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As_xSe_{100-x} system ($0 \leq x \leq 16$) studied by StepScan DSC and Raman spectroscopy

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Thermal properties of glassy As_xSe_{100-x} system (x = 0, 1, 2, 4, 8, 16) were studied by means of novel calorimetric method StepScan DSC. This method allows separating both reversible (fast) and kinetic (slow) processes. The glass transition temperature, independent of thermal history of glass, was determined from reversible part of StepScan DSC record. The Raman spectra of glasses studied are discussed, especially the assignment of band in the high-energy part of spectrum in the range 200-300 cm^{-1}. The attention was also focused on the crystallization of undercooled melts of this system.

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1. Introduction

Chalcogenide glasses, as selenium and As-Se glassy system, have been intensively studied during the past decades, predominantly due to its important potential applications. They are applied to switching devices, to optical fibers in non-linear optics and very important is their application as memory media [1,2].

We have performed the StepScan DSC (Perkin-Elmer) measurements in present work. This is a relatively new technique for the enhanced characterization of the thermal properties of materials. An advantage of this method over conventional DSC is that enthalpy effects often accompanied the phase transitions are removed, thus it is used to facilitate the taking of accurate specific heat capacity data. StepScan DSC allows the separation of complex transitions such as the glass transition into two parts. The temperature dependent process (denoted as thermodynamic or reversible part) is separated from the time dependent one (kinetic or irreversible part). In our previous works [3,4] we have found that the reversible part of the glass transition, the temperature dependence of the isobaric specific heat capacity (C_p vs. T), is completely independent on both experimental conditions (especially on heating or cooling rate) and thermal history (relaxation) of glass. It means that this part depends only on the chemical composition of material. Results obtained by StepScan DSC method are similar to ones obtained by other dynamic or temperature modulated DSC (TMDSC) techniques, see e.g. [5,6], but in comparison with TMDSC the StepScan DSC method shows some benefits. This method is straightforward and utilizes the traditional approach for measuring the heat capacity ("two curves method") without the need for deconvolution or the extraction of sine wave amplitudes.

Selenium has been known as a very complicated substance. In the solid state, it exists in one of four allotropes. Trigonal selenium is thermodynamically the most stable crystal form consisting of helical Se_n-chains. Both monoclinic α a β selenium consist of Se_8 rings. Se atoms in the same chain or ring are bonded with covalent bond and the chains or rings are bonded each other by van der Waals forces. The last form of selenium is amorphous one consisting of the mixture of chains and rings according to the way of its preparation [7,8].

The structure of As-Se glassy system with low content of As is described by "chains crossing model" based on the assumption that arsenic atoms are homogeneously distributed among the selenium network. The Se-chains are cross-linked by the $AsSe_3$ pyramids, the richer is the composition in As, the shorter are chains and no signature of any clustering process is evidenced. The validity of this model for the description of As-Se system structure was confirmed, for example by NMR experiments [9,10].

The study of the structure of selenium and of As-Se glassy system by means of Raman spectroscopy has been the subject of many works [11-17], however, the results are relatively inconsistent and up to now an unambiguous vibrational analysis, especially in the high energy range 200 - 300 cm^{-1}, was not published. In the majority of papers authors analyzed only the spectral envelope. It means that they are able to recognize only the main composite peak and some shoulders, depending on spectrometer resolution. This fact could bring some difficulties in determination of the number of vibration modes. As concerned selenium, various authors have found different number of bands in this range (two or three) and proposed their different assignment. Some authors [11,12] have discussed two bands, the most intensive one at 250 cm^{-1} was attributed to vibration of Se_8 rings, while the less intensive band (low energy shoulder) was assigned to the vibration of Se-chains. This assignment is the most frequently used up to now. Recently, thanks to improving technical possibilities of measurement and following analysis of spectra, the papers with different results appear. Authors [13-15] have found three bands in the high energy spectral range at 234, 250 a 260 cm^{-1}. The first one at 234 cm^{-1} was assigned to the intra-chain bond-stretching vibration of Se chains in configuration resembling trigonal selenium. The most intensive band at 250 cm^{-1} was attributed to the intra-chain bond-stretching vibrational mode of the disordered Se chains while the low intensity one at 260 cm^{-1} was assigned to the intra-ring bond-stretching vibrational mode of Se_8 molecule. In the low energy region (70 - 140 cm^{-1}) they found two peaks that were considered to originate from bond-bending vibration of ringlike (112 cm^{-1}) and chainlike (138 cm^{-1}) species. This assignment is in accordance with this one, done by Lucovsky [11].

