

Structural and thermal properties of Ge-Sb-Se chalcogenide glasses for an application in infrared optical product design and manufacture

Jun Bin Ko* and Tea-Sik Myung

Division of Mechanical Engineering, Hanbat National University, San. 16-1. Dukmyung, Yuseong, Daejeon, 305-719, Korea

Chalcogenide glasses based on the Ge-Sb-Se system have drawn a great deal of attention because of their use in preparing optical lenses and fibers transparent in the range of 3-12 μm . In this study, amorphous Ge-Sb-Se chalcogenide for an application in infrared optical product design and manufacture was prepared by a standard melt-quenching technique. Results of the structural analysis and differential scanning calorimetry of high purity Ge-Sb-Se chalcogenide glasses are reported during various annealing processes. An anomaly of crystallization was observed in the DSC result of the chalcogenide glass and the activation energy of $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ calculated by the Ozawa method was approximately 3.2 eV.

Key words: Chalcogenide glass, Ge-Sb-Se, Amorphous, Crystallization, Activation energy, Infrared lens.

Introduction

Chalcogenide glasses are based on the chalcogen elements S, Se, and Te [1]. These glasses are formed by the addition of other elements such as Ge, As, Sb, Ga, etc [2-4]. They are low-phonon-energy materials and are generally transparent from the visible up to the infrared(IR). Chalcogenide glasses can be doped by rare-earth elements, such as Er, Nd, Pr, etc., and hence numerous applications of active optical devices have been proposed [5-7]. Since chalcogenide-glass fibers transmit in the IR, there are numerous potential applications in the civil, medical, and military areas. In addition, one of the most promising classes of materials for solid state batteries, memory devices, electro chemical devices, catalysts, and anticorrosion media seems to be chalcogenide glasses containing metals [8, 9].

In many cases, the important optical properties of an infrared lens have been determined by a conventional IR-VIS-UV measurement method, but to improve their optical properties we must study the basic characteristics of a chalcogenide, which have thermal and structural properties, using analytical methods such as temperature-modulated DSC or X-ray diffraction [10].

The purpose of the present study was to establish the crystallization process and to clarify the crystalline phases in chalcogenide materials for an application in infrared optical product design and manufacture. The chalcogenide glasses were fabricated by a standard melt-quenching technique with the starting materials placed in evacuated quartz ampoules. The influence of the treatment-temperature on the microstructure, which is a fundamental property of

optical lens devices, was investigated structurally and thermally. In particular, the activation energy of chalcogenide was calculated by the Ozawa method [11].

Experimental

The samples of the Ge-Sb-Se system were prepared from 5N elements by a standard melt-quenching technique with the starting materials placed in evacuated quartz ampoules [12]. For the quantitative chemical analysis, inductively coupled plasma-atomic emission spectrometry (ICP-EDS) was used to determine the exact Ge, Sb, and Se contents of the samples.

The microstructure and morphology of the amorphous states were analyzed using X-ray diffraction (XRD, Rigaku, Japan) and a scanning electron microscope (SEM, JEOL, UK). The XRD experiments were performed every 20 °C from room temperature to 360 °C in order to investigate the crystallization temperature and to inspect whether the sample prepared was indeed amorphous. The endothermic and exothermic properties of the samples were measured by differential scanning calorimetry (DSC, SEIKO Co., Japan). The crystallization temperature was also measured more precisely by DSC experiments with various heating rates.

Results and Discussion

Figs. 1 shows the XRD patterns of amorphous and post-annealed Ge-Sb-Se samples. The samples were post-annealed from room temperature to 360 °C for 10 hours with flowing nitrogen to form a crystalline phase which was identified by XRD using nikel-filtered $\text{CuK}\alpha$ radiation. The intervals of the annealing temperatures were 20 °C. Below 280 °C, no patterns are shown in Fig. 1, meaning that crystallization had not occurred in the Ge-Sb-Se

*Corresponding author:
Tel : +82-42-821-1833
Fax: +82-42-821-1587
E-mail: koo9424@hanmail.net

