

Infrared and Raman Studies on $\text{Sn}_x\text{-Sb}_5\text{-Se}_{95-x}$ 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 $\text{Sn}_x\text{-Sb}_5\text{-Se}_{95-x}$ 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 $210\text{-}254\text{ cm}^{-1}$ and the occurrence of pyramidal SbSe_3 around $147\text{-}210\text{ cm}^{-1}$ and asymmetrical of tetrahedral SnSe_4 mode around $117\text{-}145\text{ cm}^{-1}$ 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 sited 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 co-ordination numbers of Sn, Sb and Se, respectively in the amorphous region, which is contained by the average coordination number, $\mu \leq 2.4$ and the fraction of Sn-Se bonds, $f_{\text{Sn-Se}} < 44.3\%$.

1- Introduction

Investigation of amorphous and crystallisation 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 [1, 2, 3] the mole % of Sn in $\text{Ge}_{1-x}\text{-Sn}_x\text{-Se}_2$, $\text{As}_{33}\text{-Se}_{67-x}\text{Sn}_x$ and Ge-Sn-Sb-Se were found to be 19.8, 7.0 and 12.5% in glass region, respectively. On other hands selenium based chalcogenide glasses have numerous applications as an efficient solar cell materials, memory switching devices, holographic recording systems, thermal imaging systems and infrared sensors [4-6]. In particular, the introduction of Sn into Sb-Se system, with 4 co-ordination number before stoichiometric compound, was assumed and expected to incorporate in glass formation up to 12.5-mole % of Sn [7-9]. However, above this range, increasing Sn-mole% causes the difficulty of glass formation owing to the distinct metallic character of Sn with 6 co-ordination numbers. 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 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 [10, 11]. In this paper the IR and Raman studies on $\text{Sn}_x\text{-Sb}_5\text{-Se}_{95-x}$ system are obtained and discussed.

2- Experimental procedures

Granules of Sn and Sb having 99.999% purity and that of Se, 99.99% were used. The containers in which these materials were stored in 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 [7, 9]. 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 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 hours was applied at rate of 5°C per minute. 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 in liquid nitrogen for fast cooling requirement. The transmission spectra were obtained at room temperature in the spectral range $300\text{-}100\text{ cm}^{-1}$ 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 $400\text{-}100\text{ cm}^{-1}$ with 4 cm^{-1} step at room temperature, on KBr technique prepared disc using a near 90° scattering configuration. The number of photons counted at each step was stored on a computer.

3. Result and Discussion

3.1. Infrared Spectra of $\text{Sn}_x\text{-Sb}_5\text{-Se}_{95-x}$ System

Figure 1 shows infrared spectra of $\text{Sn}_x\text{-Sb}_5\text{-Se}_{95-x}$ system (where $x = 0, 5, 10$ and 12.5). Infrared transmission (%) versus the wave number (cm^{-1}) in the bottom spectrum shows at least five to six transmission bands. The band that extended from $100\text{-}131\text{ cm}^{-1}$ is assigned to Se_8 -ring bending mode whereas a $115\text{-}131\text{ cm}^{-1}$ band was assigned to Se_8 chain in Ge-Se alloy [12]. The band situated between $131\text{-}190\text{ cm}^{-1}$, with its two shoulders at 147 and 181 cm^{-1} are attributed to SbSe_3 stretching mode as reported in [13]. Furthermore, the band located around $190\text{-}210\text{ cm}^{-1}$ is ascribed to Se-Se stretching mode or Sb-Se bending mode, while the band around $210\text{-}239\text{ cm}^{-1}$ with a shoulder at 220 showed SbSe_3 stretching mode and Se_8 chain mode, respectively. On the other hand, the band around $177\text{-}210\text{ cm}^{-1}$ was assigned to Sb-Se bond in Sb-Ge-Se glass [14]. The transmission cut-off at 254 cm^{-1} is clearly assigned to 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 [10].

The second spectrum demonstrates the sample Sn = 5-mole %. A new band ranging $117\text{-}145\text{ cm}^{-1}$ is assigned to SnSe_4 tetrahedral mode. This band was not observed in the preceding spectrum. However, the fraction of Sn-Se bond showed the possibility of the first chance of forming Sn-Se covalent bond in this composition as reported in [7]. Further, support of this assigning is deduced from Raman analysis on binary Sn-Se, which showed a high intensity peak at

