Journal of Alloys and Compounds 480 (2009) 934–937

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Far-infrared study of amorphous $Ge_{0.17}Se_{0.83-x}Sb_x$ chalcogenide glasses

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ARTICLE INFO

Article history:
Received 30 October 2008
Received in revised form 17 February 2009
Accepted 21 February 2009
Available online 5 March 2009

Keywords:
Chalcogenide glasses
Far-infrared transmission
Bond energy
Force constant

ABSTRACT

Far-infrared transmission spectra of $Ge_{0.17}Se_{0.83-x}Sb_x$ ($x = 0, 0.03, 0.09, 0.12, 0.15$) glassy alloys are obtained in the spectral range 500–200 cm^{-1} at room temperature. The results are interpreted in terms of the vibrations of the isolated molecular units, in such a way as to preserve fourfold and twofold coordination for Ge and Se atoms, respectively. In the $Ge_{0.17}Se_{0.83}$ bulk glass the main absorption bands appear at ~250 cm^{-1} and 300 cm^{-1}. With the increase in Sb content some new bands start appearing at 228–231 cm^{-1} and 250–260 cm^{-1}. Theoretical calculations (bond energy, relative probability density of bond formation, force constant and wave number) were also made to justify the results.

1. Introduction

Chalcogenide glasses have drawn colossal attention over the past three decades because of their potential in photoresist [1,2], microelectronic [3–5], optoelectronic [6–9], holographic [10,11] applications and especially their ability to transmit light in the mid- to far-infrared region. Impurity effects in chalcogenide glasses may have importance in fabricating glassy semiconductors. The infrared transparency of chalcogenide glasses allows their use in optical fibers for transmission of light generated by CO and CO_2 lasers operating in infrared region and such fibers are applied towards high-precision tools in surgery, industrial cutting, welding, etc. The study of the IR spectra of chalcogenide glasses provides a pave way into the molecular structure of these glasses. Recently several workers have reported [12–15] vibrational spectroscopic studies of these glasses and have tried to assign the observed absorptions to the different chemical bonds in the system.

Amorphous solids display a characteristic extreme far-infrared (FIR) and microwave absorption as a result of phonon coupling to modes which are not active in the corresponding crystalline counterpart material. For many years infrared spectroscopy is used as an important tool for investigating chemical processes and structure. The combination of infrared spectroscopy with the theories of reflection has made advances in surface analysis possible. Specific IR reflectance techniques are divided into the areas of specular reflectance, diffuse reflectance and internal reflectance [16–19]. The latter is often termed as attenuated total reflectance. Recent advances in low frequency IR and Raman spectroscopy and Brillouin scattering have given a great stimulus to studies on vibrations in solids and liquids to provide data which supplements that obtained from measurements of elastic properties from the velocities of acoustic waves and by neutron and X-ray inelastic scattering. It is important to have the low frequencies for two reasons: they are needed to complete the vibrational assignments and they are essential for calculating the thermodynamic properties. Sometimes the low frequencies cannot be obtained from the Raman spectrum because the selection rules forbid them, the sample is unsuited for the experiment because of colour or instability or the Raman bands are just too weak. The only source of data may be the far-infrared [20].

Optical transmission is among one of the major applications of Ge–Se–Sb thin films which generally offer IR transparency in the wavelength (λ) regions of 3–5 μm and 4–14 μm [21]. Ge–Se–Sb thin films family is emerging as one of the most promising families which feed the material requirements for the fabrication of optical fibers, such as large band gap, low material dispersion, low light scattering and long wavelength multiphonon edge along with good thermal, mechanical and chemical properties. These properties of Ge–Se–Sb thin films makes several groups [22,23] to work on these glasses to prepare IR optical fibers for the 2–14 μm regions. Structural properties of both amorphous and crystalline solids can be explained with topological models [24], chain crossing model (CCM) [25], random covalent network model (RCNM) [26] and chemical bond approach (CBO) [27]. In these models, some of the properties can be discussed in terms of the average coordination number, which is indiscriminate of the species or valence bond. The glass network has either a mechanical threshold or critical

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doi:10.1016/j.jallcom.2009.02.101