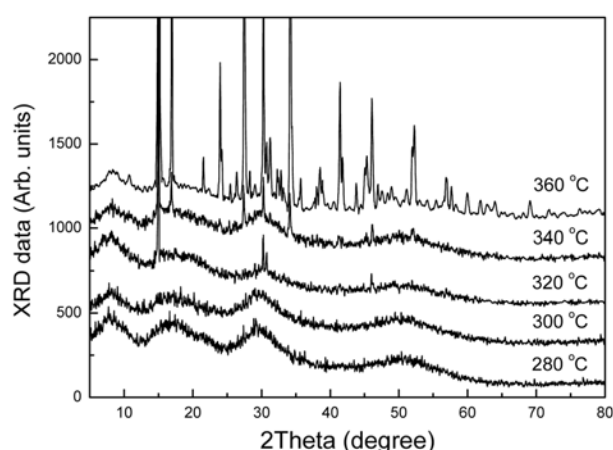


Fig. 1. XRD patterns of annealed chalcogenide glass of Ge-Sb-Se. Patterns were obtained on heating the samples every 20 °C from 280 °C to 360 °C.

sample. Upon elevating the annealing temperature above 320 °C in the Ge-Sb-Se sample, some diffraction lines were detected in the XRD patterns. The XRD peaks represented nearly the stoichiometric crystal of $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$. From the result of ICP-EDS analysis, the qualitative elemental compositions of Ge, Sb, and Se were 17.7, 22.5, and 59.8, respectively.

Figs. 2(a), 2(b), and 2(c) illustrate the SEM images of $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ specimens post-annealed at 320 °C, 340 °C, and 360 °C, respectively. The post-annealing time was 10 hours. The image from amorphous $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ showed only a dark and smooth region. In the cases of samples annealed at 340 °C and 360 °C, some crystallite-like bodies were detected in the amorphous base and their average size was approximately 1 μm . From the XRD results, these bodies in the amorphous $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ are likely to be crystals.

To investigate the crystallization processes of amorphous $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ in detail, their thermal properties were measured by DSC and the crystallization temperature was also measured more precisely by DSC experiments with various heating rates. Fig. 3 gives the DSC curves of $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ with heating rates between 2 $\text{K}\cdot\text{minute}^{-1}$ to 70 $\text{K}\cdot\text{minute}^{-1}$. The weak endothermic anomaly observed in the first heating process of $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ disappeared in the first cooling process and therefore it was an anomaly of crystallization. The anomalies of crystallization changed according to the heating rates. To get a sophisticated peak-value of the anomalies, the DSC curves of the chalcogenides were corrected by the base line, as shown Fig. 4, and the activation energy of crystallization was calculated by a non-isothermal Ozawa method [11]. As the heating rate increased, the crystallization temperatures shifted to higher temperature and the intensity of the anomalies also increased. The Ozawa approach is used for analyzing the dependence of the crystallization or glass transition temperature (T) on the heating rate (α). The first empirical relationship has the following form [13]:

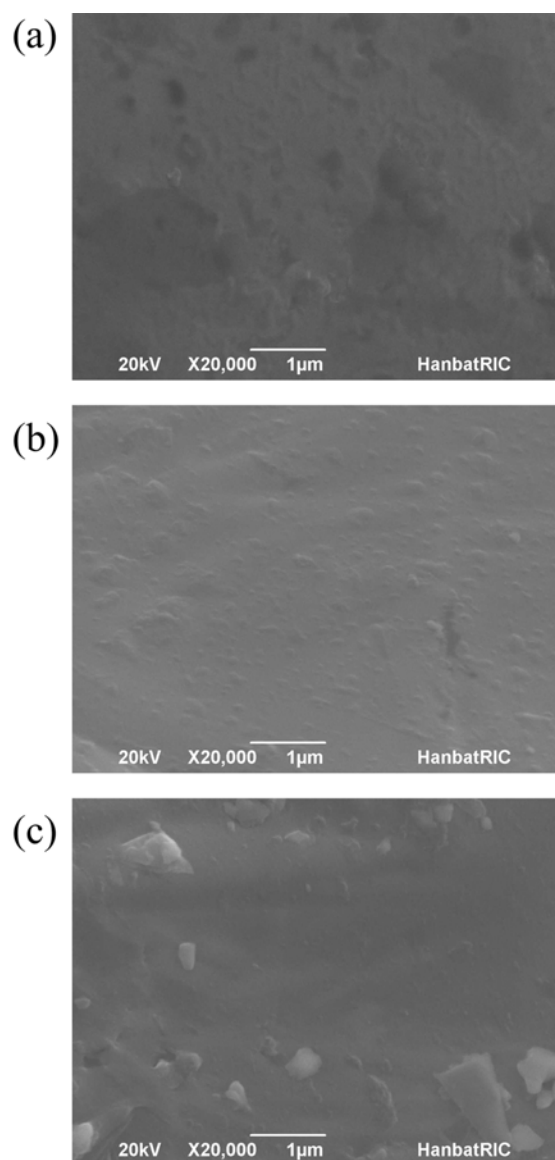


Fig. 2. SEM images of three $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ specimens annealed at (a) 320 °C, (b) 340 °C, and (c) 360 °C for 10 hours.

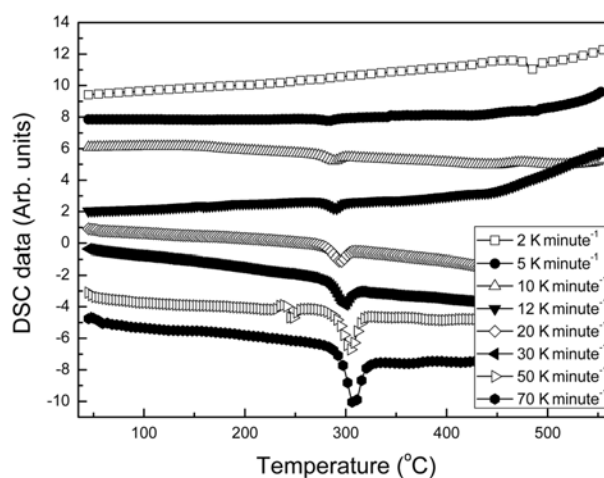


Fig. 3. DSC curves of $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ glasses as a function of the heating rate. The crystallization temperatures changed according to the heating rate between 2 $\text{K}\cdot\text{minute}^{-1}$ and 70 $\text{K}\cdot\text{minute}^{-1}$.

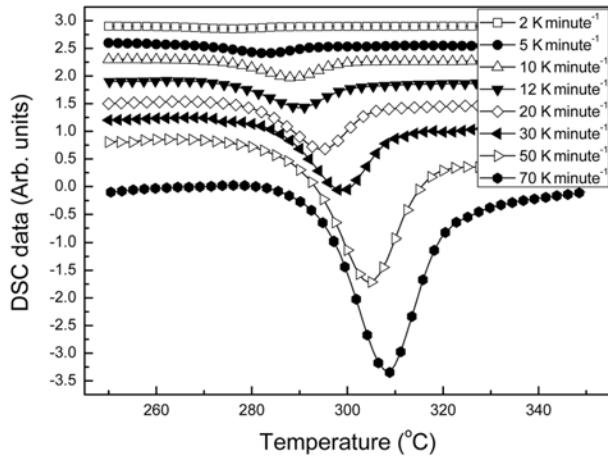


Fig. 4. DSC curves of $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ glasses corrected by the base line.