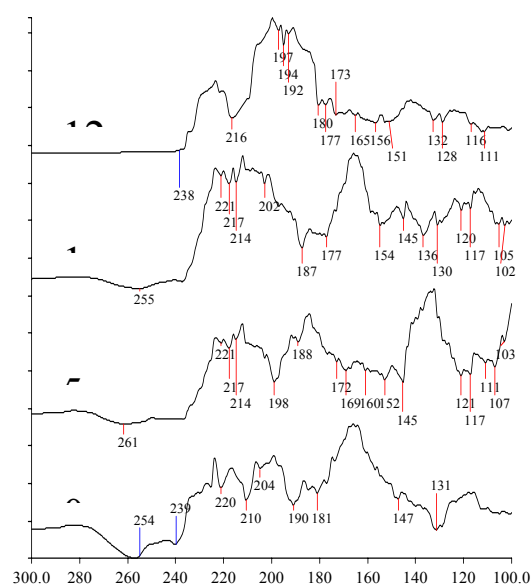


Fig. (1). Infrared Transmission Spectra of $\text{Sn}_x\text{-Sb}_5\text{-Se}_{95-x}$ System.

$150\text{-}150\text{ cm}^{-1}$ [9]. Further change in the spectrum is observed when the intensity of the band between $147\text{-}181\text{ cm}^{-1}$ in $\text{Sb}_5\text{Se}_{95}$ is reduced and shifted to the new band between $169\text{-}198\text{ cm}^{-1}$, 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 $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$ glasses [15]. The third band at $198\text{-}238\text{ cm}^{-1}$ 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 $117\text{-}145\text{ cm}^{-1}$ at $x = 5$ to $154\text{-}187\text{ cm}^{-1}$ are detected. This new band is ascribed to SnSe_4 mode. The stretching pyramidal SbSe_3 's band is extended between $187\text{-}237\text{ cm}^{-1}$ with a series of shoulders around $202, 214, 217$ and 221 . However, the shoulders that allocated around 217 and 237 cm^{-1} are attributed to Se-chain mode, which also can be assigned to pyramidal SbSe_3 mode. Shift and reduction in the band location and intensity are observed when the spectrum of Sn = 12.5-mole % is examined. The band between $132\text{-}151\text{ cm}^{-1}$ shows a tetrahedral SnSe_4 bending mode. However, the band at $180\text{-}194\text{ cm}^{-1}$ is ascribed to tetrahedral SnSe_4

stretching mode, while that extended between 194-216-cm⁻¹ is assigned to pyramidal SbSe₃ stretching mode. The last band between 216-238-cm⁻¹ could be assigned to a pyramidal SbSe₃ bending mode or Se₈-chain mode.

3.2. Raman Vibration Spectra of Sn_x-Sb₅-Se_{95-x} System

Raman spectra for amorphous Se and Sn_x-Sb₅-Se_{95-x} system are shown in Figure 2. A peak at 250.64-cm⁻¹ dominates the Raman spectrum of amorphous Se. This peak was also a characteristic of monoclinic selenium [16]. The Raman peak at 250-cm⁻¹ is therefore assigned to totally symmetric vibration mode of Se₈-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 [16]. Hence, the low frequency band at 239-cm⁻¹ is assigned to Se₈-bending mode. On the other hand, Raman vibrations at 235-cm⁻¹ and 255-cm⁻¹ were assigned to Se-Se chains in Ge_xSe_{1-x} glasses [17].

As shown in Fig. 2, Raman spectra of Sn_x-Sb₅-Se_{95-x} system, many-bands are identified around 250, 239, 190, 183 and 150-cm⁻¹. It is observed that for Sb₅Se₉₅ spectrum ($x = 0$), the peak at 190-cm⁻¹ is ascribed to SbSe₃ pyramidal vibration symmetrical stretching mode. The two short peaks at 250 and 239-cm⁻¹ are assigned to Se₈ stretching and bending modes, respectively. The fourth peak at 150-cm⁻¹ is attributed to symmetrical bending pyramidal SbSe₃. 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 assigned for a pyramidal SbSe₃ stretching mode. This change implies the occurrence of Sn-sharing the bonds in Sn-Se-SbSe₃ net instead of Se-Se bonds. A little higher peak than that of Sb₅Se₉₅ is observed at 150 cm⁻¹ and assigned to symmetric bending mode of SnSe₄ tetrahedral. The peak-intensities are increased at 250 and 239-cm⁻¹ and implied the existence of Se chains.

Extreme shift of Raman's peak is occurred in the spectrum of Sn = 10-mole %. The pyramidal SbSe₃ stretching is still dominant and approaching the symmetric stretching of SnSe₄ tetrahedral mode at 185-cm⁻¹. The peak at 184-cm⁻¹ was reported for SnSe₄ bending mode [2]. The trend is continued in Sn = 12.5-mole % spectrum while the peak at 184-cm⁻¹ is more reasonably attributed to symmetric stretching of SnSe₄ tetrahedral mode than pyramidal SbSe₃ stretching.

