

## MICROHARDNESS OF Pb MODIFIED CHALCOGENIDE GLASSES

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Microhardness of bulk  $Pb_xGe_{42-x}Se_{58}$  ( $3 \leq x \leq 15$ ),  $Pb_{20}Ge_xSe_{80-x}$  ( $17 \leq x \leq 24$ ),  $Pb_xGe_{42-x}Se_{48}Te_{10}$  ( $3 \leq x \leq 15$ ) and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  ( $17 \leq x \leq 24$ ) glasses was measured at room temperature. In  $Pb_{20}Ge_xSe_{80-x}$  and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  glasses, microhardness attained a maximum value at the composition with 21 at. wt. % Ge. In the case of  $Pb_xGe_{42-x}Se_{58}$  and  $Pb_xGe_{42-x}Se_{48}Te_{10}$  glasses, the microhardness decreased with the addition of Pb. The variation in microhardness with composition and the effect of Te substitution on the microhardness of these glasses are discussed in the light of the change in the average bond energy of the glasses.

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### 1. Introduction

Chalcogenide glasses are p-type semiconductors [1]. The p-type conduction is attributed to pinning of the Fermi energy level near the middle of the band gap by charge defects present in these glasses [2]. Through their pioneering work in early eighties, Tohge et al. [3, 4] showed that n-type glasses could be obtained when Ge-Se glasses were prepared with appropriate amounts of Bi or Pb as additives. In Pb-Ge-Se glasses, majority charge carrier reversal (MCCR) has been reported [4] in two series of glasses, namely,  $Pb_xGe_{42-x}Se_{58}$  (Series-I,  $0 \leq x \leq 15$ ) and  $Pb_{20}Ge_xSe_{80-x}Te_{10}$  (series-II,  $15 \leq x \leq 24$ ) at  $x = 9$  at. wt. % Pb and  $x = 21$  at. wt. % Ge, respectively. Murugavel et al. [5] reported the occurrence of carrier reversal in  $Pb_xGe_{42-x}Se_{48}Te_{10}$  glasses at  $x = 9$  at. wt. % Ge. Vaidhyanathan et al. [6] proposed that the MCCR in  $Pb_xGe_{42-x}Se_{58}$  glasses is a consequence of the energetically disposed  $Pb^{2+}$  ion. Differential scanning calorimeter [6, 7], photo-acoustic spectroscopy [8] and spectrophotometry [9] studies on Pb-Ge-Se(-Te) glasses showed that even physical properties of non-electronic nature exhibited anomalous behaviour at the MCCR composition.

Hardness of glasses is a function of the strength of the strength of individual bonds and the atomic packing density [10]. The Vickers hardness number (VHN), obtained by measuring the diagonal length of the indentation produced by the penetration of a square-based pyramid indenter is normally taken as a measure of the microhardness of the material. VHN is determined using the relation [11],

$$H (VHN) = \frac{1854 F}{d^2} \quad (1)$$

where F is the load applied (in kg) and d is the length (in mm) of the diagonal of the indentation. During indentation, a glass undergoes both compression and shear, resulting in its elastic deformation, flow and densification [12]. The bond strength of a certain compound determines the ratio of recoverable and irreversible deformation. High bond strength results in high elastic modulus, which in turn prevents bond breakage. On the other hand, low bond strength results in bond breaking concomitant irreversible, plastic flow. It is often convenient to understand the variation in VHN of a

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glass in terms of the variation in the average bond energy of the glass. The average bond energy could be estimated by Pauling's method [13] from the single covalent bond energy and electronegativity of the constituent elements. Microhardness has also been related to the dilatometric softening point  $T_d$  [10] of glasses. It has been pointed that microhardness and softening temperature of glasses show the same behaviour [14]. This work is aimed at understanding the composition dependence of the microhardness and the effect of Te substitution on the microhardness of Pb modified chalcogenide glasses.

## 2. Experimental

Bulk  $Pb_xGe_{42-x}Se_{58}$  ( $3 \leq x \leq 15$ ),  $Pb_{20}Ge_xSe_{80-x}$  ( $17 \leq x \leq 24$ ),  $Pb_xGe_{42-x}Se_{48}Te_{10}$  ( $3 \leq x \leq 15$ ) and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  ( $17 \leq x \leq 24$ ) glasses were prepared by the melt quenching technique [7]. Appropriate amounts of high purity elements were taken in a quartz ampoule. The ampoule was flame sealed after evacuating the ampoule to  $10^{-5}$  Torr pressure. The sealed ampoule was then loaded into a rotary furnace, heated to 1050 °C and then dropped into cold brine water solution. To check the amorphous nature of these glasses x-ray diffraction method was used. The glass transition temperature ( $T_g$ ) was determined from Differential Scanning Calorimeter (Perkin-Elmer DSC 7) under a constant heating rate of  $10^\circ C \cdot min^{-1}$ . The  $T_g$  (on-set) values are tabulated in Table 1. Polished samples were indented using a Buehler Micromet 2100 automated Vickers microhardness tester. All glass samples were uniformly subjected to a load of 50 g for 15 seconds duration. Each microhardness value tabulated in table 1 is the average of at least ten indents made on each sample. All measurements were made at room temperature.

