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COMPOSITIONAL DEPENDENCE OF HARDNESS OF Ge-Sb-Se GLASS FOR MOLDED LENS APPLICATIONS

ZALEŻNOŚĆ STĘŻENIOWA TWARDOŚCI SZKŁA Ge-Sb-Se DO ZASTOSOWAŃ NA FORMOWANE SOCZEWKI

Chalcogenide glass in the ternary Ge-Sb-Se system is inherently moldable, thus being considered as a strong candidate material for use in infrared-transmitting lens applications from the viewpoint of thermal and mechanical stability. In an effort to experimentally determine compositional region suitable for the molded lens applications, we evaluate its compositional dependence of hardness. Among the constituent atoms, Ge content turns out to exert a most conspicuous correlation with hardness. This phenomenological behavior is then explained in connection with the structural evolution that Ge brings about.

Keywords: Chalcogenide glass, Ge-Sb-Se glass, Infrared lens, Molded lens, Infrared camera

1. Introduction

Chalcogenide glass refers in general to an amorphous inorganic solid that contains chalcogen elements such as S, Se and (or) Te as a major constituent, and normally takes shape via processing route of melt-quenching technique. Its optical properties are quite unique, which can be represented by extended infrared transmittance up to $\sim 20 \mu\text{m}$ (for tellurium-based one) and enhanced optical nonlinearity. Among numerous (potential) applications that exploit its characteristic optical properties, infrared-transmitting lens is definitely very promising since the blackbody radiation from a homeothermic body normally peaks at around $\sim 10 \mu\text{m}$ in its emission spectrum. In order to take such a thermal image by using an IR camera system, optical components such as lens and filter should be transmitting at the mid-infrared wavelengths. With the increasing demand upon the night vision system for use in transportation and surveillance, in addition to its existing military applications, cost effectiveness of IR transmitting lens becomes rapidly critical. As such, inorganic glasses that are readily moldable are certainly competitive against their counterparts such as single-crystalline Ge and chemical-vapor-deposited polycrystalline ZnSe. Since sulfur-based glasses are less transparent at mid-IR wavelengths around $\sim 10 \mu\text{m}$ and tellurium-based ones are thermally less stable, selenium-based chalcogenide glasses are thus considered as the material of choice for optical-grade lens working at the mid-IR wavelength region [1].

Among several Se-based glass-forming systems, ternary Ge-Sb-Se system is most promising for molded infrared-transmitting lens from the viewpoint of its thermal and mechan-

ical stability. Glass formation out of this ternary system has been known, and various aspects of this unique glass have been studied so far. However, we notice that compositional optimization needs to be carried out in terms of thermal, mechanical and optical properties for the purpose of molding process to be applied to this chalcogenide glass. In particular, hardness plays an important role during service as well as process of chalcogenide glass lens, so that we need to define compositionally optimized region as to hardness of this ternary glass because there has been a lack of experimental data concerning hardness of potential candidate compositions

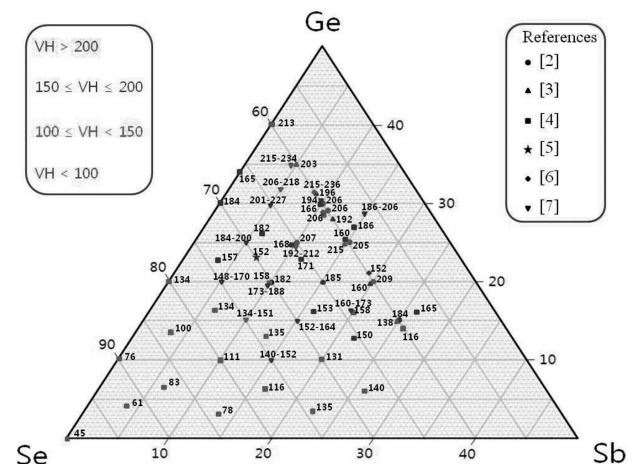


Fig. 1. Vickers hardness of ternary Ge-Sb-Se glass reported in previous studies. Note that the Vickers hardness data appearing in these seven references are merged in this plot, all of which have not intended explicitly to compositional study for the infrared lens applications

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out of this ternary glass system for the molded lens applications [2-7]. Specifically, even though hardness data are available across the glass-forming region, as depicted in Fig. 1, a refined compositional region is needed to explicate the correlations between hardness and composition in a more comprehensive fashion. Based on these considerations, in this study, we have aimed to evaluate its compositional dependence upon hardness: Changes of micro Vickers hardness are plotted as a function of compositional variation in order to find which constituent is most influential, and these phenomenological correlations are explained in connection with the corresponding structural evolutions.

