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ORIGINAL ARTICLE

Infrared and Raman studies on Sn_x–Sb_5–Se_{95-x} chalcogenide glasses

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Abstract Tin–antimony–selenium (Sn–Sb–Se)-based systems belong to the ternary chalcogenide compounds of *IV–V–VI* group. They have potential applications in infrared region due to their heavy elemental masses, continuous variation of band gap-energies and lattice constants as well as electrical properties, with compositions. Structures of melt quench-synthesized samples of Sn_x–Sb_5–Se_{95-x} system, where $x = 0$, 5, 10 and 12.5-mole% have been studied using Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. FTIR spectra illustrates that addition of Sn-mole% to the system causes a shift in IR-peak's intensity and width from long to the short wavelength. This change implies the breaking of Se chains that appeared around 210–254 cm^{-1} and the occurrence of pyramidal SbSe_3 around 147–210 cm^{-1} and asymmetrical tetrahedral SnSe_4 mode around 117–145 cm^{-1} for Sn = 5 mole% up to 180 cm^{-1} in Sn = 12.5 mole% spectra. Raman spectra show that a pyramidal SbSe_3 peak is cited at 190-cm^{-1}. The intensity of this peak is shifted towards -183 cm^{-1} when Sn-mole% is added to the system. The results confirm the validity of using 4, 3 and 2 as co-ordination numbers of Sn, Sb and Se, respectively, in the amorphous region, which is contained by the average co-ordination number, $\mu \leqslant 2.4$ and the fraction of Sn–Se bonds, $f_{\mathrm{Sn-Se}} < 44.3\%$.

1. Introduction

Investigation of amorphous and crystalline regions of chalcogenide glasses is of practical interest for obtaining new materials with semiconducting properties. It is also of theoretical interest for determining the influences of short and long-range orders on properties of substances. In previous studies (Jagtap and Zope, 1990; Mikurt and McNell, 1890; Kislitskaya et al., 1971) the mole% of Sn in Ge_{1-x}–Sn_x–Se_2, As_{33}–$\mathrm{Se}_{67-x}\mathrm{Sn}_x$ and Ge–Sn–Sb–Se was found to be 19.8%, 7.0% and 12.5% in glass region, respectively. On the other hand selenium-based chalcogenide glasses have numerous applications as efficient solar cell materials, memory switching devices, holographic recording systems, thermal imaging systems and infrared sensors (Bureau, 2005; Padiyan et al., 2004; Kumar et al., 2006). In particular, the introduction of Sn into the Sb–Se system, with co-ordination number of 4 before stoichiometric compound, was assumed and the incorporation of 12.5-mole%

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of Sn (Adam et al., 2005, 2006, 2002) in glass formation is expected. However, above this range, increasing the mole% of Sn causes the difficulty in glass formation owing to the distinct metallic character of Sn with co-ordination number 6. It should be mentioned that in binary stoichiometric Sb_2Se_3 and $SnSe_2$, Sb and Sn were coordinated with Se at their stoichiometric compositions with 5 and 6 as co-ordination numbers, resulting in changing the co-ordination number of Se from 2 to 3. Their stoichiometric average co-ordination numbers were $\mu = 3.8$ and 4, respectively (Zhenhua, 1991; Philips, 1979). In this paper the IR and Raman studies on Sn_x–Sb_5–Se_{95-x} system are obtained and discussed.

