



Fabrication and Investigation of Se-Ge Glass-Ceramics in the Presence of Ga and Sn Additives

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ABSTRACT

The Chalcogenide glasses were fabricated by melting and quenching techniques in the Se-Ge system in the presence of 1% mol of Ga and 3, 5 and 7 % mol of Sn. Differential scanning calorimetry (DSC) analysis was conducted to extract the glass transition temperature of the samples. Fourier Transform Infrared (FTIR) spectroscopy analysis was also performed in range of 400-4000 cm⁻¹. The Glass samples were heated at 450 °C for 1-10 h. The precipitated nanoparticles were observed using a Field Emission Scanning Electron Microscope (FESEM). The size of crystals were in the range of 100-1000 nm. The precipitated phases were identified using X-ray Diffraction (XRD) analysis on glass-ceramics powder. The hardness of the glass-ceramics has been increased from 200 to 250 Kg/mm².

1. INTRODUCTION

Low phonon energy of heavy anions in chalcogenide glasses as well as their transparency in a wide range of FTIR spectra has resulted in their extensive applications such as infrared laser, thermal imaging, chemical sensors, and medicine [1,2]. Other unique properties of these glasses, such as their high refractive index have increased the focus on their development and applications. As the production cost of chalcogenide glasses and preparation of germanium element is high, substitution of the Ge with other elements can decrease the cost and therefore improve the glass properties [3,4]. Significance of semiconductor chalcogenide glasses has resulted in numerous researches on this special type of glass in recent years. Lots of researchers have addressed the effect of various elements such as Sn, Ga, and Indium on Se-Ge systems [5-7].

In this study, we chose Se₆₀Ge₄₀ [8] as the base glass. The stability of this bi-components system is very low toward crystallization and its glass forming zones is also wide. To increasing the solubility, 1 % mol of Ga

(solution) was added to all glass samples. Application of the Ga or Sn element can increase the glass forming zones and prevent from crystallization during melting and quenching. The fourth element, Sn, significantly affects density and nonlinear optical properties due to its high molar mass and high polarizability, respectively [9-12]. The aim of this study was to investigate the effect of Sn addition on optical properties of Se-Ge glass in the presence of 1% mol of Ga to increase their hardness. Despite all the extraordinary properties of these glasses, they mainly suffer from low mechanical hardness. Creation of nanocrystals is one of the major methods to resolve this weakness [13,14], Some substances may be created between the glass and ceramic during crystallization by thermal treatment and reheating of the glasses. By controlling the rate of addition of Sn and heat treatment program, the thermal and optical properties can be controlled and optimized.

2. MATERIALS AND METHODS

To fabricate Se-Ge glass systems, pure Sn, Ga, Ge and Se (99.999% purity) were employed. Glass

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compositions are listed in Table 1. The amounts of 3, 5, and 7 % . mol of Sn were added to 3 different glass batches to create phase segregation and provide the conditions for crystallization. 1 % . mol of Ga (solution) was added to all glasses as it can enhance the elements solubility and systems stability for glass formation and also increase the polarization effect. Moreover, it has been experimentally proven that in glasses containing Ga, crystallization is more controllable due to more stability. Silica capsules were washed with HF acid (75 Molar) to remove all contaminants, they were then heated up at 600 °C for 2 h. Elements were weighed and added to Silica capsules. The capsules were then sealed under 10^{-2} mPa vacuum. The glasses were heated up at 850 °C for 15 h in a rocking furnace. In the next step, the capsules were quenched at 240 °C in molten salt. After cooling down, the capsules were cut down into disks with 2.5 mm of thickness. To prepare glass-ceramics, the samples were heated up in Muffle furnace for 1-10 h according to DSC curves.

3. RESULTS AND DISCUSSION

The X-ray diffraction patterns of the fabricated glasses were evaluated by Philips Xpert-MDD System (Cu- K_{α} , 1.542Å, 300 KV) as shown in Figure 1. Absence of sharp peaks confirmed an amorphous structure of the glasses. The broad peak has appeared in the XRD pattern shows that there were not crystalline phases occurred during the glass formation up to 7 % . mol Sn.