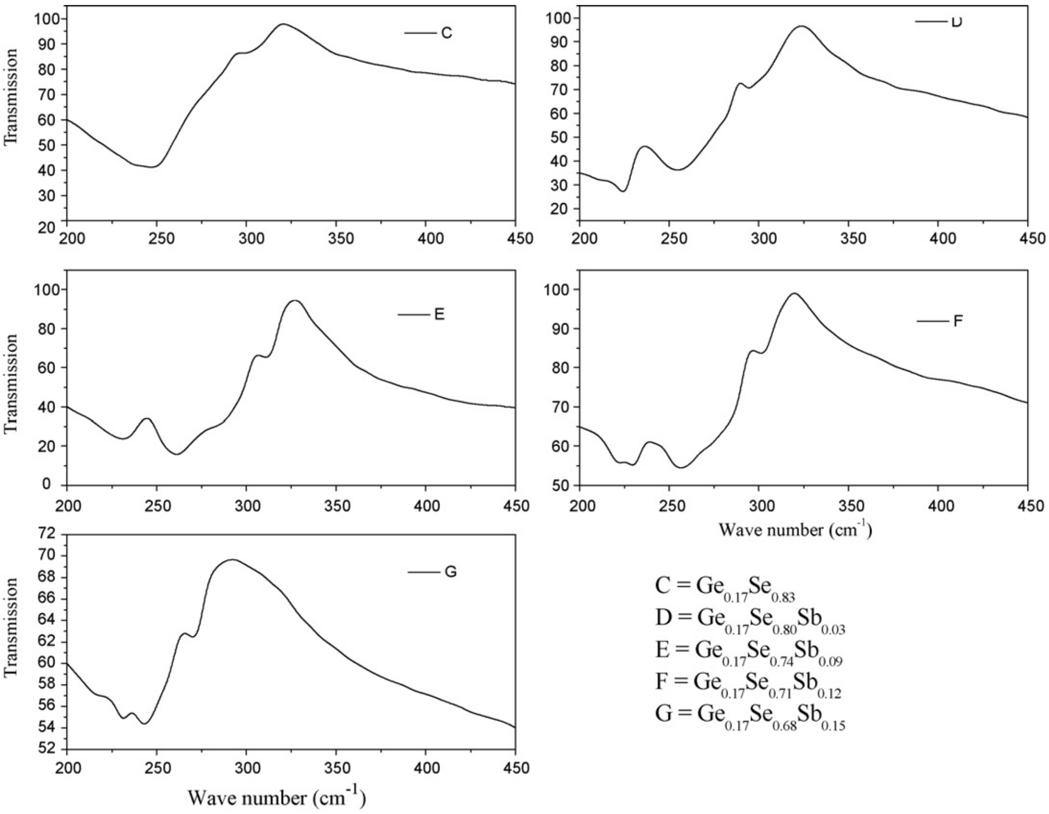

Fig. 1. Far-IR transmission spectra of amorphous $Ge_{0.17}Se_{0.83-x}Sb_x$ glassy alloys.

composition, at which the network changes from an elastically floppy (polymeric glass) mode to a rigid (amorphous solid) mode. The particular base composition of our study $Ge_{0.17}Se_{0.83}$ is the bearer of short-range order of initial components and also exhibit compound short-range order formed from both the initial components [28].

In the present work far-IR absorption studies have been carried out on $Ge_{0.17}Se_{0.83-x}Sb_x$ ($x = 0, 0.03, 0.09, 0.12, 0.15$) thin films. The results are discussed in the light of probabilities and the bond energies of various chemical bonds possible in this glass.

2. Experimental details

Glassy alloys of $Ge_{0.17}Se_{0.83-x}Sb_x$ ($x = 0, 0.03, 0.09, 0.12, 0.15$) system were prepared by melt quench technique. Materials (99.999% purity) were weighed according to their atomic percentages and sealed in evacuated (at $\sim10^{-4}$ Pa) quartz ampoules. The sealed ampoules were kept inside a furnace where the temperature was increased up to 950 °C at a heating rate of 3–4 °C/min and then the ampoules were frequently rocked for 8 h at the highest temperature to make the melt homogeneous. Ice-cold water was used for quenching. The bulk samples were characterized by X-ray diffraction technique and found to be amorphous in nature as no prominent peak was observed in the spectra [29].

The far-IR transmission spectra of different alloys were recorded on a Fourier transform IR (NICOLET 5700) used in conjunction with the KBr disc technique, over the spectral range of 500–200 cm^{-1} at room temperature. Powdered samples of 4 mg were thoroughly mixed and ground with 200 mg KBr; after which the mixtures were pressed at 10 tons cm^{-2} for 5 min under vacuum.