2. Experimental procedures

Granules of Sn and Sb having 99.999% purity and those of Se having 99.99% purity were used. The containers in which these materials were stored were opened under a controlled way to minimise contamination. A 5.00-g sample was batched in a closed scale balance on which Sn, Sb and Se were weighted using sample percentage procedures (Adam et al., 2005, 2002). Batched elements were placed in a pre-cleaned quartz ampoule. The ampoule was attached to the vacuum pump and evacuated to 66.5 Pa. Then an inert argon gas was supplied for half an hour while pumping continued. The ampoule was later sealed using an oxygen–natural gas flame melt by heating its wall, bending it carefully and sealing it up. Selenium is recognised to have high vapour pressure and also a tendency to react with oxygen. Thus, care and precaution were taken to avoid any explosion during the sealing of the tube. Then, the ampoule was transferred into a specially designed orbital-shaking furnace. Heating cycle up to 700 °C for 6 h was applied at a rate of 5 °C min^{-1}. In order to prepare homogenous samples, agitation of 100.0 rotations per minute (rpm) was applied using an attached orbital shaker. The ampoule was dropped into liquid nitrogen for fast cooling requirement. The transmission spectra were obtained at room temperature in the spectral range 300–100 cm^{-1} with 2.0 cm^{-1} resolutions (FTIR Shimadzu- spectrophotometer 8000). Polarised Raman spectrum (Magna-spectrometer 560 in Rubber Research Center-Malaysia) was recorded in the range 400–100 cm^{-1} with 4 cm^{-1} step at room temperature, on a KBr technique prepared disc using a near 90° scattering configuration. The number of photons counted at each step was stored in a computer.

3. Result and discussion

3.1. Infrared Spectra of Sn_x–Sb_5–Se_{95-x} system

Fig. 1 shows infrared spectra of Sn_x–Sb_5–Se_{95-x} system (where x = 0, 5, 10 and 12.5). Infrared transmission (%) versus the wave number (cm^{-1}) spectrum at the bottom shows at least five to six transmission bands. The band that extends from 100 to 131 cm^{-1} is assigned to the Se_8-ring bending mode, whereas a 115-cm^{-1} band was assigned to Se_8 chain in Ge–Se alloy (Goyal and Maan, 1995). The band situated between 131 and 190 cm^{-1}, with its two shoulders at 147 and 181 cm^{-1}, is attributed to the $SbSe_3$ stretching mode as reported in Kato et al. (1983). Furthermore, the band located around 190–210 cm^{-1} is ascribed to the Se–Se stretching mode or to the Sb–Se bending mode, while the band around 210–239 cm^{-1} with a shoulder at 220 showed $SbSe_3$ stretching mode and Se_8 chain mode, respectively. On the other hand, the band around 177–210 cm^{-1} was assigned to Sb–Se bond in Sb–Ge–Se glass (Sharma et al., 1989). The transmission cut-off at 254 cm^{-1} is clearly assigned to the Se_8 chain ring, as the absorption peaks around 227 and 247 cm^{-1} were assigned to the Se polymeric chain and Se_8 ring modes, respectively (Zhenhua, 1991).

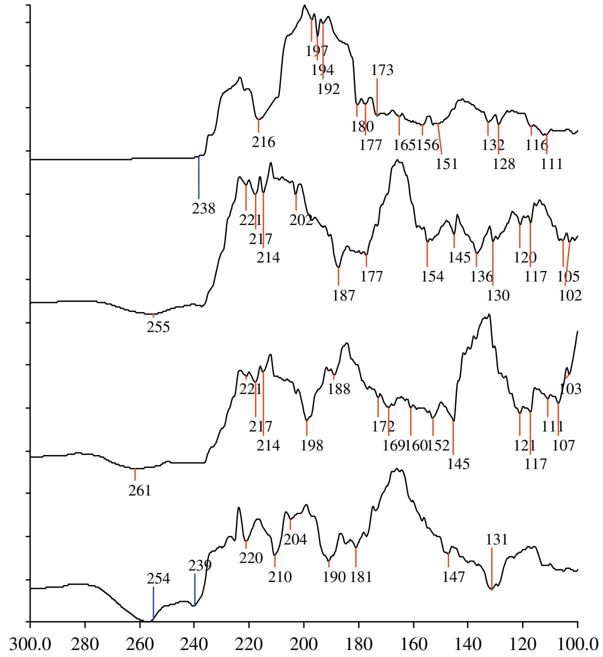

Figure 1 Infrared transmission spectra of Sn_x–Sb_5–Se_{95-x} system.