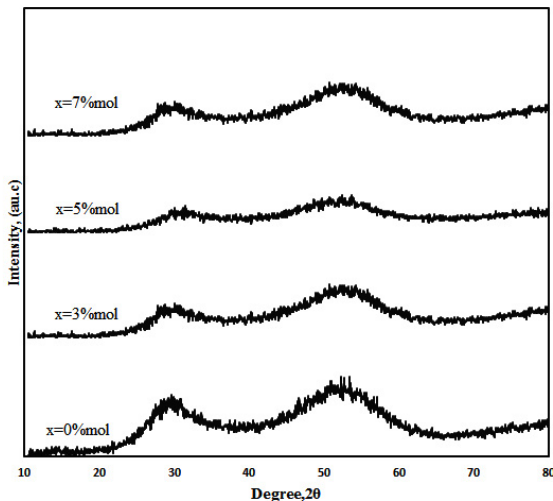


Figure 1. XRD patterns of glasses containing different amount of Sn and 1 % . mol of Gallium

3.1. Fourier Transform Infrared Spectra (FTIR)

The most important feature of the chalcogenide glasses is their transmittance at infrared wavelengths. Figure 2. shows the FTIR spectra of the samples, by increasing of Sn amount up to 7 % . mol, the network former role of Sn has increased. By increasing the amount of Sn, the

Ge-O absorption band was eliminated, which could be due to higher tendency and capacity of Sn toward O compared to Ge. The enhancement in the glass transition temperature also confirmed the increase in glass integrity. Increase of rigidity and reduction in multi-phonon interactions augmented the FTIR transmittance of the glass structure [9,15,16].

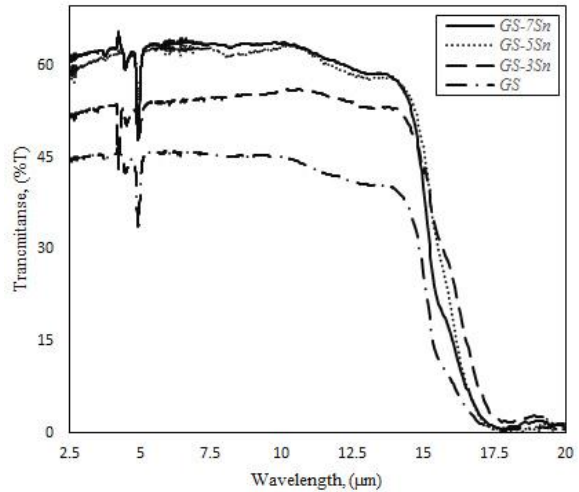


Figure 2. FTIR spectra of glass samples before heat-treatment

The hardness value of the produced glasses was in the range of 190-220 Kg/mm². With increasing Sn content, the hardness and density of glasses increased which confirmed the network former role of Sn element. Tin is a heavy element and had the greatest impact on the glass density.

3.2. Differential Scanning Calorimetry (DSC) Analysis

DSC curves of GS (Glass-Ceramic), GS-3Sn (Glass-Ceramic with 3% . mol), GS-5Sn (Glass-Ceramic with 5% . mol), and GS-7Sn (Glass-Ceramic with 7% . mol) glasses which are shown in Figure 3, indicate an increase in glass transition temperature (T_g) with increasing Sn content in the structures. T_g is known to be dependent on many parameters including mean bond energy, band gap, coordination number, elemental mass, molar fraction, cooling and agitating rate, etc. In general, the more rigid a solid structure, the higher its T_g .

Average coordination number is an important parameter when it comes to variations of the glass transition temperature. It is calculated using the following formula (Eq. (1)):

$$\langle Z \rangle = \frac{(\alpha Z_{Ge} + \beta Z_{Se} + \gamma Z_{Sn} + \delta Z_{Ga})}{(\alpha + \beta + \gamma + \delta)} \quad (1)$$

Where Z_{Ge} , Z_{Se} , Z_{Sn} and Z_{Ga} are the coordination numbers of Ge, Se, Sn, and Ga and α , β , γ and δ are atomic weight percentages of Ge, Se, Sn and Ga, respectively.