After addition of As into selenium matrix the new band at 227 cm^{-1} was found in the Raman spectrum [16,17]. This one was attributed to As-Se stretching vibrational mode of the $AsSe_3$ pyramidal molecule.

The crystallization of system As_xSe_{100-x} up to x = 10 were studied by conventional DSC [18]. Authors found for glasses with $x \geq 2$ that the melting enthalpy of the same composition is lower than enthalpy of crystallization. Surprisingly they did not comment this result. According to our opinion their samples were very probably partly crystallized before DSC scans and so results obtained should be used with caution.

The main aim of this work is using StepScan DSC and Raman spectroscopy to elucidate the influence of chemical composition on both structure and thermal properties of As_xSe_{100-x} glassy system with arsenic content lower then eutectic composition (x < 20). The attention was focused on the influence of low arsenic content on the crystallization ability of selenium.

2. Experimental

Non-crystalline selenium was prepared by the melt-quenching technique. The selenium of high-purity (5N) was sealed in evacuated silica ampoule and melted for 2 hours at 850 °C, than quenched in air. As_xSe_{100-x} bulk glasses were prepared by conventional method of direct synthesis from high-purity (5N) elements. The mixture of elements was placed into evacuated silica ampoules and synthesized in a rocking furnace (850 °C, 7 hrs.) Melt was quenched in cold water.

The DSC measurements were carried out with help of differential scanning calorimeter Pyris 1 (Perkin-Elmer). Finely powdered glassy samples (approx. 4 mg for conventional DSC and 10 mg for StepScan DSC measurements) were encapsulated into sealed aluminium pans. Empty pan was used for baseline run.

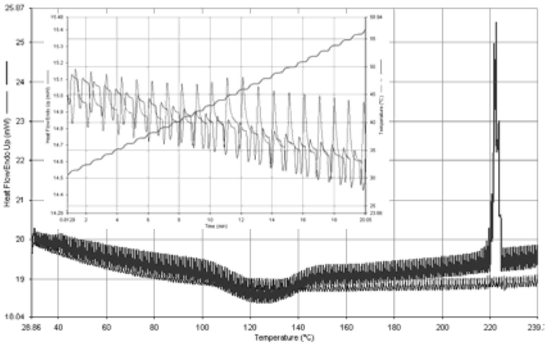

Fig. 1. Typical StepScan DSC scans (glassy-Se and baseline run); the inset shows detail of the scan in the glass transition range and stepwise temperature profile.

To obtain values of glass transition temperature, T_g, and the change of isobaric specific heat capacity at glass transition, ΔC_p, independent on experimental conditions (especially on heating or cooling rate) and thermal history of glass the StepScan DSC software (Perkin Elmer) was used. StepScan DSC technique is based on repeatedly measured heat flow of a known amount of sample at a constant heating rate, q, compared to that of the heat flow in an adjacent isotherm. The duration of isotherm at each step depends on the response of sample and is software controlled. Hence, the equilibration time is minimized during temperature region where the sample response is rapid, and extended when more time is required. Typical StepScan DSC scan is in Fig. 1 and the final result after calculation is in Fig. 2. Reversible part corresponds to temperature dependence of C_p. The irreversible part reflects enthalpy of kinetic processes.

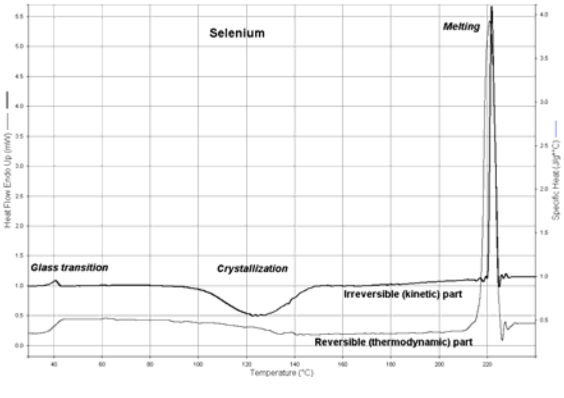

Fig. 2. The result of StepScan DSC measurement (glassy-Se).