3. Results

Far-IR transmission study provides valuable information about the atomic configuration of glasses. The IR spectra of $Ge_{0.17}Se_{0.83-x}Sb_x$ ($x = 0, 0.03, 0.09, 0.12, 0.15$) glassy system is shown in Fig. 1.

The bond energies of various possible heteropolar bonds Ge–Se, Ge–Sb and Se–Sb bonds have been calculated on the basis of the relation postulated by Pauling [30]:

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

where X_A and X_B are the electronegativities of atoms A and B, and $D(A-A)$ and $D(B-B)$ are the bond energies of A–A and B–B bonds, respectively [31]. The relative probabilities of the different bonds have also been calculated using the probability function $\exp(D/k_BT)$ at room temperatures as well as at the temperature of 950 °C at which the sample was prepared. The results are shown in Table 1.

Table 1
Bond energies and their relative probabilities of formation at 27 °C and 950 °C of $Ge_{0.17}Se_{0.83-x}Sb_x$ ($x = 0, 0.03, 0.09, 0.12, 0.15$) glassy alloys.

Bond	Bond energy (kcal mol^{-1})	Relative probability of bond formation	
		27 °C	950 °C
Ge–Se	49.4	1	1
Se–Se	44.0	1.18×10^{-4}	1.08×10^{-1}
Se–Sb	43.9	1.08×10^{-4}	1.06×10^{-1}
Ge–Sb	39.7	9.31×10^{-8}	1.88×10^{-2}
Ge–Ge	37.6	2.57×10^{-9}	7.78×10^{-3}
Sb–Sb	30.2	1.06×10^{-14}	3.70×10^{-4}

4. Discussion

Researchers have applied various methods and models to explain the structure of amorphous solids. Chain crossing model and random covalent model has been proposed for the structural analysis of Ge–Se amorphous glasses [25,26]. In chain crossing model the fourfold tetrahedrally coordinated Ge atoms acts as chain crossing points in the Se chain structure. In random covalent model the tetrahedrally coordinated Ge atoms bond to the other Ge atoms as readily as to the twofold coordinated Se atoms.

Table 2
Experimentally and theoretically calculated values of wave number (ν), reduced mass and force constant of the probable bonds.

Bond	Reduced mass 10^{-26} (kg U^{-1}) (μ)	Bond length (nm) (d)	Force constant K_{AB} (eV)	Wave number	
				Experimental (cm^{-1})	Theoretical (cm^{-1})
Ge–Ge	6.060	0.224	1.29	–	231
Ge–Sb	7.584	0.263	1.07	–	206
Ge–Se	6.301	0.239	1.93	300	277
Sb–Sb	10.129	0.282	0.87	–	173
Se–Sb	7.962	0.258	1.54	226	201
Se–Se	6.559	0.234	1.91	250–260	270

From an energy point of view heteropolar bonds are preferred over homopolar bonds. This can be largely explained on the basis of CBO proposed by Biecerano and Ovshinsky [27]. In this approach, the glass structure is assumed to be composed of cross-linked structural units of the stable chemical compounds (heteropolar bonds) of the system and excess if any, of the elements (homopolar bonds). Due to the chemical ordering, features like extremum, a change in slope or kink [32], occur for the various properties at the tie line or stoichiometric compositions. In this case the glass structure is made up of cross-linked structural units consisting of heteropolar bonds only. Heteropolar bonds thus have pre-eminence over homopolar bonds and bonds are formed in the sequences of decreasing bond energy until all the available valances of the atoms are saturated. Each constituent is coordinated by 8-*N* atoms, where *N* is the number of electrons in outer shell and this is equivalent to neglecting the dangling bonds and the other valence defects.

In the $Ge_{0.17}Se_{0.83}$ bulk glass the main absorption bands appear at ∼250 cm^{-1} and 300 cm^{-1}. The existence of the absorption band at 250 cm^{-1} is assigned due to the presence of Se_8 (A_1, E mode) and the absorption band appearing at 300 cm^{-1} is due to the presence of Ge–Se–Ge (ν_1 mode). These results are in good agreement with Goyal and Maan [22]. On addition of Sb to the base sample it is seen that the Se–Se absorption band is bifurcated into 228–231 cm^{-1} and 250–260 cm^{-1}. The new absorption band appearing at 228–231 cm^{-1} having lower bond energies is assigned to Se–Sb bonds. The absorption band at 250–260 cm^{-1} is assigned due to the presence of Se_8. The absorption band near 250–260 cm^{-1} in the spectra corresponds well to the value of 250 cm^{-1} calculated by Somayayulu [33]. As the amount of Sb goes on increasing heteropolar Se–Sb bonds starts forming on the expense of Se–Se bonds [34]. So formation of Se–Sb bonds reduces the average energy of the system which consequently supports the decrease in optical band gap [29].