2. Experimental

The compositional region we set in this study is displayed in Fig. 2, which also reveals all the different compositions that were actually fabricated as glass specimens for test. Note this compositional boundary has been drawn taking into consideration previously reported values of Vickers hardness as well as thermal properties such as temperatures for glass transition, softening and crystallization.

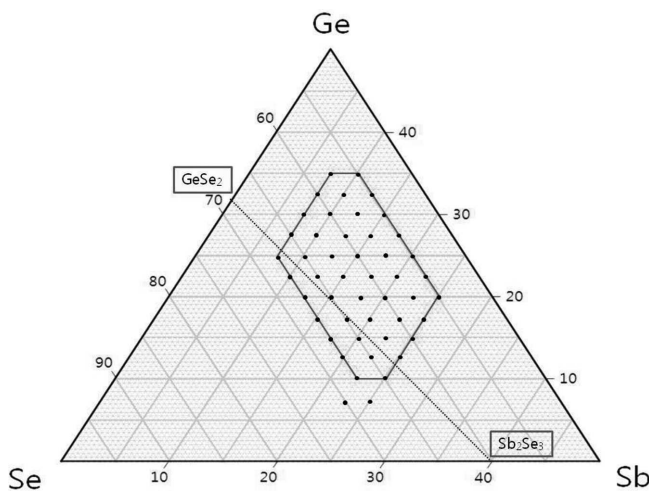


Fig. 2. Compositional region set in this study to pursue the compositional dependence of Vickers hardness. Note that the circles indicate compositions actually fabricated into glass specimens

Starting materials of elemental Ge, Sb (Advanced Materials) and Se (Alfa Aesar) were all better than 99.999% in purity. Synthesis of glass specimen was carried out following the conventional processing technique for chalcogenide glass [8-10]. Each silica ampoule containing desired composition was kept for 12 hours at 1200°C and then water-quenched. All the glass specimens were annealed to relax any thermal stresses induced during the melt-quenching process at proper temperatures determined according to their glass transition temperature. After being inspected by using optical microscope and X-ray diffractometer, each glass rod was cut into a 2-mm-thick disk with both surfaces optically polished. For the measurement of hardness, a tester capable of micro Vickers hardness (Future Tech, FM-700) has been used. For each specimen, measurements were repeated for 10 times, and hardness values thus obtained were averaged after rejecting both the maximum and the minimum ones.

3. Results and discussion

The measured Vickers hardness values of ternary Ge-Sb-Se glass are plotted against content of each constituent (Fig. 3) and fitted to a linear function with no assumption to find which constituent dominates in hardness. Goodness of such fittings is evaluated in terms of R^2 parameter which is calculated with the equation below;

$$R^2 = 1 - \frac{SSE}{SST}$$

where SSE and SST represent sum of squares error and sum of squares total, respectively. It is thus implying that both the measured data and the fitted straight line become to satisfy a better linear correlation as the R^2 parameter approaches unity. As shown in Fig. 3(a), hardness turns out to be proportional to Ge content with R^2 parameter of 0.74, conspicuously surpassing 0.46 for Sb content (Fig. 3(b)) and 0.20 for Se content (Fig. 3(c)). This implies that phenomenologically Ge content prevails over the other constituents in hardness of the present chalcogenide glass.

