keywords: Crystallization; Glass–ceramics

1. Introduction

Transparent glasses from 0.8 μm to 16 μm, synthesized in the Ge–As–Se or Ge–Sb–Se systems such as GASIR [1], could be an alternative solution to replace expensive single crystalline Ge usually used for thermal imaging devices. It has been demonstrated that ionic compound addition such as alkali halide facilitates the controlled submicron crystals growth in chalcogenide glasses [2]. The generation of crystals inside a glass matrix is a proven technique for improving the mechanical properties of glasses such as the tenacity and hardness and examples are often given for silicate glasses and glass ceramics [3–7]. While the crystallization of chalcogenide glasses have been intensively studied [8–10], results of controllable and reproducible crystal growth have only been recently reported [2].

In a previous study on the $GeSe_2$–Sb_2Se_3–RbI glass system, we have demonstrated that Sb_2Se_3 and RbI crystals can be generated by heating a glass with a rate of 1 °C/min up to $T_g + 50$ °C, T_g being the glass transition temperature [11]. Observations under scanning electronic microscope and X-rays diffraction show however that Sb_2Se_3 crystals are only on the glass surface, while the RbI is homogeneously distributed inside the glass matrix.

In this paper, we will present a complete thermal study on these glasses. The objective is to optimize the thermal annealing process for controllable and homogenous crystallization.

The thermal expansion coefficient and thermal conductivity of the glasses and glass ceramics have been measured in order to evaluate their resistance to thermal shocks.

2. Experimental

Bulk glasses were prepared by melting the pure raw materials (99.999% Ge, Sb, Se and 99.9% for the RbI) under vacuum in a sealed silica tube of 10 mm inner diameter. The sealed ampoule containing the mixture was heated up to 750 °C in a rocking furnace for several hours

* Corresponding author.
E-mail address: x.zhang@univ-rennes1.fr (X.H. Zhang).

0022-3093/$ - see front matter
doi:10.1016/j.jnoncrysol.2007.06.059

and quenched in water. Samples were annealed 10 °C below T_g for 6 h to minimize inner constrains. The purification process by distillation under dynamic vacuum was described elsewhere [11]. The obtained glass rods were sliced into disks of 2 mm thickness and heat treated in a ventilated furnace at different temperatures for different durations.

The crystalline phases obtained by ceramization were analyzed by X-ray diffraction on polished disk and powder, and by scanning electronic microscope (SEM) coupled with an energy dispersive spectrometer to analyze the composition.

For transmission measurement, a double beam spectrometer (CARY 5) was used in the visible and near infrared region. A BRUKER Fourier transform infrared spectrometer was used for mid and far infrared region.

Hardness (H_v) and toughness (K_c) were determined by using a Vickers micro indenter with a charge of 100 g for 5 s. Image of nanocrystals were obtained using a scanning electronic microscope (SEM). The technique to observe sub-micron crystals and the methods used to calculate the hardness and the toughness were described elsewhere [12]. The flash-laser method was used on 16 mm diameter and 2 mm thickness glass and glass–ceramics sample with a surface precision of $\lambda/4$ to measure thermal diffusivity. In the flash-laser method, a flash of radiant energy is applied to one surface of a small disk, and the temperature increase of the opposite face is registered. The thermal diffusivity is calculated from the sample thickness and the time required for the opposite face temperature rise to reach a known percentage of its maximum value. Heat capacity was measured on glass slice by differential scanning calorimetry experiments.

In order to determinate the evolution of the crystallization rate versus annealing time, crucibles containing 10 mg powder of the $60GeSe_2$–$30Sb_2Se_3$–10RbI base glass, which has been identified as the best glass composition for controlled crystallization [11] were annealed at 290 °C for different durations. As described in a previous paper, a crystallization temperature from 30 °C to 40 °C above T_g allows a controlled crystallization [2]. The heat treatment of crucibles containing the sample is realized in a high precision ventilated furnace (±2 °C). The crucibles are cooled down at a rate of about 50 °C/s to room temperature. Finally, thermal analysis is performed with a heating rate of 10 °C/min.

3. Results

The DSC curve of the $60GeSe_2$–$30Sb_2Se_3$–10RbI base glass powder gives a glass transition temperature of 248 °C. This glass is stable against crystallization, as the difference between the glass forming temperature and the crystallization temperature is larger than 140 °C. We can observe in the Fig. 1 that the base glass presents a large crystallization peak at 395 °C. After 120 min of heat treatment at 290 °C, the main peak splits up into two exothermal peaks. By increasing the heat treatment time, the second crystallization peak shifts towards lower temperature while the T_x of the initial peak does not change and the full width at half maximum strongly decreases. After 480 min of heat treatment, the second crystallization peak totally disappears indicating the total crystallization of the phase associated with this peak. According to the thermograms, the dissociation of the two crystallization peaks can be obtained by annealing samples for 300 min at 290 °C, keeping a very good thermal stability illustrated by a large T_x–T_g.

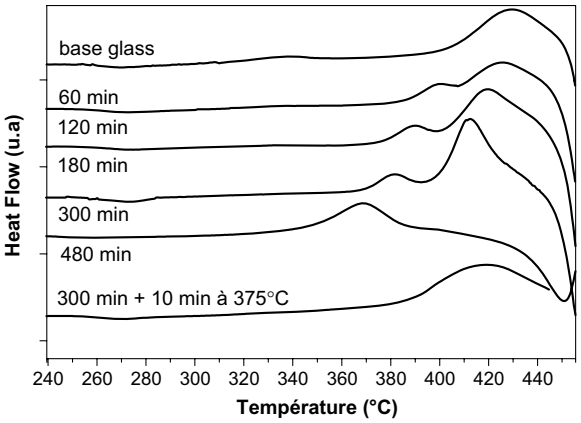

Fig. 1. DSC curves of the base glass heat treated at 290 °C for different times.

As demonstrated by Ray et al. the height of the crystallization peak permit to determine the evolution of the nucleus number [13–15]. Hence, the height of the main and initial crystallization peak versus heat treatment time at 290 °C was reported in the Fig. 2. This curve permits to determinate that the best nucleation time is around 300 min at 290 °C for the second peak.

By using the same method, it can be determined that the best nucleation time at 290 °C, for the crystalline phase corresponding to the 1st crystallization peak in Fig. 1, is 480 min. In this case, the second phase will be completely crystallized. To avoid uncontrollable crystal growth, a nucleation step of 300 min is the best compromise.

Now, in order to determine the best nucleation temperature, a series of samples have been annealed at different temperatures for 300 min. The DSC analysis for different

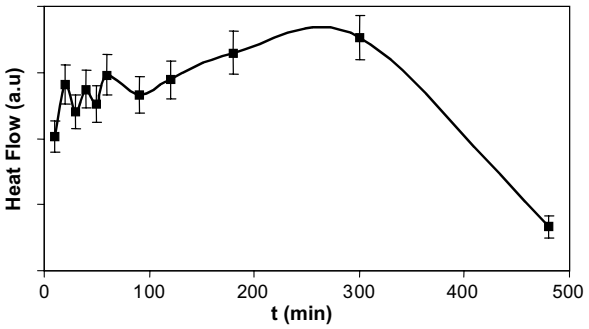

Fig. 2. Crystallization peak height versus heat treatment time at 290 °C.