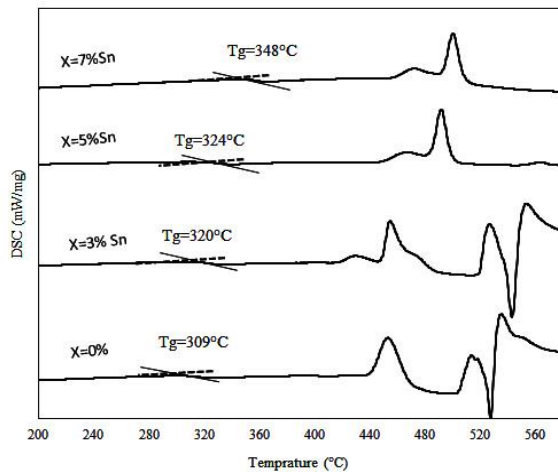


Figure 3. DSC curves of the glass samples containing different amounts of Sn ($\text{Se}_{60}\text{Ge}_{40}\text{Sn}_x$, $x=0, 1, \text{ and } 3$)

TABLE 1. Chemical Composition, Hardness, Density and Coordination number of samples

Sample Lable	Chemical Composition	T_g ($^{\circ}\text{C}$)	Z	Z_{eff}	Hardness (Kg/mm^2)	Density (gr/cm^3)
GS	$\text{Ge}_{40}\text{Se}_{60}$	309	2.80	2.8	191 ± 3	4.23
GS-3Sn	$\text{Ge}_{36}\text{Se}_{60}\text{Ga}_1\text{Sn}_3$	320	2.82	2.82	199 ± 7	4.51
GS-5Sn	$\text{Ge}_{34}\text{Se}_{60}\text{Ga}_1\text{Sn}_5$	324	2.82	2.82	211 ± 5	4.53
GS-7Sn	$\text{Ge}_{32}\text{Se}_{60}\text{Ga}_1\text{Sn}_7$	348	2.82	2.82	225 ± 3	4.71

Average coordination number is associated with average bond energy across the network. Actually, variations of T_g are related to the bond circumstance and chalcogen atom interactions across the network. Given the large elemental mass of Sn, an increase in Sn content of a glass structure leads to increased T_g . Effective coordination number is calculated as follows:

$$\langle \bar{Z}_{\text{eff}} \rangle = \frac{2}{5} (N_c + 3) \quad (2)$$

where N_c is the following mechanical constraint (Eq. (3)):

$$N_c = N_b + N_a \quad (3)$$

in which N_a is the bond stretching and N_b is bond bending energies (18,19)

$$N_b = 2\bar{Z} - 3 \quad (4)$$

$$N_a = \bar{Z} / 2 \quad (5)$$

According to covalent network model (CONM), chalcogen elements are more likely to form hetero-polar bonds rather than homo-polar bonds. The results of

hetero-polar bond energy, calculated from Eq. (6), are tabulated in Table 2.

$$E_{A-B} = (E_{A-A} \times E_{B-B})^{0.5} + 30 (X_A - X_B)^2 \quad (6)$$

The amount of additives in the network can also affect T_g . Accordingly, if the content of additives goes beyond a certain threshold, molecules of the additive(s) agglomerate, which can thereby decrease T_g and increase the susceptibility of the network to crystallization. This degrades the system stability and initiates the crystallization process. An increase in coordination number, enhances the structural integrity and solidity. As an important parameter describing compactness of a glass network, density can be increased by increasing Sn content in the structure. Increasing the density as a result of decrease in molar volume, indicates higher degree of sorting across the network. Hardness of the samples ranged from 190 to 220 Kg/mm^2 . Due to bond energy and formation of the Sn-Se bonds, an increase in the content of Sn enhanced solidity and rigidity of the network.