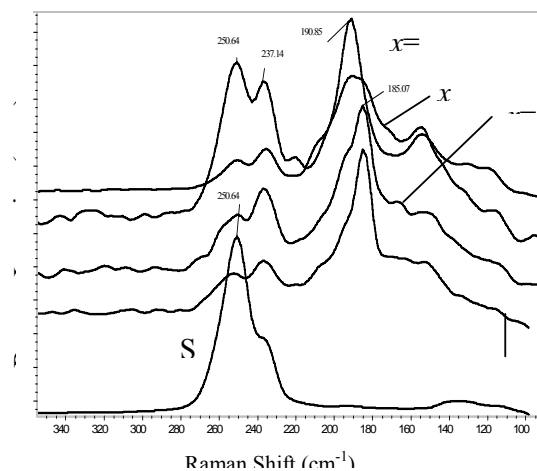


Fig. (2). Raman Spectra of amorphous Se and Sn_x-Sb₅-Se_{95-x} system, where $x = 0, 5, 10$ and 12.5 .

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 with 4-co-ordination number 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 [18]. The structure of Se glasses was believed to consist of long chains of selenium atoms, each having co-ordination number of 2 [19]. 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 SnSe₂ and Sb₂Se₃ 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 SnSe₂ glass is made of SnSe₄ tetrahedral and that of Sb₂Se₃ glass is made of SbSe₃ pyramidal. These units spread out among Se chains and form a net of Se₃-Sn-Se-Se-Sb-Se₂ glass structure. The occurrence of a new IR transmission band around 125-145 cm⁻¹ and the shift of Raman peak from 190 cm⁻¹ to 183 cm⁻¹, which happen due to increasing Sn-mole % while Sb-mole % fixed at 5, are strong evidences that support the configuration of this net structure.

4- Conclusion

IR-transmission-results on Sn_x-Sb₅-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 a new transmission bands around $117\text{-}145\text{ cm}^{-1}$ in Sn = 5 mole % until 180 cm^{-1} in Sn = 12.5 mole %, 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 co-ordination numbers of Sn, Sb and Se, respectively are the most preferable co-ordination numbers that enhance the glass-formation in Sn-Sb-Se system.

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دراسات لطيفي رامان والاشعة تحت الحمراء على زجاج الكالسيوم لمركب
(القصدير^س - الأنتيمون^ه - السيلينيوم^{س-٩٥}) $Sn_x-Sb_5-Se_{95}$

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(قدم للنشر في ٢٤ / ٢ / ١٤٢٩هـ؛ وقبل للنشر في ٢٨ / ٧ / ١٤٢٩هـ)

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

ملخص البحث. المركب الثلاثي من عناصر القصدير، الأنتيمون، السيلينيوم يتبع للمركبات الثلاثية المسماه بالكالسيوم لعناصر المجموعة الرابعة - الخامسة - السادسة من الجدول الدوري للعناصر وله تطبيقات عديدة في مجال طيف الأشعة تحت الحمراء نظرا لثقل الوزن الذري لعناصره الثلاثة مجتمعة وطاقة الفجوة الممتدة للمركب والثوابت البلورية وخصائصه الكهربيه المميزه مع تغير نسب الوزن الجزيئي لعناصر المركب الثلاثة. لقد تم دراسة التركيب الداخلي لمصهور عينات مبردة فجائيا من المركب (القصدير^س - الأنتيمون^ه - السيلينيوم^{س-٩٥}) حيث قيم س تساوي صفر، ٥، ١٠، ١٢.٥ من نسبة التركيب الكلي للمركب بواسطة طيف الأشعة تحت الحمراء وتحويلات فورير 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 والتي تظهر في المدى ٢١٠ - ٢٥٤ سم^{-١} ومع تكون مركبي ثلاثي سيلانيد الأنتيمون الهرمي في المدى ١٤٧ - ٢١٠ سم^{-١}، ورباعي سيلانيد

القصدير في المدى ١١٧ - ١٤٥ سم^{-١} للتركيز ٥٪ ووزن جزيئي للقصدير وتصل الى المدى ١٨٠ سم^{-١} في حالة إضافة القصدير بنسبة ١٢.٥٪ ووزن جزيئي.

اثبتت دراسة طيف رامان للمركب ان رأس القمة للمركب ثلاثي سيلانيد الانتيمون حدثت لها إزاحة إلى المدى ١٩٠ سم^{-١} من المدى ١٨٣ سم^{-١} عندما يضاف عنصر القصدير بنسبة الوزن الجزيئي للمركب. وهذه النتائج تؤكد إمكانية استخدام عناصر ذات أعداد تناسقية ٤، ٣، ٢ لعناصر القصدير، الأنتيمون، السيلينيوم على الترتيب في المدى الأمورفي (غير المتبلور) كما يمكن استخدام عدد التناسق $\mu \leq 2.4$ للرابطة بين عنصري القصدير والسيلينيوم. f $\text{Sn-Se} < 44.3$ ٪.