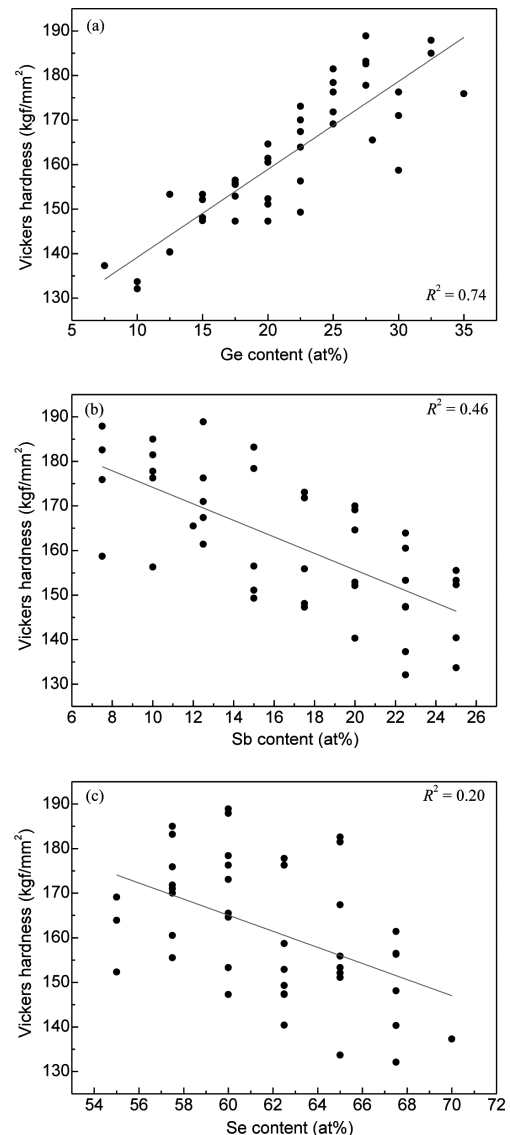


Fig. 3. Vickers hardness plotted as a function of (a) Ge content, (b) Sb content and (c) Se content. The red straight line is obtained from the least-squares fit to a linear function

The amorphous structure of chalcogenide glass would be characterized in terms of three structure-related parameters: First, free volume is capable of accounting for packing density of constituent atoms inside this kind of amorphous covalent solid. It would be reasonably inferred that as the free volume decreases the atoms become more densely packed, thus resulting in more strengthened amorphous structure. Free volume of the current glass specimens was obtained by using measured apparent density, and we observe that it is nicely correlated with hardness. However, such a correlation between the free volume and hardness is not described here since the free volume turns out to be less affecting than the other two structure-related parameters, i.e., mean coordination number (MCN) and average bond energy (ABE).

MCN would be utilized as a crude but convenient measure for network connectivity of chalcogenide glass. According to the topological model based on the constraint counting theory [11], MCN of the present chalcogenide glass with composition of $\text{Ge}_x\text{Sb}_y\text{Se}_z$ (at%) can be simply calculated to $4x+3y+2z$ [12], based on the fact that coordination number of Ge, Sb and Se is set to be 4, 3 and 2, respectively, thus satisfying the $8-N$ rule. It has been known that when plotted against MCN, various physical and chemical properties of chalcogenide glass exhibit interesting behaviors upon change of MCN. For example, the amorphous structure would change from ‘floppy’ state to ‘rigid’ state at MCN of ~ 2.4 [13], and as a result extrema or inflections in changes of properties are observed at around this point. Another interesting opinion associated with such MCN-dependent behaviors is that the dimensionality of amorphous structure evolves to three-dimensional network from two-dimensional layer at MCN of ~ 2.67 [14]. As for the $\text{Ge}_x\text{Sb}_{40-x}\text{Se}_{60}$ glasses, it was reported that their Vickers hardness is maximized at around 2.67 [15]. The compositional range used in this study roughly covers MCN values ranging from 2.425 to 2.775 with a lot more specimens, so that it is a good chance to check whether such a behavior is also evident in this much broadened compositional range. As shown in Fig. 4, the measured Vickers hardness tends to increase with increasing MCN, but it is quite difficult to assert that the maximum occurs at around 2.67. It is clear, however, that hardness of the present glasses is probably proportional to their MCN, which is taken in this study as a measure of the network connectivity. Intuitively, this sounds quite reasonable since one can anticipate that hardness goes up as the constituent atoms are more connected with each other. Here, as noted above, the coordination number of Ge atom is 4, the highest among the three constituent atoms. This is significant since a change in Ge content should affect MCN most sensitively, thus supporting from the structural viewpoint the phenomenological dominance of Ge content observed from Vickers hardness of this ternary glass (see Fig. 3 again).