## 3. Results and discussion

Fig. 1a shows the variation of Vickers hardness number VHN of  $Pb_xGe_{42-x}Se_{58}$  and  $Pb_xGe_{42-x}Se_{48}Te_{10}$  ( $3 \leq x \leq 15$ ) glasses as a function of Pb at. wt. %. VHN of these glasses decreases as the concentration of Pb is increased. This behaviour can be interpreted in terms of the variation in the average bond energy of the glasses with change in composition. Pauling proposed [13] that single covalent bond energy of heteronuclear bonds  $D(A-B)$  can be estimated from the single covalent bond energy of homonuclear bonds  $D(A-A)$  and  $D(B-B)$  and the electronegativity,  $x_A$  of atom A and  $x_B$  of atom B using the formula,

$$D(A-B) = [D(A-A) \times D(B-B)]^{1/2} + 30(x_A - x_B)^2 \quad (2)$$

The single bond energy values [15,16] of Ge-Ge ( $205.2 \text{ kJ} \cdot \text{mol}^{-1}$ ), Pb-Pb ( $85.7 \text{ kJ} \cdot \text{mol}^{-1}$ ), Se-Se ( $206.1 \text{ kJ} \cdot \text{mol}^{-1}$ ) and Te-Te ( $158.8 \text{ kJ} \cdot \text{mol}^{-1}$ ) and Allred-Rockow electronegativity values were used to estimate the single covalent bond energies of Ge-Se ( $234.9 \text{ kJ} \cdot \text{mol}^{-1}$ ), Pb-Se ( $231.2 \text{ kJ} \cdot \text{mol}^{-1}$ ), Se-Te ( $201.1 \text{ kJ} \cdot \text{mol}^{-1}$ ), Pb-Te ( $183.1 \text{ kJ} \cdot \text{mol}^{-1}$ ), etc.

In  $Pb_xGe_{42-x}Se_{58}$  glasses, substitution of Ge with Pb atoms results in the reduction of Ge-Se bonds and an increase in Pb-Se bonds. Since Pb-Se bonds have a lower energy than Ge-Se bonds, addition of Pb results in a reduction in the average bond energy of  $Pb_xGe_{42-x}Se_{58}$  glasses. This reduction in the average bond energy of the glasses is reflected in the reduction in the microhardness of these glasses. In the case of  $Pb_xGe_{42-x}Se_{48}Te_{10}$  glasses, Te content remains constant throughout this series, whereas Ge is substituted by Pb. Te bonds have lower energy as compared to Se bonds. The presence of a finite number of Te bonds in  $Pb_xGe_{42-x}Se_{48}Te_{10}$  glasses results in an overall reduction in the average bond energy of this series of glasses as shown in Fig. 1a, as compared to the corresponding  $Pb_xGe_{42-x}Se_{58}$  glasses. The glass transition temperature  $T_g$  of  $Pb_xGe_{42-x}Se_{58}$  and  $Pb_xGe_{42-x}Se_{48}Te_{10}$  glasses is listed in Table 1 along with the VHN data. Since  $T_g$  is also a property that depends on the average bond energy of the glass, its variation with Pb content is similar to that of the microhardness.

