Materials Chemistry and Physics 134 (2012) 834–838

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Kinetic parameters of glass transition and crystallization for glassy Se and glassy $Se_{98}M_2$ (M = In, Sb and Sn) alloys

H. Kumar, N. Mehta*

Department of Physics, Banaras Hindu University, Varanasi 221005, India

ARTICLE INFO

Article history:
Received 30 July 2011
Received in revised form
6 March 2012
Accepted 9 March 2012

Keywords:
Amorphous materials
Chalcogenides glasses
Differential scanning calorimetry (DSC)
Glass transition
Crystallization

ABSTRACT

The calorimetric measurements have been made in glassy Se and glassy $Se_{98}M_2$ (M = In, Sb and Sn) alloys using non-isothermal DSC Technique. The effects of In, Sb and Sn additives on the glass transition and crystallization kinetics of glassy Se have been studied. From the heating rate dependence of glass transition temperature T_g and crystallization temperature T_c, different kinetic parameters of glass transition and crystallization have been evaluated.

1. Introduction

Phase-change memory (also known as PCME, PRAM, PCRAM, Ovonic Unified Memory, Chalcogenide RAM and C-RAM) is a type of non-volatile computer memory [1–3]. PRAMs exploit the unique behavior of chalcogenide glasses. With the application of heat produced by the passage of an electric current, these materials can be switched between two states, crystalline and amorphous. The crystalline and amorphous states of chalcogenide glass have dramatically different electrical resistivity, and this forms the basis by which data is stored. The amorphous state (high resistance state) is used to represent a binary 0, and the crystalline state (low resistance state) represents a binary 1. Recent versions can achieve two additional distinct states, effectively doubling its storage capacity.

Chalcogenide glasses have recently attracted the attention of solid-state physicists, chemists and electronic engineers on account of their potential application in various solid-state devices [1–3]. The effect of impurities on the transport and structural properties has been an important issue since the discovery of these glasses. The addition of a metallic impurity to amorphous chalcogenides enhances their conductivity and produces a significant decrease in the activation energy for conduction, making them more suitable for device applications.

The effect of foreign additives on chalcogenide glasses has been of considerable interest in recent years [4–7]. It was suggested by various workers that the foreign metal impurities in chalcogenide glasses induce changes in the intermediate ordering, which restrict mutual slip motion of the structure clusters [8]. These days our lab is also engaged in studying the effect of different metallic additives on the physical properties of selenium based chalcogenide glasses [9,10].

The binary alloys of Se–In, Se–Sb and Se–Sn system have numerous advantages over amorphous Se [11–15]. In past, some attempts have been made to utilize the binary Se–In alloys in solar cells [11]. Mikla et al. reported the effect of Sb alloying on the electrographic properties of a-Se as well as laser-induced amorphous to crystalline phase transition in glassy $Se_{100-x}Sb_x$ alloys [12,13]. Most recently, composition dependence of density of states and dielectric properties in $Se_{100-x}Sn_x$ glassy alloys has been reported by Sharma et al. [14,15]. From above mentioned literature, one can see that attempts have been made to see the effects of In, Sb and Sn additives on various physical properties of glassy Se by changing the composition, but no attempts have been made to see the effect of changing the additive for a fixed composition. The present paper is our new work in this direction. We have studied the effect of In, Sb and Sn additives on the glass transition and crystallization kinetics of glassy Se.

* Corresponding author. Tel.: +91 542 2307308 (244); fax: +91 542 2368174.
E-mail address: dr_neeraj_mehta@yahoo.co.in (N. Mehta).

0254-0584/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2012.03.077

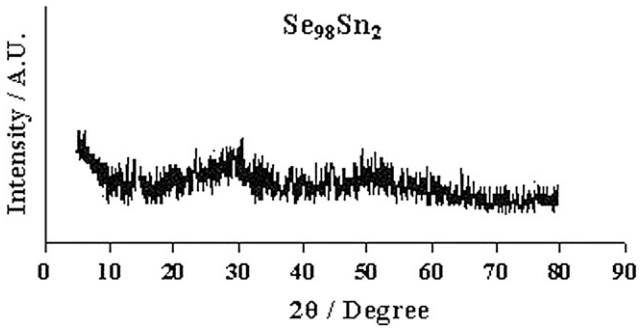

Fig. 1. XRD pattern of glassy $Se_{98}Sn_2$ alloy.

2. Material preparation

Glassy alloys of Se and $Se_{98}M_2$ (M = In, Sb and Sn) were prepared by quenching technique. The exact proportions of high purity 5 N (99.999%) pure elements, in accordance with their atomic percentages, were weighed using an electronic balance with the least count of 1 mg. The materials were then sealed in evacuated quartz ampoules (length ~5 cm and internal diameter ~8 mm). A high vacuum pumping system (Hindhivac, Model VS65D) was used to achieve the vacuum (~10^{-5} Torr). Each ampoule was kept inside the furnace at 800 °C (where the temperature was raised at a rate of 3–4 °C/min.). During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 h, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The ingots of the samples were then taken out by breaking the quartz ampoules.