The experiments were carried out with following parameters. The temperature step 1 °C was used and heating rate in the scanning step was 20 °C/min. The maximal allowed heat flow difference during isotherm before next step was $\Delta Q = \pm 0.1$ μW.

Isothermal crystallization was studied by conventional DSC technique. Sample was heated up to the temperature of isothermal crystallization (160 °C) with rate 2 °C/min to ensure nucleation. Crystallization was checked by Raman spectroscopy.

Raman spectra were measured by FTIR spektrometer IFS 55 (Bruker) with Raman module FRA 106 and Nd:YAG excitation laser (1064 nm). Ge-detector cooled by liquid nitrogen was used.

3. Results and discussion

3.1 StepScan DSC measurement

Glassy system As_xSe_{100-x} (x = 0, 1, 2, 4, 8 and 16 at.%) was studied by StepScan DSC. The glass transformation temperature, T_g, was determined as the midpoint at the reversible part of StepScan DSC scan. The glass transition temperature increases with increasing content of As, see Fig. 3. Only one glass transition was found and thus this system is homogeneous.

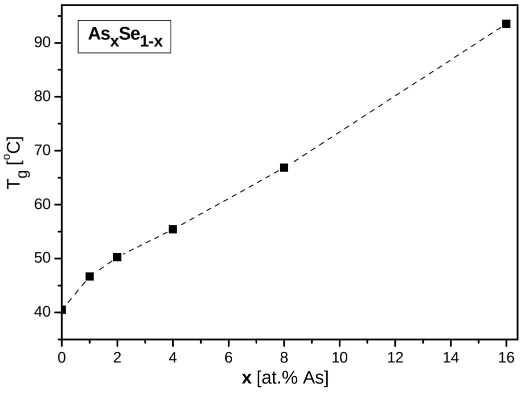

Fig. 3. The compositional dependence of glass transition temperature for As_xSe_{100-x} glassy system (StepScan DSC). Dashed line is merely to guide the eye.

The values of glass transition temperature taken from conventional [19] and temperature modulated data [20] agree with our measurements, but only in general trend. As we mentioned above, in comparison with these methods, T_g found by StepScan DSC is completely unaffected by any kinetic process, so that this value depends only on composition of glass.

The change of isobaric specific heat capacity at the glass transition, ΔC_p, was also determined for the glassy system studied from reversible part of the StepScan DSC trace. The values of ΔC_p (difference between isobaric heat capacity of glass and undercooled melt) did not change significantly with increasing content of As, within an experimental error, for composition 1 - 8 at.% of As, the mean value was found to be $\Delta C_p = 0.156 \pm 0.006$ J/(g∗K). In the case of glass $As_{16}Se_{84}$, ΔC_p fell down to the value $\Delta C_p = 0.129$ J/(g∗K).

This reduction of ΔC_p means that structure of $As_{16}Se_{84}$ glass and its undercooled melt is closer each other than in the case of samples with lower arsenic content.

3.2 Raman spectroscopy

Experimentally obtained Raman spectra of all glasses studied can be divided into two parts - energy region from 50 to 150 cm^{-1} (bond-bending vibrational modes) and higher energy region in the range 200 - 300 cm^{-1} (bond-stretching vibrational modes).

At low energy region less intensive band at 112 cm^{-1} was found. The presence of this band is considered as direct evidence of the existence of Se_8 rings in the glass structure [11,13].

In this work the main attention was paid to the study of high energy region, because analysis of this part of Raman spectrum found in literature contradict each other. The high energy part of Raman spectra of glassy selenium and As-Se system studied are shown in Fig. 4. One can see intensive band at 254 cm^{-1} and two shoulders at 226 and 262 - 283 cm^{-1}, respectively.

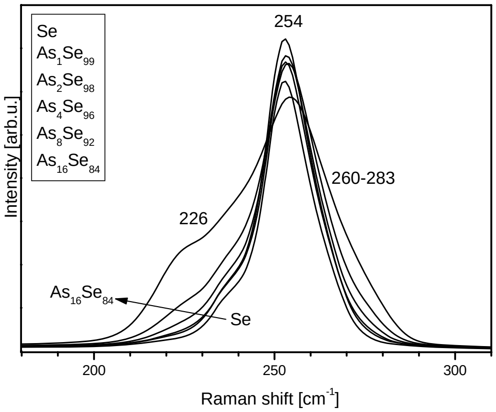

Fig. 4. Higher energy part of Raman spectra of As-Se system glasses; As content changes from 0 to 16 at.%. For details see text.