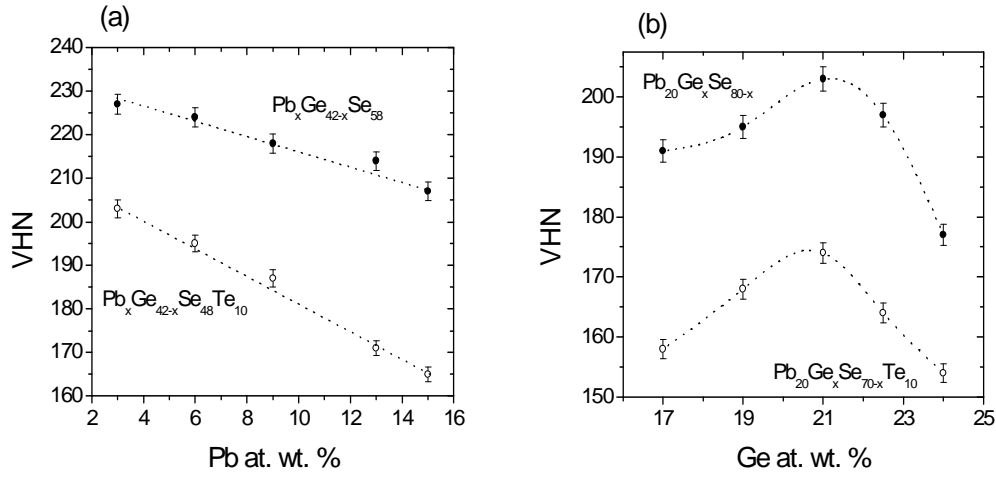


Fig. 1. Vickers hardness number (VHN) of (a)  $Pb_xGe_{42-x}Se_{58}$  and  $Pb_xGe_{42-x}Se_{48}Te_{10}$  ( $3 \leq x \leq 15$ ) glasses, (b)  $Pb_{20}Ge_xSe_{80-x}$  and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  ( $17 \leq x \leq 24$ ) glasses as a function of composition.

Table 1. Vickers hardness number (VHN) and glass transition temperature ( $T_g$ ) recorded at a constant heating rate of  $10^\circ C \cdot min^{-1}$  of various Pb-Ge-Se(-Te) glasses.

Glass composition	VHN	$T_g$ (K)	Glass composition	VHN	$T_g$ (K)
$Pb_{03}Ge_{39}Se_{58}$	227	544	$Pb_{03}Ge_{39}Se_{48}Te_{10}$	203	536
$Pb_{06}Ge_{36}Se_{58}$	224	527	$Pb_{06}Ge_{36}Se_{48}Te_{10}$	195	522
$Pb_{09}Ge_{33}Se_{58}$	218	524	$Pb_{09}Ge_{33}Se_{48}Te_{10}$	187	517
$Pb_{13}Ge_{29}Se_{58}$	214	527	$Pb_{13}Ge_{29}Se_{48}Te_{10}$	171	514
$Pb_{15}Ge_{27}Se_{58}$	207	528	$Pb_{15}Ge_{27}Se_{48}Te_{10}$	165	515
$Pb_{20}Ge_{17}Se_{63}$	191	495	$Pb_{20}Ge_{17}Se_{53}Te_{10}$	158	506
$Pb_{20}Ge_{19}Se_{61}$	195	533	$Pb_{20}Ge_{19}Se_{51}Te_{10}$	168	510
$Pb_{20}Ge_{21}Se_{59}$	203	544	$Pb_{20}Ge_{21}Se_{49}Te_{10}$	174	516
$Pb_{20}Ge_{22.5}Se_{57.5}$	197	535	$Pb_{20}Ge_{22.5}Se_{47.5}Te_{10}$	164	516
$Pb_{20}Ge_{24}Se_{56}$	177	524	$Pb_{20}Ge_{24}Se_{46}Te_{10}$	154	489

Fig. 1b depicts the variation of VHN of  $Pb_{20}Ge_xSe_{80-x}$  and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  ( $17 \leq x \leq 24$ ) glasses as a function of Ge at. wt. %. Tohge et al. [4] estimated the variation in the number of Ge-Se, Ge-Ge and Se-Se bonds in this glass system (the number of Pb-Se bonds remains constant throughout this series). They showed that Ge-Se bonds increase in number, reach a maximum at 20 mol % of Ge and, thereafter, decrease in number. Se-Se bonds decrease in number as Ge content increases and disappear at 20 mol % Ge, whereas Ge-Ge bonds, which start appearing at 20 at. wt. % Ge, attain a maximum value at 24 at. wt. % Ge. Since Ge-Se bonds are maximum at 20 at. wt. % Ge. The average bond energy of the glass with this composition is the maximum in the series. This explains the maximum value in VHN at this composition for  $Pb_{20}Ge_xSe_{80-x}$  series of glasses. In the  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  series of glasses, Te content remains constant at 10 at. wt. % throughout and hence the VHN of this series is also expected to exhibit a maximum at the composition with 20 at. wt. % Ge. It is evident from Fig. 1b that the presence of low energy Te bonds has resulted in a lower VHN value for all  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  glasses as compared to the  $Pb_{20}Ge_xSe_{80}$  glasses. The composition dependence of  $T_g$  of  $Pb_{20}Ge_xSe_{80}$  and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  glasses (Table 1) exhibits similar dependence with composition. This is to be expected since both these properties depend on the average bond energy of the glass.

