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Structural characterization and phase transformation kinetics of $Se_{58}Ge_{42-x}Pb_x$ ($x = 9, 12$) chalcogenide glasses

Deepika *, Praveen K. Jain, K.S. Rathore, N.S. Saxena

Semi-conductor and Polymer Science Laboratory, 5-6, Vigyan Bhawan, University of Rajasthan, Jaipur 302004, India

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ABSTRACT

The glass transition behavior and crystallization kinetics of $Se_{58}Ge_{42-x}Pb_x$ ($x = 9, 12$) have been investigated using Differential Scanning Calorimetry (DSC) at five different heating rates under non-isothermal conditions. It has been observed that these glassy systems exhibit single glass transition and double crystallization on heating. The XRD pattern revealed that the considered glasses get crystallized into $GeSe_2$ and PbSe/Se phases after annealing at 633–643 K for 2 h. The $GeSe_2$ and Se phases were found to crystallize in monoclinic structure while, PbSe phase crystallizes in cubic structure. Besides this, a mixed phase was also observed in DSC thermograms after annealing. The kinetic studies include determination of various parameters such as Avrami exponent (n), frequency factor (K_o), dimensionality of growth (m), the activation energy for glass transition (E_t) and for crystallization (E_c). The values of E_t increases while that of E_c decreases after annealing. Also, dimensionality of growth decreases to one dimension from two and three dimensions after annealing.

1. Introduction

Chalcogenide glasses are generally p-type semiconductors and doping is very difficult, since the presence of charged defect states pins the fermi level at the mid gap. However, the addition of Pb or Bi to Ge–Se or Ge–Te glasses is found to reverse the conduction from p-type to n-type at certain concentration of Pb/Bi [1–3]. These amorphous semiconductors with tailored properties have a potential for thermoelectric and photovoltaic device applications [4]. The last decades have seen a strong interest in the study of the glass–crystal transformation. An understanding of the kinetics of crystallization in glasses is important for the manufacturing of glass-ceramics and in preventing devitrification. Thermal analysis is widely used in investigating the crystallization kinetics of glasses. Differential Scanning Calorimetry (DSC) is valuable technique for the quantitative study of crystallization in different glassy systems. It is very quick and needs very small quantities of glass samples to acquire kinetic parameters of the crystallization of glasses by thermal analysis. The study of crystallization kinetics has been widely discussed in the literature [5–9]. The most widely used model, the Johnson–Mehl–Avrami (JMA) model, is derived for isothermal crystallization. Attempt has been made to apply the JMA model for non-isothermal kinetics. This has been shown to be possible under the following conditions: the nucleation rate is proportional to the growth rate and nucleation occurs at the start leading to site saturation. The JMA model implies that the Avrami exponent n and the effective activation energy E_c should be constant during the transformation process and thus many authors applied the (JMA) [10,11] equation to the non-isothermal crystallization process [12–14].

In the present work, structural and thermal analysis using X-ray diffraction (XRD) and Differential Scanning Calorimetry (DSC) for $Se_{58}Ge_{42-x}Pb_x$ ($x = 9, 12$) have been presented. Se-Ge-Pb system has been investigated because very few attempts have been made to study chalcogenide glasses with Pb as one of the component. It

* Corresponding author.
E-mail addresses: deepika.spsl@gmail.com (Deepika), n_s_saxena@rediffmail.com (N.S. Saxena).

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is due to the fact that lead is the last element in radioactive series, which is more stable, or lead is one with which it is difficult to form a glass. Moreover, the charge reversal from usual p-type to n-type has created interest in these glasses. Glasses with 9 at wt% and 12 at wt% Pb were of interest as glasses formed below 9 at wt% of Pb were not showing any sharp glass transition and any transformation kinetics for such glasses would have not lead to any important conclusions. Glasses above 12 at wt% of Pb (15%, 18%, 20% Pb) show the similar phases in XRD and DSC as shown by the glass with 12 at wt% Pb. Also, different behavior of 9 at wt% Pb than 12 at wt% Pb concentration of glasses invoked interest in studying these two compositions. The results obtained from DSC were interpreted using many theoretical models. These models were used to extract the kinetic parameters of the phase transformation. The main aim of the paper is to report the effect of annealing on the phase transformation of the system under investigation. Annealing of samples at an intermediate temperature between first and second crystallization leads to origination of a modified phase with a shift in glass transition and crystallization region towards a lower temperature side. Thermal stability of the phases has also been derived using the evaluated kinetic parameters.