TABLE 2. Bonds energy of chalcogenide elements

Bonds	Energy (KJ)	Bonds	Energy (KJ)
Se-Se	330.5	Se-Sn	401.2 ± 5.9
Ge-Ge	264.4 ± 6.8	Ge-Sn	230.1 ± 1.3
Sn-Sn	187.1 ± 0.3		
Se-Ge	484.7 ± 1.7		

3.3. Preparing Glass-Ceramic

The glass samples with IR transmittance above 55% were placed in a Muffle furnace and reheated according to their DSC peaks. The glasses were heated at (450°C) for 1 to 10 hours at their initial peak temperature. The results are shown in Figure 4. The sharp peak appeared after 3 hours of heat treatment indicates crystallization of GeSe_2 , SnSe and GeSe_2 .

Figure 5 presents the microstructure images of the prepared glass-ceramics and Figure 6 shows the FTIR spectra variations. For better resolution in the study of deposited crystals, Fe-SEM microscope (Mira 3-XMU) equipped with a LVSTD detector was used.

After 3 to 4 hours of heat treatment at 450°C , a few dispersed crystals were observed in the glass structure. The transmittance reduction was low in these glass samples ($\sim 10\%$). By increasing the heat treatment time up to 6 hours, more crystallites germinated and grew in glass, whose size reached to 100-300 nm. A significant decrease was observed in transmittance of these samples. The hardness of these glass-ceramics was reported in the range of 250-280 kg/mm^2 after 5 to 6 hours of heat treatment. These hardness values of the prepared glass-ceramic samples were higher than that of crystal-free samples. Further increase in heat treatment

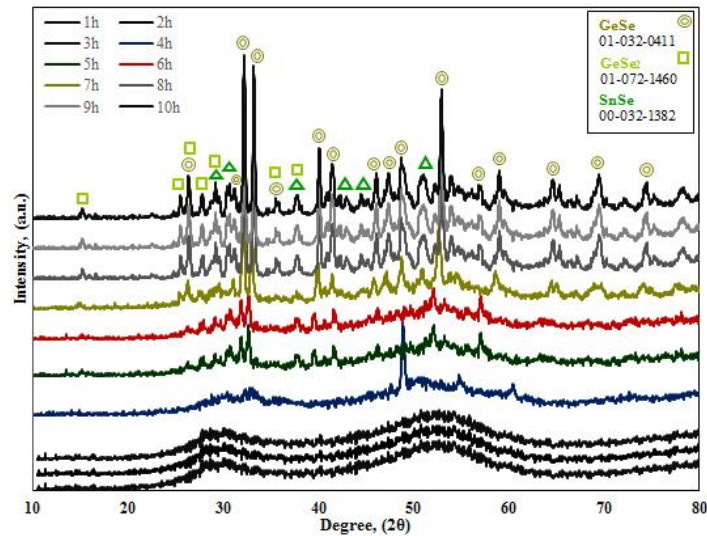


Figure 4. XRD patterns of prepared glass-ceramic samples

time up to 8 hours resulted in the crystals growth and binding which gave rise to masses with dimension of 500-1000 nm. These masses caused severe scattering and a great reduction in the transmittance. The changes in refractive index of diffraction and scattering due to the different refractive indexes of the crystals in the glass matrix, which can reduce transmittance. At the same time, nano-crystals germination significantly improved the mechanical properties of these glasses. Beyond 8 hours of heat treatment, a huge part of glass was

occupied by crystals, leading to apparently opaque surfaces.

The transmittance of such glass-ceramics was zero. The remarkable point is the significant loss of hardness in the glass-ceramic with extreme crystallization. This could be due to the rupture of the main bonds of the glass as a result of creation of several large crystals (dimensions in the range of micrometer). The hardness of the glass-ceramic after more than 7 h of heat treatment reduced to 120 kg/mm². The hardness of these glass-ceramics was in the range 120-160 kg/mm².