The second spectrum demonstrates the sample Sn = 5-mole%. A new band ranging from 117 to 145 cm^{-1} is assigned to $SnSe_4$ tetrahedral mode. This band was not observed in the preceding spectrum. However, the fraction of Sn–Se bond shows the possibility of the first chance of forming Sn–Se covalent bond in this composition as reported in Adam et al. (2005). Further, support of this assignment is deduced from Raman analysis on binary Sn–Se, which shows a high intensity peak at 150 cm^{-1} (Adam et al., 2002). Further change in the spectrum is observed when the intensity of the band between 147 and 181 cm^{-1} in Sb_5Se_{95} is reduced and shifted to the new band between 169 and 198 cm^{-1}, with a shoulder at 188 cm^{-1}. This band is ascribed to another pyramidal $SbSe_3$ mode. In contrast, the shoulder at 188 cm^{-1} is assigned to $SnSe_4$ tetrahedral mode. Whereas Raman shift at 189 cm^{-1} was assigned to $SnSe_4$ units in $Ge_{1-x}Sn_xSe_2$ glasses (Stevens et al., 1985). The third band at 198–238 cm^{-1} is attributed to Se–Se or $SbSe_3$ bending modes and its shoulders around 214 and 221 cm^{-1} are assigned to Se_8 chains. It should be mentioned here that since the atomic masses of Sn and Sb are almost similar, their frequency vibrations are not clearly identified from IR analysis. Comparing and supporting the IR analysis with Raman study will clarify any sort of overlapping.

In Sn = 10-mole% spectrum reduction and shift of the band's intensity from around 117–145 cm^{-1} at x = 5 to 154–

187 cm^{-1} are detected. This new band is ascribed to $SnSe_4$ mode. The stretching pyramidal band of $SbSe_3$ is extended between 187 and 237 cm^{-1} with a series of shoulders around 202, 214, 217 and 221. However, the shoulders around 217 and 237 cm^{-1} are attributed to Se-chain mode, which can also be assigned to pyramidal $SbSe_3$ mode. Shift and reduction in the band location and intensity, respectively, are observed when the spectrum of Sn = 12.5 mole% is examined. The band between 132 and 151 cm^{-1} shows a tetrahedral $SnSe_4$ bending mode. However, the band at 180–194 cm^{-1} is ascribed to tetrahedral $SnSe_4$ stretching mode, while that extending between 194 and 216 cm^{-1} is assigned to pyramidal $SbSe_3$ stretching mode. The last band between 216 and 238 cm^{-1} could be assigned to a pyramidal $SbSe_3$ bending mode or to Se_8-chain mode.

3.2. Raman vibration spectra of Sn_x–Sb_5–Se_{95-x} system

Raman spectra for amorphous Se and Sn_x–Sb_5–Se_{95-x} system are shown in Fig. 2. A peak at 250.64 cm^{-1} dominates the Raman spectrum of amorphous Se. This peak is also a characteristic of monoclinic selenium (Mort, 1973). The Raman peak at 250 cm^{-1} is therefore assigned to totally symmetric vibration mode of Se_8-ring based on this evidence and the fact that this line is polarisation dependent. Weak shoulder at 239 cm^{-1} was observed in amorphous Se, which coincided with a dominant peak of crystalline trigonal Se (Mort, 1973). Hence, the low frequency band at 239 cm^{-1} is assigned to Se_8-bending mode. On the other hand, Raman vibrations at 235 and 255 cm^{-1} are assigned to Se–Se chains in Ge_xSe_{1-x} glasses (Wong et al., 1998).

