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Ambient temperature Raman scattering studies on $Se_{70}Te_{30-x}Pb_x$ glass systems

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The effect of doping Se-Te glass system with Pb is investigated using Raman spectroscopy. The relation between rigidity percolation based on the prediction of the mean field constraint theory, and a relative degree of fragility, representing the structural relaxation of the network is demonstrated. An observed decrease of fragility with the increase of average coordination number up to 2.4 can be attributed to the predicted rigidity percolation threshold where the glass changes from floppy to rigid. The Raman spectra and possible glass structures are discussed for different Pb content. It is seen that the addition of lead results in the formation of Se-Pb and Te-Pb bonds.

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1. Introduction

The narrow gap IV-VI semiconductors have been the subjects of extensive research as they are suited for the fabrication of photovoltaic infrared sensors [1]. The structural studies of these materials are very important for better understanding the transport mechanism in them [2-6]. The addition of selenium into a tellurium alloy improve the corrosion resistance. Therefore, Te-Se based chalcogenide glasses are thought to be a promising media, which make use of a phase change between an amorphous state and crystalline state. Te containing glasses have good chemical durability, stability against crystallization, low thermal expansion coefficient and are relatively easy to fiberize [7]

The chalcogenide glasses containing lead are important material for the tunable radiations in the mid infrared wavelength region. They are used in the advanced measurement system for detecting hydrocarbon pollutants in atmosphere, high-resolution spectroscopy, and trace gas analysis and also to a new optical fibre communication system over super long distances [8-10]. The carrier concentration in lead chalcogenides can be controlled by adjusting the lead: chalcogen ratio.

Chalcogen elements such as Sulphur, Selenium and Tellurium usually have two-fold coordination. The addition of network formers such as lead establishes a cross –linking between chains and facilitates glass formation. Since the electro negativities of the chalcogen elements are similar to those of the network formers, the chemical bonding of the chalcogenide glasses is predominantly covalent with well-defined directional bonds. The amorphous chalcogenide glass structure can be best described by using the random covalent model (RCM) in which all the local valence requirements are satisfied. Mott's '8-N' bonding rule is applicable to chalcogenide glasses and this rule states that all electrons are taken up in bonding so that changes in conductivity are small (~1%) changes of composition. Thus the long-range structure of chalcogenide glass is completely random and disordered.

The average coordination number <r> of the elements in these glasses varies from 2 to 2.4 by adding Pb to $Se_{70}Te_{30-x}Pb_x$ glasses at the expense of Te from x=0 to 10. A qualitative change in the network glasses; from being easily deformable at <r> < 2.4 to being rigid at <r> >2.4,has been demonstrated by many experimental results [11-18]. In this work we had studied the low frequency Raman spectra of Se Te Pb glasses in the range [0-800 cm^{-1}] and the relation between the fragility and rigidity percolation in the glasses are discussed.

An attempt has also been made to analyze the spectrum using average coordination number and bond energy of the bonds present in spectrum. Direct evidence of structural changes in the glasses studied is obtained from the Raman scattering.

2. Experimental

High purity Se, Te and Pb in appropriate weight proportions are weighed in a quarts ampoule. The contents of the ampoules are sealed in vacuum of 10^{-5} Torr and heated in a furnace where temperature is raised at a rate of $3\text{-}4^0$c per minute up to 750 k and kept at that temperature for 12 hours. The ampoules are frequently rocked to ensure the homogeneity of the samples. The molten samples were then rapidly quenched in ice-cooled water. The amorphous nature of the alloy in general is ascertained through X-ray diffraction pattern of the samples. The Raman measurements are done on a Raman Spectrometer and the spectra are recorded in the wave number range from 50-800cm^{-1}. Micro Raman spectroscopy was performed with a Lab Ram HR 800 instrument from HJY using a 9mW He- Ne laser beam (633nm) focused in to a ~1 micron diameter spot in a back

scattering geometry, where the incident beam is linearly polarized and the spectral detection unpolarised. Olympus microscope was used to view the images of the surface of the sample and a Mplan 50x lens was used during the entire measurements. The spectral resolution of the spectrometer is ~1cm$^{-1.}$ The incident laser light (He-Ne laser at 632nm) is focused on the sample with a microscope objective. A closed circuit video camera is used to monitor the sample surface under excitation.

3. Results and discussion

Figure shows Raman Spectra of samples Se_{70} T_{30-x} Pb_x (x=0,4,6,10). In glassy materials, the low frequency Raman scattering comes from two kinds of contributions,[19] quasielastic scattering, which is usually ascribed to some kind of relaxation motion, and the boson peak, a vibrational motion Sokolov et.al used the ratio I_{min}/I_{max} (defined as the ratios of the intensities at the minimum to that at the boson peak maximum), to describe the fragility (i.e. departure from the Arrehenius dependence of viscosity or relaxation time)[20]. In an under coordinated network glass (<r> < 2.4), the mean field constraint theory predict the existence of floppy-modes [21,22]. The reported floppy modes should affect the Raman spectra particularly in the low frequency region.

In these glasses a decrease of fragility is observed at the rigidity percolation threshold of <r>= 2.4 when the glass changes from a floppy to a rigid structure Table 1. Either a large boson peak or a smaller relaxation distribution, which reduces the intensity at the minimum between the Raleigh line and the Boson peak or both, can explain the decrease of the low frequency intensity ratio, I_{min}/I_{max}. The intensity ratio, I_{min}/I_{max}, at the percolation threshold, <r>=2.4 will be regarded by us as important evidence of the floppy mode in the under coordinated and disappearing in the over coordinated network glasses.