Thermoelectric power measurements (TEP) made [17] on  $Pb_xGe_{42-x}Se_{58}$  and  $Pb_xGe_{42-x}Se_{48}Te_{10}$  glasses confirmed that the p-type to n-type transition in these glasses occurred near  $x = 9$  at. wt. % Pb. Similarly, TEP measurements showed [17] that the carrier type reversal occurs near  $x = 21$  at. wt. % Ge in  $Pb_{20}Ge_xSe_{80}$  and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  glasses. The present studies on microhardness of these glasses, especially,  $Pb_{20}Ge_xSe_{80}$  and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  glasses show that the VHN data exhibits an anomaly at the  $x = 21$  at. wt. % Ge composition. From the simple interpretation of the composition dependence of VHN of these glasses provided above, it is evident that there is a preponderance of heteronuclear (Ge-Se) bonds at this composition. It is interesting to note that a non-electronic property such as microhardness, which depends on the average bond energy of the glass, is exhibiting an anomaly at the composition at which the electronic (p-type to n-type) transition was observed. This observation suggests that there is considerable amount of change in the chemical bonding at this composition. Earlier reports on other non-electronic properties such a thermal diffusivity [8], optical band gap [9], and  $T_g$  [7,18] on Pb-Ge-Se(-Te) glasses lend support to this argument.

#### 4. Conclusion

Microhardness of bulk  $Pb_xGe_{42-x}Se_{58}$  ( $3 \leq x \leq 15$ ),  $Pb_{20}Ge_xSe_{80-x}$  ( $17 \leq x \leq 24$ ),  $Pb_xGe_{42-x}Se_{48}Te_{10}$  ( $3 \leq x \leq 15$ ) and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  ( $17 \leq x \leq 24$ ) glasses was measured at room temperature. In  $Pb_{20}Ge_xSe_{80-x}$  and  $Pb_{20}Ge_xSe_{70-x}Te_{10}$  glasses, microhardness attained a maximum value at the composition with 21 at. wt. % Ge. In the case of  $Pb_xGe_{42-x}Se_{58}$  and  $Pb_xGe_{42-x}Se_{48}Te_{10}$  glasses, microhardness decreased with the addition of Pb. The variation in microhardness with composition and the effect of Te substitution on the microhardness of these glasses have been interpreted in terms of the variation in the average bond energy of the glasses with composition. This simple interpretation enables one to satisfactorily account for the variation of VHN with composition in these glasses and the effect of Te substitution. These observations suggest that there is a preponderance of heteronuclear bonds at the composition with 21 at. wt. % Ge in  $Pb_{20}Ge_xSe_{80-x}$  and  $Pb_{20}Ge_xSe_{70}Te_{10}$  glasses.

#### References

- [1] S. R. Elliot, *Physics of Amorphous Materials*, Longman, London, 1984.
- [2] M. Kastner, D. Adler, H. Fritsche, *Phys. Rev. Lett.* **37**, 150 (1976).
- [3] N. Tohge, T. Minami, Y. Yamamoto, *J. Appl. Phys.* **51**, 1048 (1980).
- [4] N. Tohge, H. Matsuo, T. Minami, *J. Non-Cryst. Solids* **95&96**, 809 (1987).
- [5] S. Murugavel, S. Asokan, *Phys. Rev. B*, **58**, 4449 (1998).
- [6] B. Vaidhyanathan, S. Murugavel, S. Asokan, K. J. Rao, *J. Phys. Chem. B*, **101**, 9717 (1997).
- [7] A. K. Pattanaik, A. Srinivasan, *J. Mater. Sci.* **37**, 1 (2002).
- [8] R. Ganesan, B. Thangaraju, K. S. Sangunni, E. S. R. Gopal, *J. Optoelectron. Adv. Mater.* **3**, 467 (2001).
- [9] A. K. Pattanaik, A. Srinivasan, *Solid State Physics (India)*, **42**, 289 (1999).
- [10] J. E. Shelby, *Introduction to Glass Science & Technology*, RSC, Cambridge (1997).
- [11] B. W. Mott, *Microindentation Hardness Testing*, Butterworths, London (1956).
- [12] A. Petzold, F.G. Withsmann, H. Von Kampiz, *Glasteck. Ber.* **43**, 56 (1961).
- [13] L. Pauling, *The Nature of Chemical Bond*, Oxford & IBH, Delhi, 3<sup>rd</sup> ed. (1967).
- [14] A. R. Hilton, C. E. Jones, M. Baru, *Phys. Chem. Glasses* **7**, 105 (1966).
- [15] R. T. Sanderson, *Chemical Bonds and Bond Energy*, Academic, London, 2<sup>nd</sup> ed. (1976).
- [16] K. J. Rao, R. Mohan, *Solid State Commun.* **39**, 1065 (1981).
- [17] A. K. Pattanaik, Ph. D. Thesis, IIT Guwahati, India (2002) (unpublished).
- [18] M. K. Rabinal, N. Ramesh Rao, K. S. Sangunni, E. S. R. Gopal, *Phil Mag. B*, **70**, 89 (1994).