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The relationship between structural and optical properties of Se-Ge-As glasses

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HIGHLIGHTS

- Investigation of connectivity of cations and anions in Se–Ge–As glasses.
- Anomalous behavior of T_g and optical properties were revealed.
- Fully amorphous phase can easily form in different Se-Ge-As systems.
- Highest T_g and optical properties were achieved in $Se_{60}Ge_{35}As_5$ glass.
- Highest connectivity of cations and anions in $Se_{60}Ge_{35}As_5$ glass network.

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ABSTRACT

In this study, the structural and optical characterization of bulk Se-Ge-As glasses has been investigated. In this regards, six different $Se_{60}Ge_{40-x}As_x$ ($0 \le x \le 25$) glasses were prepared by conventional melt quenching technique in quartz ampoule. The produced samples were characterized using X-ray diffraction (XRD), Raman spectroscopy, differential thermal analysis (DTA), ultraviolet–visible (UV–Vis) and Fourier transform infrared (FTIR) spectroscopy. The fundamental absorption edge for all the glasses was analyzed in terms of the theory proposed by Davis and Mott. According to achieved results, fully amorphous phase can easily form in different Se-Ge-As systems. The thermal and optical characteristic of $Se_{60}Ge_{40-x}As_x$ glasses shows anomalous behavior at 5 mol% of As for the glass transition temperature, transmittance, absorption edge, optical energy gap and Urbach energy. The highest glass transition temperature, transmittance, optical energy gap and Urbach energy properties were achieved in $Se_{60}Ge_{35}As_5$ glass as a result of the highest connectivity of cations and anions in glass network.

1. Introduction

Chalcogenides glasses are materials containing one or more of the chalcogen elements (S, Se, and Te) covalently bonded to the elements such as Ge, As, Si and Sb [1]. These glasses have attracted the attentions of many researchers due to the fact that they are potential candidates for the applications in infrared optics, photonics device, reversible optical recording, memory switching, inorganic photo resists and antireflection coatings. They exhibit semiconductor behavior with band gap energies from 1 to 3 e.V. and good transparency in both 3–5 and 8–12 μm infrared spectral regions [2–4].

It is well known that, the physical and mechanical properties of chalcogenide glasses are in direct relation with the structural units that form the basic building blocks of the glassy network [5]. On the other hands, the knowledge about short-range order structure of chalcogenide glasses is particularly valuable in order to establish useful correlations between their structural and macroscopic properties [6]. Several models such as continuous random network (CRN), chemically ordered network (CON) and topological model, have been presented to depict the possible special structure in covalent chalcogenide glasses. Among these models, the topological model is the popular model for describing the structural properties of chalcogenide glasses [7,8].

It is well known that, different properties of this glassy system can be modified by addition of one or more alloying elements to the composition [9,10]. The Ge-As-Se system is the most interesting group of chalcogenide glasses due to its very broad glass formation region and tenability of their physical and optical properties by the chemical compositions [11–15]. The size and electronegativity of the constituent components in this alloying system

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provide close-to-ideal covalent network. Although there are a lot of studies about the preparation and characterization of Se-Ge-As chalcogenide glasses, the correlation between composition and properties of this glass system has not been properly investigated. Moreover, there is lack of information about the relation between network connectivity and properties of this system in the literatures. So, in this study, the structural, thermal and optical characterizations of $Se_{60}Ge_{40-x}As_x$ $(0 \le x \le 25)$ glasses will be investigated in details.

2. Experimental procedure

Bulk $Se_{60}Ge_{40-x}As_x$ $(0 \le x \le 25)$ glassy samples were prepared by the conventional melt quenching technique using high purity Se (Changsha Santech material, 99.99% purity), Ge (single crystal, 99.999% purity) and As (Changsha Santech material, 99.999% purity) elements (see Table 1). About 15 g of each batch was weighed and transferred into a high purity quartz ampoule (with internal diameter of about 11 mm and cleaned with 0.4%HF for 15 min), evacuated under vacuum and then sealed. The prepared samples were homogenized at 900 °C for 8 h in a rocking furnace and then were subsequently quenched at a salt batch ($NaNO_3 + KNO_3$ melt) with 220 °C temperature (for avoiding the breaking samples). After that, as-prepared samples were annealed at the temperature about 20 °C below the glass transition temperature (T_g) for 4 h and slowly cooled down to room temperature.

Table 1
The chemical composition of different Se-Ge-As specimens which were investigated in this work.