The X-ray diffraction patterns of as-prepared samples were recorded using Philips PW-1700 powder diffractometer (operating at 20 kV) with Cu-K_α ($\lambda = 1.54056$ Å) radiation to confirm the glassy nature of alloys. The XRD pattern of glassy $Se_{98}Sn_2$ alloy is shown in Fig. 1. Absence of any sharp peak confirms the amorphous nature of the sample. Similar XRD patterns were obtained for other glasses.

3. Experimental

The glasses, thus prepared, were ground to make fine powder for DSC studies. The thermal behavior was investigated using differential scanning calorimeter (Model:Mettler ToledoDSC1). 10–20 mg of the powder was heated at constant heating rate and the changes in heat flow with respect to an empty reference pan were measured. Fig. 2 shows typical DSC scans at heating rate of 10 K min^{-1} for glassy Se and glassy $Se_{98}M_2$ (M = In, Sb and Sn) alloys. Each DSC scan showed a well-defined endothermic peak at the glass transition temperature T_g and an exothermic peak at the crystallization temperature T_c. Similar scans were obtained for the other heating rates.

4. Results and discussion

4.1. Glass transition kinetics

Glass transition studies are important from the viewpoint of understanding the mechanism of glass transformations and in evaluating the structural rigidity of the glasses. The glass transition temperature reflects the strength or rigidity of the glasses.

The glass transition peak shifts with increasing heating rate, indicating the kinetic nature of the glass transition. The glass transition temperature T_g dependence on the heating rate (β) has been analyzed using the following three different approaches.

The empirical relation between T_g and β according to Lasocka [16] is

$$T_g = A_g + B_g \log \beta \quad (1)$$

The value of A_g is equal to the glass transition temperature for the heating rate of 1 K min^{-1} and B_g is constant for a given glass composition. The plots of log β vs. T_g are shown in Fig. 3 for present glasses. The value of A_g and B_g of different alloys are listed in Table 1.

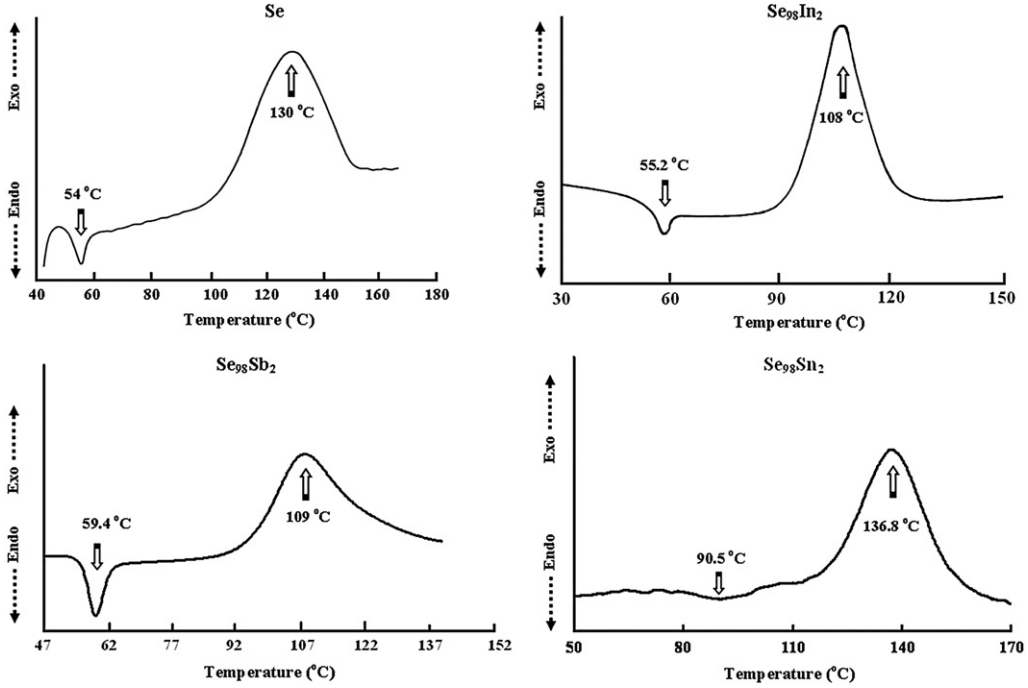

Fig. 2. DSC scans of glassy Se and glassy $Se_{98}M_2$ (M = In, Sb, Sn) alloys at a heating rate 10 min^{-1}.