From Table 2, the order of bond energies and the probability functions indicate that the Se atoms will preferentially first saturate Ge atoms and thereafter Se–Sb and Se–Se bonds will be formed. The result also shows that there is least probability of forming Ge–Ge, Sb–Sb and Ge–Sb bonds. The Se atoms will form chain like structures and these chains will be interlinked by Ge and Sb atoms. The bond energy results exclude the random covalent model structure where germanium atoms can be linked with other germanium atoms. These leads to the exemption of bonds like Ge–Sb and Sb–Sb whose bond energies are very low.

5. Theoretical justification of some absorption bands

Two assumptions are generally employed for discussing the IR transmission measurements for Ge–Se–Sb materials: (1) the valence force field model (VFF) [35]; (2) the position of the intrinsic IR features is influenced mainly by stretching force constants of corresponding chemical bonds.

The wave number of the vibration modes in the IR spectra is determined by the mass of the atoms and the interatomic force within the groups of the atoms comprising the glass network. The wave number is given by the following formula:

$$\nu = \left(\frac{K_r}{\mu}\right)^{1/2}$$

where K_r is the bending or stretching force constant of the bond and μ is the reduced mass of the molecule and is given by the following relation:

$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

where M_1 and M_2 are the atomic masses of two atoms. The force constant K_r can be calculated by the following relation obtained by Gordy [36]:

$$K_r = aN\left(\frac{\chi_A \chi_B}{d^2}\right)^{3/4} + b$$

Here *a* and *b* are constants which depend on the structural unit type, *d* is the bond length, χ_A and χ_B are the electronegativities (Ge = 1.8, Se = 2.4, and Sb = 1.9) in Pauling scale [37] and *N* is the bond order, which can be determined from the expression [30]

$$N = \frac{d + 2r_1 - 3r_2}{2d + r_1 - 3r_2}$$

where r_1 and r_2 are the covalent radii for the single bond and double bond respectively. By using the elemental covalent force constant electronegativities Somayayulu [33] has developed a method for predicting the force constant as follows:

$$K_{AB} = (K_{AA}K_{BB})^{1/2} + (\chi_A - \chi_B)^2$$

where K_{AB} is the force constant between the elements *A* and *B* and K_{AA} and K_{BB} are the force constants for bonds *A*–*A* and *B*–*B* respectively the values of which are (10^5 dyne cm^{-1}) 1.29 eV for Ge–Ge, 0.87 eV for Sb–Sb and 1.91 eV for Se–Se.

Both the experimental and theoretical values of wave number (ν) are listed in Table 2, together with the calculated reduced mass and the force constants of the probable bonds. From Table 2 it can be seen that the experimental values of the wave number for the stretching vibrational modes for Ge–Se and Se–Sb bonds are greater than the theoretically observed values but the wave number for the stretching vibrational modes for Se–Se bond the experimental values are lesser than the theoretically observed one. This could happen because of the existence of more closely lying modes which leads to the broadening in the absorption bands.

6. Conclusion

The structure of the taken glassy system is based on the chain structure of selenium atoms interlinked by the tetrahedrally coordinated germanium and conceivably trivalent antimony atoms. The bond energies and probability functions conclude the least existence of bonds like Ge–Ge, Sb–Sb and Ge–Sb whose bond energies are very low. The comparison of theoretical and experimental values of the wave numbers for the stretching vibrational modes shows that the experimental wave number value for Ge–Se bond and

Se–Sb bonds are greater than their corresponding theoretical values but it is just reverse for the Se–Se bonds. This may be due to the existence of more closely lying modes which leads to the broadening in the absorption bands.

Acknowledgements

One of us (Parikshit) is thankful to Dr. S.S. Bhatt, Chemistry Department, Himachal Pradesh University Shimla, for helping to obtain Far-IR transmission spectra.