2. Experimental details

Glassy alloy of $Se_{58}Ge_{33}Pb_9$ and $Se_{58}Ge_{30}Pb_{12}$ were prepared by melt-quenching technique. High purity (99.999%) of all constituent materials in appropriate atomic weight proportions were weighed into a quartz ampoule. The content of the ampoule (4 g) was sealed in a vacuum of 10^{-5} Torr. The ampoules were heated in two stages to avoid the sudden evaporation and deposition of the selenium to the inner wall of the quartz tube. The ampoules were heated slowly and maintained at 600 °C for about 6 h with continuous rotation. The temperature is then subsequently raised to 900 °C and kept under constant rotation for 30 h to facilitate the homogenization of the sample. The molten sample was rapidly quenched in ice-cooled water to obtain glassy state. The ingot of so produced glassy sample was taken out of the ampoule by breaking the ampoule and then grinded gently in mortar and pestle to obtain its powder form.

Differential Scanning Calorimetry (DSC) Rigaku Model 8230 is used to measure the caloric manifestation of the phase transformation and to study the crystallization kinetics under non-isothermal condition. The accuracy of heat flow measurement is ±0.01 mW and the temperature precision as determined by the microprocessor of the thermal analyzer is ±0.1 K. DSC runs have been taken at five different heating rates, i.e. 10, 15, 20, 25, 30 K/min on accurately weighed samples taken in aluminum pans under non-isothermal conditions. The temperature range covered in DSC was from room temperature (300 K) to 753 K.

The amorphous nature of the alloy was ascertained through X-ray diffraction pattern of the samples using Bragg–Brentanno geometry on Panalytical X'pert Pro differactometer in 2θ range of 20–60° with CuK_α radiation source (λ = 1.5406 Å). The X-ray tube was operated at 45 kV and 40 mA.

3. Experimental results

3.1. XRD studies

Fig. 1 shows the X-ray diffraction patterns of as-prepared and annealed $Se_{58}Ge_{33}Pb_9$ and $Se_{58}Ge_{30}Pb_{12}$ glassy systems. The absence of any sharp peak confirms the amorphous nature of these samples. For the identification of the phases, which were obtained through DSC thermograms, both the glasses i.e. $Se_{58}Ge_{33}Pb_9$ and $Se_{58}Ge_{30}Pb_{12}$ were annealed at 633 and 643 K, which lie between the first and second crystallization in the case of these glasses, respectively. The annealed samples were then subjected to XRD. The XRD study reveals that $Se_{58}Ge_{33}Pb_9$ glassy alloy crystallizes into $GeSe_2$ and Se phases while the $Se_{58}Ge_{30}Pb_{12}$ glass crystallizes into $GeSe_2$ and PbSe phases. The $GeSe_2$ phase is found to crystallize in the monoclinic structure with a unit cell defined by a = 7.016 Å, b = 16.79 Å and c = 11.83 Å. The PbSe phase crystallizes in the cubic structure with unit cell a = 6.128 Å while, Se phase crystallizes in the monoclinic structure with a unit cell defined by a = 15.01 Å, b = 14.71 Å and c = 8.789 Å.

3.2. DSC studies

Fig. 2 shows the DSC curves of as-prepared and annealed samples of $Se_{58}Ge_{33}Pb_9$ and $Se_{58}Ge_{30}Pb_{12}$ glasses at a heating rate of 20 K/min as a representative case. The characteristic features of

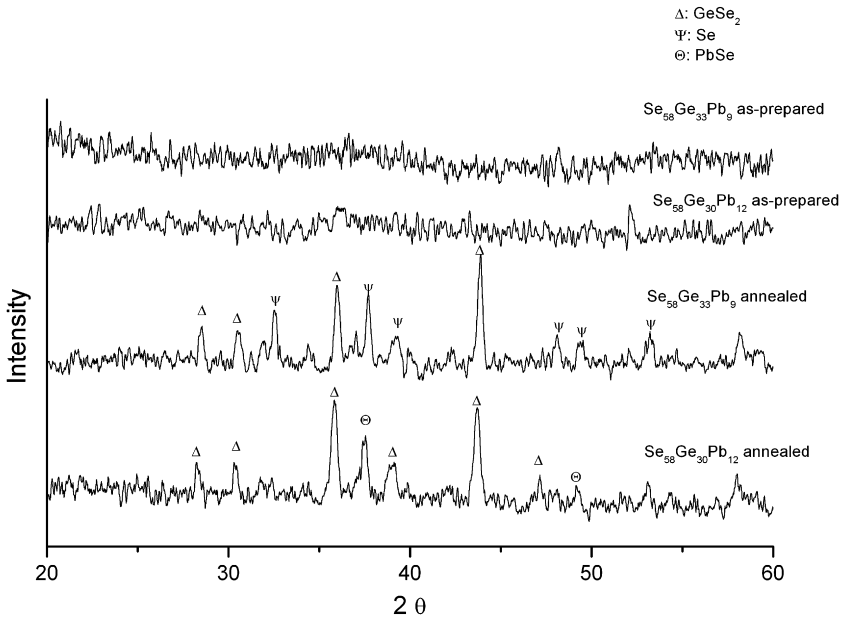

Fig. 1. X-ray diffraction patterns of as-prepared and annealed $Se_{58}Ge_{33}Pb_9$ and $Se_{58}Ge_{30}Pb_{12}$ glassy systems.