Table 1.

Composition	<r>	I_{min}/I_{max}
Pb_0	2	.722
Pb_4	2.16	.954
Pb_6	2.24	.935
Pb_{10}	2.4	.8668

The decrease of fragility in the range <r> < 2.4 corresponding the Pb content is related to an enlargement of population of randomly distributed Se-Pb and Te-Pb bonds, since such a glass structure is more rigid than that of Se-Te bonds. According to Y-Wang et al. the fragility decreases as the <r> increases and becomes minimum at the composition for which <r>= 2.67 and then increases. In our study also a similar decrease in fragility with increase in <r> was observed.

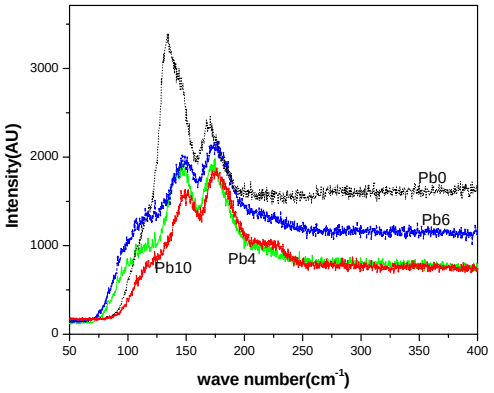
At x=0 (i.e. for Se_{70} Te_{30}) the homopolar Se-Se bond vibrations dominate the spectrum, corresponding to the main band at 134 cm^{-1}[23]. The feature at about 170 cm^{-1} is associated with heteropolar Se-Te bonds [24]. The introduction of lead leads to the formation of heteropolar Se-Pb bonds and Te-Pb bonds. The formation of Se-Pb bonds is enhanced since these bonds have higher bond energy than any other heteropolar bond in the $Se_{70}Te_{30-x}$ Pb_x system under consideration [25]. With increasing 'x' the fraction of Se-Pb bonds increase at the expense of Se-Te ones. After the addition of Pb first band in the spectrum represents Te-Pb bond and the second band represents Se-Pb bond. In addition to these two bands the spectrum shows a wider band at around 120cm^{-1}. The vibrations at around 120cm^{-1} are related to Se-Se bonds [23]. The atomic mass of Te is 127.6 and Pb is 207.19 and that for Se is 78.96. When Pb content in the glass system increases both the bands shift to higher frequency side.

When x==0, there are two bands in the spectrum. Main band at134 cm^{-1} and the second band at 170 cm^{-1}. The intensity of the first band is 3407 a.u and for the second is 2461 a.u. When Pb (x=4) is added to Se Te system the position of the two bands shifts to higher frequencies (first band at 149 cm^{-1} and the second at 176 cm^{-1}) and the intensity of the two bands decreases to 1901 a.u. and 1992 a.u. respectively. When Pb content again increased (x=6) the position of the two bands again shifts to higher frequency side (first at 150 cm^{-1} and the second at 177 cm^{-1}) and the intensity of the two bands increase to 2022 a.u. and 2162 a.u, respectively. When x==10, position of the first band is at 151 cm^{-1} and the second at 179 cm^{-1}. Accordingly intensity of the bands decreases to 1634 a.u. and 1885 a.u. respectively. Some kind of discontinuity is observed for this glass composition. This is because for Se_{70} $Te_{20}Pb_{10}$ glass the average coordination number is 2.4. In chalcogenide glasses a discontinuity in the various macroscopic physical properties has been observed [26,27] at a particular composition when the average coordination number reaches 2.4, which is explained by Phillips and Thorpe in terms of a mechanically optimized structure at critical, glass composition. The IV-VI glasses show a discontinuity at Z= 2.4 as suggested by Phillips [28,29]. Similar type of discontinuity is observed in $Se_{96}In_4$ glasses.

This band shift is due to the increase in concentration of Se-Pb and Te-Pb heteropolar bonds. Band corresponding to the Te-Pb bond will shift to the lower frequency side due to the increased reduced mass compared to Se-Pb bond [7]. But the intensity of the band corresponding to Te-Pb bond is lower than that corresponding to Se-Pb bond because the bond energy of Te-Pb bond is smaller than that of Se-Pb bond (for Se-Pb, bond energy=72.4 Kcal/mol and for Te-Pb bond energy =60 Kcal/mol) [30]. Thus the intensity of lower wave number peak is lower than that of the higher wave number peak in each glass systems. The ratio of intensities of two bands corresponding to Se-Pb and Te-Pb for each composition of the glass system increases with the increase of Pb content.

Table 2.

Composition	Ratio
$Se_{70}Te_{26}Pb_4$	1.047
$Se_{70}Te_{24}Pb_6$	1.069
$Se_{70}Te_{20}Pb_{10}$	1.1536



4. Conclusion

We had investigated the low frequency Raman spectra of glassy $Se_{70}Te_{30-x}Pb_x$ in a range 0-800 cm^{-1}. The variation of fragility with average coordination number is evaluated and it is found to decrease with average coordination number. This is assumed to be an evidence for the rigidity threshold predicted by mean field constraint theory. The distribution of the chemical bonds determined by strong chemical ordering model supports such structural changes. The addition of Pb to the Se-Te chalcogenide glass system disrupts the Se-Se and Se-Te bonds and forms Te-Pb and Se-Pb bonds. The ratio of intensities of the Se-Pb and Te-Pb bonds increases with increase in average coordination number.

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