To discuss Raman spectra of studied system, the spectrum of glassy selenium must be analyzed first. The high energy part of the glassy selenium spectrum should be fitted unambiguously with three peaks (see first derivative of experimental data, Fig. 5). Their frequencies were found at 239, 252 and 262 cm^{-1}. Contrary to Lucovsky, who has found only two vibrations at 235 and 250 cm^{-1} [11], our result agrees well with Yannopoulos [13]. To elucidate the nature of bands found we dissolved glassy selenium in CS_2 and undissolved part was separated by filtration. Monoclinic α and β selenium, that are comprised of Se_8 rings, was prepared by crystallization from red colored CS_2 solution. Raman spectra of both undissolved part and monoclinic selenium were measured, see Fig. 6.

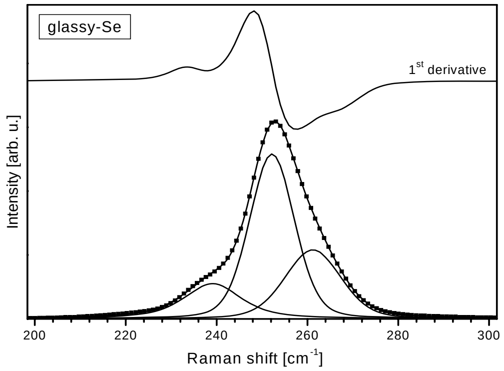

Fig. 5. Raman spectrum of glassy Se; squares - experimental spectrum, full lines - computer fit; first derivative of experimental spectrum is included, see text.

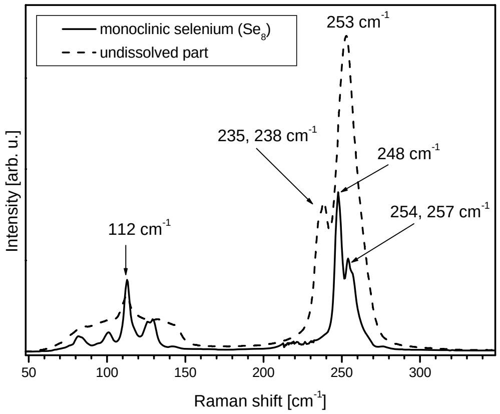

Fig. 6. Raman spectra of both crystalline cyclooctaselenium and the rest of glassy selenium after dissolution in CS_2; band at 253 cm^{-1} indicates that the dissolution of Se_8 rings wasn't complete.

The spectrum of undissolved part is characterized by the considerable increase of 239 cm^{-1} band. This energy has been commonly assigned to the vibration of trigonal selenium chains (*trans*-conformation), see e.g. [11,12]. As concerns the main composite spectral peak we have found that its intensity decreased during dissolution but without shape changing. From it follows that intensities of both 252 and 262 cm^{-1} band, creating this composite peak, decrease in the equally so these two bands have to be related to Se_8-like vibrations. Thus the undissolved part is composed of both the unsoluble Se_n chains and residual undissolved Se_8 rings.

Raman spectrum of crystals obtained by recrystallization of selenium CS_2 solution (monoclinic selenium) contains in this frequency range two narrow bands close each other (248 and 256 cm^{-1}). Their frequencies correspond to broad band at 252 cm^{-1} of glassy selenium. We must stress that there is no band at approx. 262 cm^{-1} in the spectrum of monoclinic selenium. From above mentioned it results that satellite band at 262 cm^{-1} arises from vibration of Se_8 residuals, e.g. selenium chains originate from Se_8-rings broken during glass preparation (*cis*-conformation of chains).

In the Raman spectra of As_xSe_{100-x} glasses (x = 1, 2, 4, 8, 16) we have found four bands in the in the range 200 – 300 cm^{-1}, for example see Fig. 7. Three ones of them are at the same energies as in the glassy selenium (239, 252 and 262 cm^{-1}), see above.