References

[1] P. Sharma, M. Vashistha, V. Ganesan, I.P. Jain, J. Alloys Compd. 462 (2008) 452.
[2] L. Petit, N. Carlie, K. Richardson, Y. Guo, A. Schulte, B. Campbell, B. Ferreira, S. Martin, J. Phys. Chem. Solid 66 (2005) 1788.
[3] O.V. Marchuk, I.D. Olekseyuk, A.G. Grebenyuk, J. Alloys Compd. 457 (2008) 337.
[4] S.R. Ovshinsky, J. Non-Cryst. Solids 141 (1992) 200.
[5] V.M. Lyubin, V.K. Tikhomirov, J. Non-Cryst. Solids 164–166 (1993) 1211.
[6] M. Mitkova, T. Petkova, R. Markovski, V. Mateev, J. Non-Cryst. Solids 164–166 (1993) 1247.
[7] P.J.S. Ewen, A. Zekak, C.W. Slinger, G. Dale, D.A. Pain, A.E. Owen, J. Non-Cryst. Solids 164–166 (1993) 1203.
[8] P.M. Nikolic, D. Lukovic, S.S. Vujatovic, K.M. Paraskevopoulos, M.V. Nikolic, V. Blagojevic, T.T. Zorba, B. Stamenovic, W. König, J. Alloys Compd. 466 (2008) 319.
[9] B.G. Aitken, R.S. Quimby, J. Non-Cryst. Solids 213–214 (1997) 281.
[10] D. Pathinettam Padiyan, A. Marikani, K.R. Murali, J. Alloys Compd. 365 (2004) 8.
[11] K. Tai, E. Ong, R.G. Vadimsky, Proc. Electrochem. Soc. 9 (1995) 82–89.
[12] G.J. Ball, J.M. Chamberlain, J. Non-Cryst. Solids 29 (1978) 239.
[13] V.P. Izvekov, M. Koos, K. Somogyi, J. Non-Cryst. Solids 59/60 (1983) 1011.
[14] P.M. Bridenbaugh, G.P. Espinosa, J.E. Griffiths, J.C. Phillips, J.P. Remeika, Phys. Rev. B 20 (1979) 4140.
[15] J.M. Chamberlain, S.S. Sirbegovic, P.M. Nikolic, J. Phys. C 7 (1974) L150.
[16] F.M. Mirabella, Principles, Theory, and Practice of Internal Reflection Spectroscopy, Wiley, New York, 1993.
[17] A.V. Prokofiev, A.I. Shelykh, A.V. Golubkov, I.A. Smirnov, J. Alloys Compd. (1995) 172.
[18] R.H. Renard, J. Opt. Soc. Am. 54 (1964) 1190.
[19] T. Hirschfield, Appl. Spectrosco. 31 (1977) 243.
[20] P. Hepple, Molecular Spectroscopy, The Institute of Petroleum, 6r New Cavendish Street, London, 1968.
[21] J.A. Savage, Infrared Optical Materials and Their Antireflection Coatings, Adam Hilger, Bristol, 1985.
[22] D.R. Goyal, A.S. Maan, J. Non-Cryst. Solids 183 (1995) 182.
[23] S.M. El-Sayed, Semicond. Sci. Technol. 18 (2003) 337–341.
[24] J.C. Phillips, J. Non-Cryst. Solids 34 (1979) 153;
J.C. Phillips, J. Non-Cryst. Solids 43 (1981) 37.
[25] P. Tronc, M. Bensoussan, A. Brenac, C. Sebenne, Phys. Rev. B 8 (1973) 5947.
[26] G. Lucovsky, F.L. Galeener, R.C. Keezer, R.H. Geils, H.A. Six, Phys. Rev. B 10 (1974) 5134.
[27] J. Biecerano, S.R. Ovshinsky, J. Non-Cryst. Sol. 74 (1985) 75.
[28] R. Fairman, B. Ushkov, Semiconducting Chalcogenide Glass I, Elsevier, Amsterdam, 2004.
[29] P. Sharma, V.S. Rangra, P. Sharma, S.C. Katyal, J. Phys. D: Appl. Phys. 41 (2008) 225.
[30] L. Pauling, The Nature of the Chemical Bonds, Cornell University Press, 1962.
[31] M. Fadel, Vacuum 52 (1999) 277.
[32] S. Mahadevan, A. Giridhar, A.K. Singh, J. Non-Cryst. Solids 103 (1988) 179.
[33] G.R. Somayayulu, J. Chem. Phys. 28 (1958) 814.
[34] S.S. Fouad, A.H. Ammar, M. Abo-Ghazala, Physica B 229 (1997) 249.
[35] L. Tichy, H. Ticha, A. Pacesova, J. Petzlt, J. Non-Cryst. Solids 128 (1991) 191.
[36] W. Gordy, J. Chem. Phys. 14 (1946) 305.
[37] L. Pauling, Uniones Quimicas, Buenos Aires, Kapelusz, 1969.