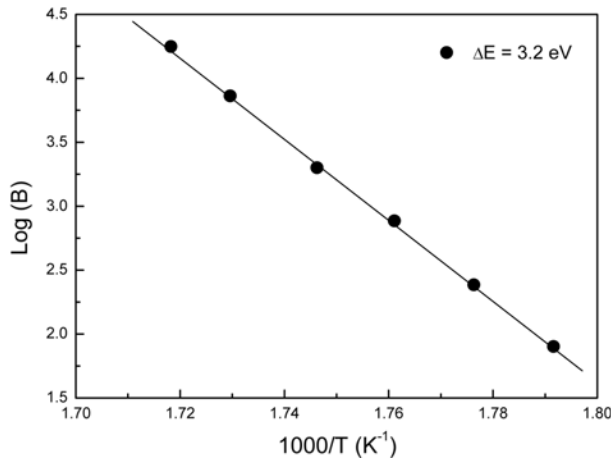


Fig. 5. Plots of $\log(B)$ versus $1000/T_c$ of $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ glass. Solid line is the fitting lines calculated by the Ozawa method.

$$T = A + B \cdot \ln \alpha \quad (1)$$

where A and B are constants. The constant B indicates the response of the configurational changes within the glass transition region to the heating rate. The values of A and B (Eq. (1)) were determined by the least squares line method from dependences of T versus $\ln(\alpha)$. Therefore, Ozawa's equation can be obtained directly from the relation between the heating rate and crystallization temperature as follows [11]:

$$\log(B) = (-0.4567) \frac{\Delta E}{R} \frac{1}{T_c} + \text{const.} \quad (2)$$

where B is the heating rate, R is the gas constant, T_c is the crystallization temperature, and E is the activation energy. The plots of $\log(B)$ versus $1000/T_c$ for the crystallization of amorphous $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ is given in Fig. 5. The solid line in Fig. 5 fits the results of Eq. (2), and the activation energy calculated from its slope for $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ was approximately 3.2 eV.

Conclusions

After producing amorphous $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ by a standard melt-quenching technique with the starting materials placed in evacuated quartz ampoules, the crystallization temperatures were determined by DSC to be from 278 °C to 308 °C with the heating rates between 2 K·min⁻¹ and 70 K·min⁻¹, respectively. The activation energy of the crystallization of $\text{Ge}_{18}\text{Sb}_{22}\text{Se}_{60}$ was calculated by the Ozawa method to be approximately 3.2 eV.

References

1. S. Surinach, M.D. Bar and M.T. Clavaguera-Mora, J. Non-Cryst. Solids 58 (1983) 209.
2. R. Chiba and N. Funakoshi, J. Non-Cryst. Solids 105 (1988) 149.
3. A.B. Seddon, J. Non Cryst. Solid 184 (1995) 44.
4. V.S. Shiryayev, J.-L. Adam, X.H. Zhang and M.F. Churbanov, Solid State Sciences 7 (2005) 209.
5. J.S. Sanghera, I.D. Aggarwal, L.B. Shaw, L.E. Busse, P. Thielen, V. Nguyen, P. Pureza, S. Bayya and F. Kung, J. Optoelectron. Adv. Mater. 3 (2001) 627.
6. M.S. Iovu, S.D. Shutov, A.M. Andriesh, E.I. Kamitsos, C.P.E. Varsamis, D. Furniss, A.B. Seddon and M. Popescu, J. Optoelectron. Adv. Mater. 3 (2001) 443.
7. J.B. Ko and J.-H. Hong, J. Ceramic Processing Research. 11[1] (2010) 116.
8. S.J. Madden, D.-Y. Choi, D.A. Bulla, A.V. Rode, B. Luther-Davies, V.G. Ta'eed, M.D. Pelusi and B.J. Eggleton, Opt. Express 15 (2007) 14414.
9. T. Usuki, O. Uemura, S. Konno, Y. Kameda and M. Sakurai, J. Non-Cryst. Solids 293-295 (2002) 799.
10. D.M. Petovic, M.V. Dobosh, V.V. Khiminets, S.R. Lukic, A.F. Petrovic and S.M. Pogoreli, J. Thermal Analysis 36 (1990) 2375.
11. T. Ozawa, J. Thermal Anal. 2 (1970) 301.
12. T. Wagner, M. Frumar and S.O. Kasap, J. Non-Cryst. Solids 256-257 (1999) 160.
13. M. Lasocka, Mater. Sci. Eng. 23 (1976) 173.