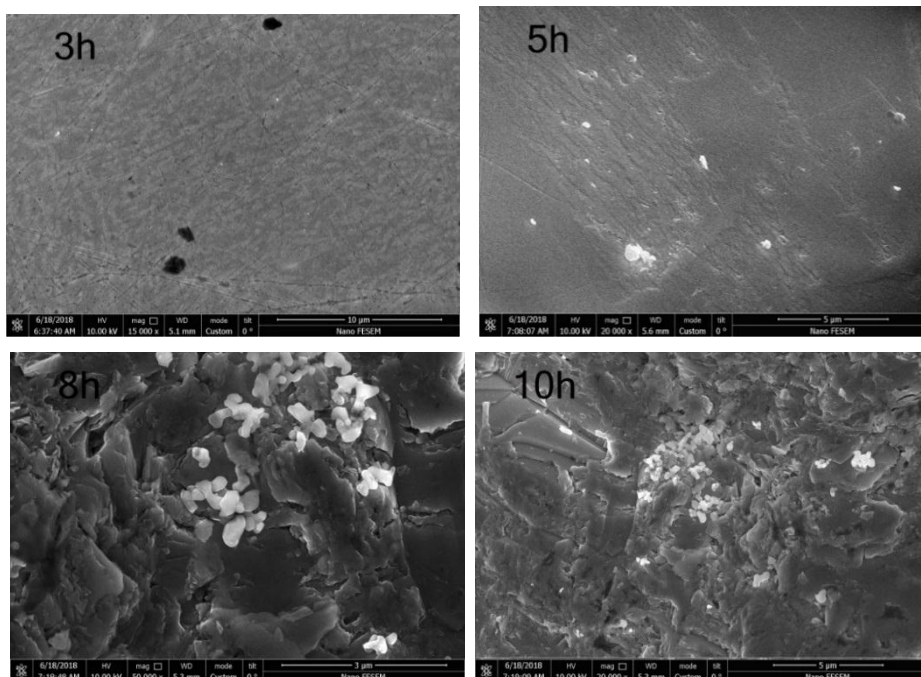


Figure 5. SEM images of glass-ceramic samples after 1-10 h of heat treatment

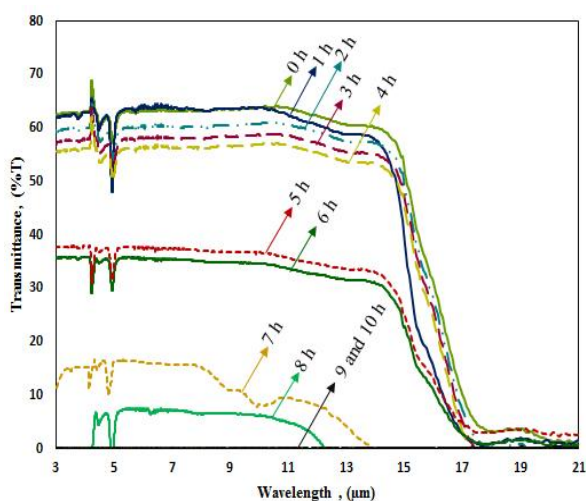


Figure 6. FTIR spectra of glass-ceramic samples after 1-10 h of heat treatment

4. CONCLUSION

In summary, tin has a network former role in the glass system and increases the infrared transmittance in FTIR spectrum. Increases in glass transition temperature, density, and hardness in the presence of Sn, confirm the network former role of this element. The role of gallium is to increase the solubility and polarization of the glasses. The melting point of Sn is 231 °C and the glass making temperature of these samples is 850 °C; hence tin will be definitely dissolved at this temperature. At these conditions, germination couldn't be the mechanism of glass-ceramic formation. The mechanism is probably a phase segregation, which provided the condition for reheat-induced crystallization. By heat treatment of glasses, fine nanocrystals were created in them. Since the germination and growth graphs of chalcogenide glasses overlap, it is very difficult to control crystal growth. Due to the greater effect of temperature on the structure rather than time, controlling the crystallization temperature can result in better outcomes. Heat treatment samples for 3-4 h at 450 °C resulted in crystallization of 100-300 nm crystals in glass samples. Increasing in the heat treatment time enhanced the number of nanocrystals resting in their combination and agglomeration. After 8 hours of heat treatment, the FTIR-transmittance of the chalcogenide glass-ceramics, as their most important feature, was destroyed and the sub-micron nanocrystals were created. During 3-6 h of heat treatment, increase in the hardness and crack growth resistance of these glass-ceramics was observed. The glass-ceramics hardness increased to 200-250 Kg/mm². The main purpose of glass-ceramics production was to increase their hardness while maintaining their high FTIR transmittance.

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