As shown in Fig. 2, Raman spectra of Sn_x–Sb_5–Se_{95-x} system, many bands are identified around 250, 239, 190, 183 and 150 cm^{-1}. It is observed that for Sb_5Se_{95} spectrum ($x = 0$), the peak at 190 cm^{-1} is ascribed to $SbSe_3$ pyramidal vibration symmetrical stretching mode. The two short peaks at 250 and 239 cm^{-1} are assigned to Se_8 stretching and bending modes, respectively. The forth peak at 150 cm^{-1} is attributed to symmetrical bending pyramidal of $SbSe_3$. It is noticeable that changing of Sn, Sb and Se-mole% varies the intensity and width of the Raman peak. The spectrum of Sn = 5 mole% shows a shift and reduction of the peak at 190 cm^{-1}, which is assigned for a pyramidal $SbSe_3$ stretching mode. This change implies the occurrence of Sn sharing the bonds in Sn–Se–$SbSe_3$ net instead of Se–Se bonds. A little higher peak than that of Sb_5Se_{95} is observed at 150 cm^{-1} and assigned to symmetric bending mode of $SnSe_4$ tetrahedral. The peak intensities are increased at 250 and 239 cm^{-1} and implies the existence of Se chains.

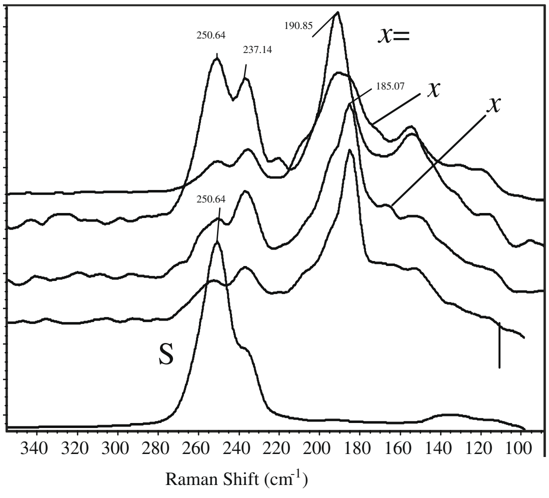

Figure 2 Raman spectra of amorphous Se and Sn_x–Sb_5–Se_{95-x} system, where $x = 0$, 5, 10 and 12.5.

Extreme shift of Raman's peak occurs in the spectrum of Sn = 10 mole%. The pyramidal $SbSe_3$ stretching is still dominant and approaching the symmetric stretching of $SnSe_4$ tetrahedral mode at 185 cm^{-1}. The peak at 184 cm^{-1} was reported for $SnSe_4$ bending mode (Mikurt and McNell, 1890). The trend continues in Sn = 12.5-mole% spectrum while the peak at 184 cm^{-1} is more reasonably attributed to symmetric stretching of $SnSe_4$ tetrahedral mode than stretching of $SbSe_3$ pyramidal mode.

Results of IR and Raman spectroscopes help us to explain the structure of Sn–Sb–Se system. Addition of Sn mole% to the system modifies the Sb–Se structure and incorporates co-ordination number 4 in glass region. Observation of Se stretching bond supports the glass formation in Se-rich region at which the Sn and Sb-mole% are less than their stoichiometric binary compounds with Se. The structure of Sn–Se and Sb–Se glasses can be envisaged as the local co-ordination that satisfies the 8-N rule of the classical valence bond theory (Lucovsky et al., 1977). The structure of Se glasses was believed to consist of long chains of selenium atoms, each having co-ordination number 2 (Aronovitz et al., 1983). To these selenium chains, small amounts of cross-linking atoms, such as Sn and Sb, were added. These amounts should be less than that required for $SnSe_2$ and Sb_2Se_3 stoichiometric compositions. Consequently, the glass structure can build up. Sn atoms are 4 coordinated when covalently bonded and each Sn atom having bonds to Se atoms, while Sb atoms are 3 coordinated and each Sb atom having bonds to Se atoms. It is deduced that the basic structural unit of $SnSe_2$ glass is made of $SnSe_4$ tetrahedral and that of Sb_2Se_3 glass is made of $SbSe_3$ pyramidal. These units spread out among Se chains and form a net of Se_3–Sn–Se–Se–Sb–Se_2 glass structure. The occurrence of a new IR transmission band around 125–145 cm^{-1} and the shift of Raman peak from 190 to 183 cm^{-1}, which happens due to increasing Sn-mole% while Sb-mole% is fixed at 5, are strong evidences that support the configuration of this net structure.