We need to take into consideration not only MCN but also ABE in order to properly account for the observed results. To derive ABE of each glass composition, information on chemical bond energy of every single covalent bond that could possibly be formed between constituent atoms should be provided first. For this information, we have used the Pauling’s empirical relation in which bond energy of a heteropolar bond can be calculated by utilizing energy of homopolar bonds together with electronegativity of involved atomic pair [16].

For example, energy of the heteropolar Ge-Se bond can be calculated by using energy of homopolar bonds, i.e., Ge-Ge and Se-Se. Arranged in Table 1 is bond energy of each atomic pair that can be formed in Ge-Sb-Se glass. One can see that bond energy of Ge-Se pair is strongest among the chemical bonds.

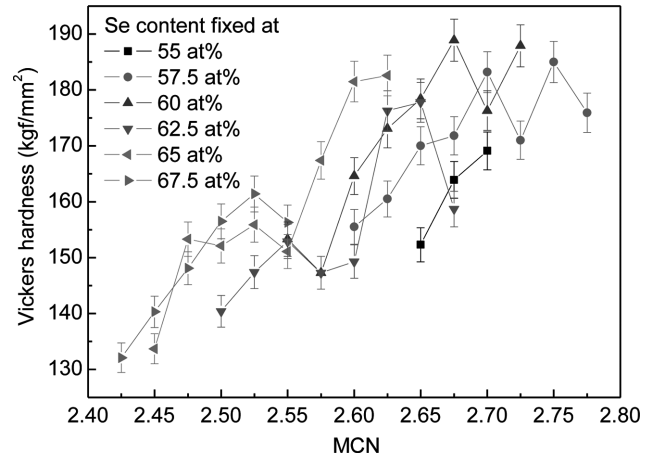


Fig. 4. Vickers hardness plotted as a function of mean coordination number. Note that hardness appears to be proportional to MCN without any distinct features at around 2.67

TABLE 1
Chemical bond energy of each atomic pair in Ge-Sb-Se glass

Atomic pair	Bond energy (eV)
Ge-Se	2.12
Sb-Se	1.86
Ge-Sb	1.48
Se-Se	1.90
Ge-Ge	1.63
Sb-Sb	1.31

We then need to count the number of chemical bonds present in each glass composition. Here, we assume that the tie line compositions, which can be simply represented with varying relative ratios of GeSe_2 to Sb_2Se_3 , consist only of heteropolar bonds without any homopolar bonds inside, but there should be additional homopolar bonds in the off-stoichiometric compositions. We thus define S parameter for glass composition of $\text{Ge}_x\text{Sb}_y\text{Se}_z$ (at%) to classify each glass composition into Se-rich, stoichiometric or Se-deficient as follows;

$$S = \frac{2z}{4x + 3y}$$

Now, ABE can be calculated in accordance with the methodology previously used [16-18]. Presented in Fig. 5 is the Vickers hardness plotted as a function of ABE, which reveals that the hardness of this glass tends to increase with increasing ABE. Taking a closer look at Fig. 5, however, one can recognize that there are two different tendencies divided by the S parameter. In short, glasses satisfying $S \geq 1$, i.e., Se-rich or stoichiometric compositions, exhibit a better correlation with ABE rather than those glasses satisfying $S < 1$. It is clear though that ABE also

acts as an important factor in hardness of this ternary glass together with MCN. Recalling that the Ge-Sb bond has the strongest bond energy (see TABLE 1 again), it is not surprising that Ge content affects ABE most sensitively compared with other chemical bonds, thus evidencing the phenomenological behavior shown in Fig. 3.