Sample	Chemical Composition (mole%)		
	Se	Ge	As
1	60	40	0
2	60	35	5
3	60	30	10
4	60	25	15
5	60	20	20
6	60	15	25

XRD technique, using a diffractometer with Cu K_α radiation (λ = 0.15406 nm; 40 kV; Philips PW3710) was used to follow the amorphous nature of the specimens (step size: 0.05°; time per step: 1 s). Differential thermal analysis was also conducted to study the thermal behavior of the as-prepared samples using the DTG-60AH model of Shimadzu corporation calorimeter. The samples were placed in Al_2O_3 pans and heated in dynamic argon atmosphere up to 550 °C at a heating rate of 10 °C/min. Optical properties of the samples were also measured using a FT-IR spectrometer (Bruker Tensor 27) in wavelength range of 2.5–25 µm and UV–Vis spectrometer (Shimadzu UV3100) in wavelength range of 0.6–1.5 µm. The Raman spectrum was obtained using a Renishaw via Raman Spectrometer equipped with an Ar ion laser with excitation wavelength of 785 nm. The excitation power applied to the measurement is approximately 700 mW and the new results showed at this below.

3. Results and discussion

There are several factors such as composition, overheat and solidification rate that influence the structure and properties of as-prepared chalcogenide glasses [16]. A slight variation in these parameters can often cause large variations in the structure and properties of the produced samples. In the present study, all of these parameters were kept nominally constant and the structural and optical properties of the $Se_{60}Ge_{40-x}As_x$ $(0 \le x \le 25)$ glasses were investigated.

To understand the effects of initial composition on the structure and physical properties of $Se_{60}Ge_{40-x}As_x$ glasses, six different compositions, listed in Table 1, were melted and quenched at the same condition. The XRD patterns of $Se_{60}Ge_{40-x}As_x$ $(0 \le x \le 25)$ as-prepared samples are presented in Fig. 1. These X-ray patterns exhibit three broad diffuse scattering halos confirming a long-range structural disorder characteristic of the amorphous network in chalcogenide glasses. This result indicates that, regardless to the difference in chemical composition, all the studied samples are in the amorphous state.

The DTA curves of these samples are presented in Fig. 2. General characterizations of these DTA curves are the same and only one changing in the slope of the base line appears in these curves.

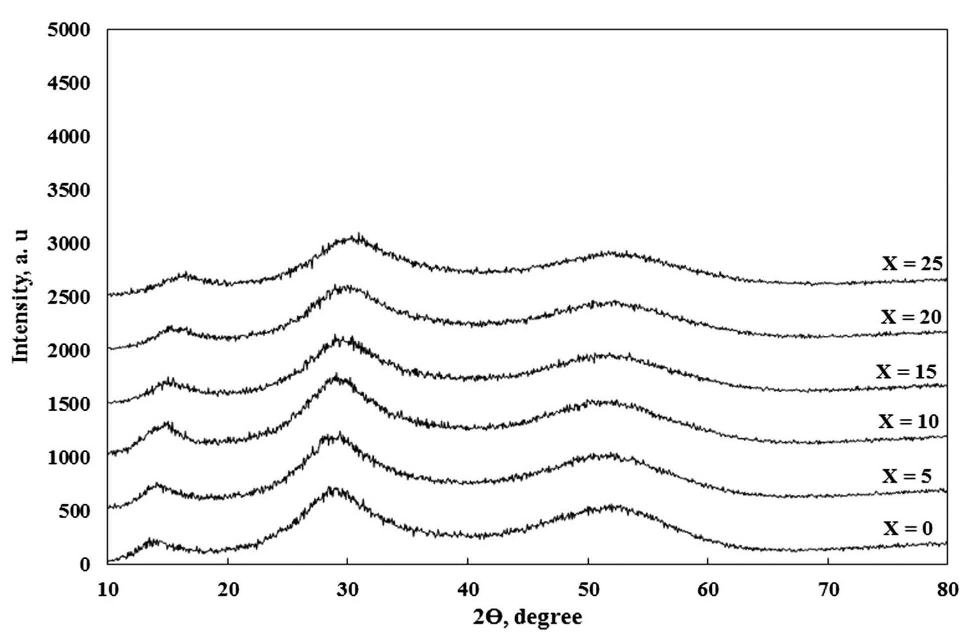

Fig. 1. The XRD patterns of $Se_{60}Ge_{40-x}As_x$ $(0 \le x \le 25)$ as-prepared samples.