4. Conclusion

IR-transmission results on Sn_x–Sb_5–Se_{95-x} system indicate that asymmetrical stretching of pyramidal $SbSe_3$ mode is dominant around 147 and 210 cm^{-1} and Se-chain mode occurs around 210–254 in binary system. Addition of Sn-mole% causes a shift of the peak and occurrence of new transmission bands around 117–145 cm^{-1} in Sn = 5 mole% until 180 cm^{-1} in Sn = 12.5 mole% spectra, which are ascribed to asymmetrical infrared active of tetrahedral $SnSe_4$ mode. Raman spectra for pyramidal $SbSe_3$ occur at 190 cm^{-1}, while addition of Sn-mole% increases the peak intensity and causes Raman shift towards 183 cm^{-1}, indicating the occurrence of Sn–Se bonds. The results suggest that 4, 3 and 2 are co-ordination numbers of Sn, Sb and Se, respectively, and are the most preferable co-ordination numbers that enhance the glass formation in the Sn–Sb–Se system.

Acknowledgements

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دراسات لطيفي رامان والاشعة تحت الحمراء على زجاج الكالجونيد لمركب (القصدير س- الأنتيمون 5 – السيلينيوم 95- س) Sn_x-Sb_5-Se_{95-x}

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الكلمات المفتاحية: الأشعة تحت الحمراء، طيف رامان ، القصدير، الأنتيمون، السيلينيوم، زجاج الكالجونيد.

ملخص البحث. المركب الثلاثي من عناصر القصدير، الأنتيمون، السيلينيوم يتبع للمركبات الثلاثية المسماه بالكالجونيد لعناصر المجموعة الرابعة - الخامسة – السادسة من الجدول الدوري للعناصر وله تطبيقات عديده في مجال طيف الأشعة تحت الحمراء نظرا لثقل الوزن الذري لعناصره الثلاثه مجتمعة وطاقة الفجوة الممتدة للمركب والثوابت البلوريه وخصائصه الكهربيه المميزه مع تغير نسب الوزن الجزيئي لعناصر المركب الثلاثه.

لقد تم دراسة التركيب الداخلي لمصهور عينات مبردة فجائيا من المركب (القصدير س- الأنتيمون 5 – السيلينيوم 95- س) حيث قيم س تساوي صفر، 5، 10 ، 12.5 من نسبة التركيب الكلي للمركب بواسطة طيف الأشعة تحت الحمراء وتحويلات فوريير وطيف رامان.

لقد اثبتت الدراسة الطيفية بأن إضافة عنصر القصدير بنسب معينه يؤدي الى تغير في الخريطه الطيفية من حيث شدة واتساع الرؤوس القمية للمركب من المدى الطويل الى المدى القصير للطول الموجي ، هذه التغيرات تدل على تكسر روابط عنصر السيلينيوم والتى تظهر في المدى 210- 254 سم$^{-1}$ ومع تكون مركبي ثلاثي سيلانيد الانتيمون الهرمي في المدى 147-210 سم$^{-1}$ ، ورباعي سيلانيد القصدير في المدى 117- 145 سم$^{-1}$ للتركيز 5% وزن جزيئي للقصدير وتصل الى المدى 180 سم$^{-1}$ في حالة إضافة القصدير بنسبة 12.5 % وزن جزيئي.

اثبتت دراسة طيف رامان للمركب ان رأس القمة للمركب ثلاثي سيلانيد الانتيمون حدثت لها إزاحة إلى المدى 190 سم $^{-1}$ من المدى 183 سم $^{-1}$ عندما يضاف عنصر القصدير بنسبة الوزن الجزيئي للمركب. وهذه النتائج تؤكد إمكانية إستخدام عناصر ذات أعدد تناسقية 4، 3، 2 لعناصر القصدير، الأنتيمون، السيلينيوم على الترتيب في المدى الأمورفي (غير المتبلور) كما يمكن إستخدام عدد التناسق $2.4 \le \mu$ للرابطة بين عنصري القصدير والسيلينيوم $f_{Sn-Se} < 44.3\ \%$.