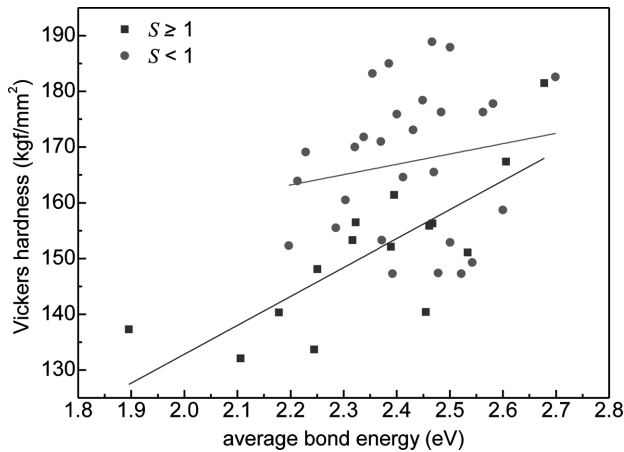


Fig. 5. Vickers hardness plotted as a function of average bond energy of each glass composition. Note that the blue straight line is obtained from the least-squares fit using a linear function to data set satisfying $S \geq 1$, while the red line satisfying $S < 1$

4. Conclusions

In this study, hardness of Ge-Sb-Se glass has been measured in an effort to compositionally optimize the glass compositions for use in molded infrared lens. Among the three constituent atoms, Ge turns out to exert a most conspicuous correlation with hardness. This phenomenological behavior can be explained in connection with the structural evolution that Ge brings about: Ge forms tetrahedral units which consist of relatively stronger chemical bonds, and as a result the amor-

phous structure becomes morphologically more connected and energetically more stable.

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REFERENCES

- [1] X.H. Zhang, Y. Guimond, Y. Bellec, *J. Non-Cryst. Solids* **326&327**, 519 (2003).
- [2] J.A. Savage, P.J. Webber, A.M. Pitt, *J. Mater. Sci.* **13**, 859 (1978).
- [3] Z.G. Ivanova, V. Pamukchieva, M. Vlcek, *J. Non-Cryst. Solids* **293-295**, 580 (2001).
- [4] D.R. Swiler, A.K. Varshneya, R.M. Callahan, *J. Non-Cryst. Solids* **125**, 250 (1990).
- [5] L. Petit, N. Carlie, K. Richardson, *J. Phys. Chem. Solids* **66**, 1788 (2005).
- [6] P. Klocek, L. Colombo, *J. Non-Cryst. Solids* **93**, 1 (1987).
- [7] A. Giridhar, P.S.L. Narasimham, S. Mahadevan, *J. Non-Cryst. Solids* **43**, 29 (1981).
- [8] Y.G. Choi, R.J. Curry, D.W. Hewak, *Chem. Phys. Lett.* **551**, 101 (2012).
- [9] J.K. Kim, B.K. Jin, W.J. Chung, B.J. Park, J. Heo, Y.G. Choi, *J. Phys. Chem. Solids* **72**, 1386 (2011).
- [10] Y.G. Choi, *J. Lumin.* **129**, 620 (2009).
- [11] J.C. Philips, *J. Non-Cryst. Solids* **43**, 37 (1981).
- [12] Y.G. Choi, B.J. Park, W.J. Chung, *Chem. Phys. Lett.* **395**, 379 (2004).
- [13] J.C. Philips, M.F. Thorpe, *Solid State Commun.* **53**, 699 (1985).
- [14] K. Tankaka, *Phys. Rev. B* **39**, 1270 (1989).
- [15] Z.G. Ivanova, V. Pamukchieva, M. Vlcek, *J. Non-Cryst. Solids* **293-295**, 580 (2001).
- [16] L. Tichy, H. Ticha, *J. Non-Cryst. Solids* **189**, 141 (1995).
- [17] M.M. Wakkad, *J. Non-Cryst. Solids* **265**, 157 (2000).
- [18] S.A. Saleh, *Mater. Sci. Appl.* **2**, 950 (2011).