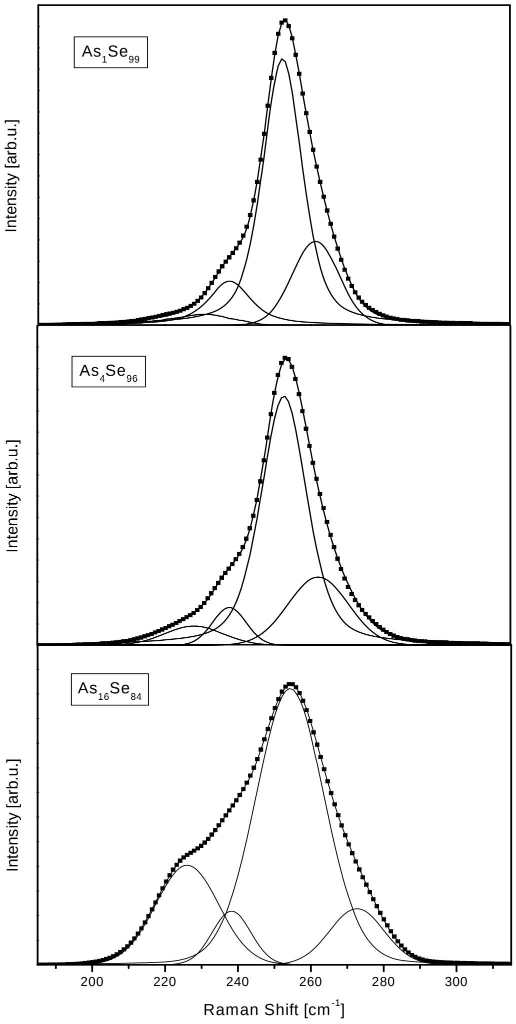

Fig. 7. Computer fit of Raman spectrum of selected $As_xSe_{(100-x)}$ glasses; squares - experimental spectrum, full lines - computer fit.

Fourth band appears at ~ 230 cm^{-1} and with increasing content of As its intensity increases and band position slightly moves to lower energies. This band has been attributed to the As-Se vibrational mode of the $AsSe_3$ pyramids [16,17]. Contrary to Mikla et al. [17], who have found this band in As-Se system for arsenic content higher then 2 at.%, we have identified this one even at composition containing 1 at.% As.

We have found that peak at 262 cm^{-1} of glassy Se moves significantly up to higher energies when arsenic content is not less than 8 at.%. For $As_{16}Se_{84}$ glass its energy is 273 cm^{-1}. In the case of glassy Se we have assigned peak at 262 cm^{-1} to the vibrations of fragments (chains) originating from Se_8 rings, as it was mentioned above. One can easily imagine that As atoms can bind readily these fragments and joining selenium chains in *cis*-conformation by $AsSe_3$ pyramids into compact net. As a result, bond-stretching vibrational mode of these selenium chains is affected by adjacent arsenic atoms and its energy moves up.

3.3 Crystallization of undercooled melts

Non-isothermal, as well as isothermal crystallization of As_xSe_{100-x} system was studied. The non-isothermal crystallization was investigated by StepScan DSC and the crystallization enthalpy was determined from kinetic part of StepScan DSC scan.

Using StepScan DSC and average heating rate 0.9 K/min, the crystallization of undercooled melts containing 1, 2 and 4 at.% As was identified. Undercooled melts with 8 and 16 at.% As did not crystallize during StepScan DSC runs. Thus long time isothermal crystallization at 160 ^oC (the temperature of sufficiently high crystal growth rate [21]) was used to test crystallization ability of these melts. The undercooled melt with chemical composition As_8Se_{92} partly crystallized after 5 hrs., contrary to melt of $As_{16}Se_{84}$ where the crystalline phase was not found even after 20 hours.

Crystallization was detected by Raman spectroscopy during. It was found that crystalline phase is formed only by selenium. Two intensive Raman bands at 144 and 237 cm^{-1} were found in spectra of crystalline phase corresponding to vibration of Se-chains in conformation belonging to trigonal selenium [11]. Due to this fact the crystallization enthalpies of As-Se system, obtained by StepScan DSC, were related to the enthalpy of crystallization of trigonal selenium. Based on it, the degree of crystallization was calculated, see Fig. 8.

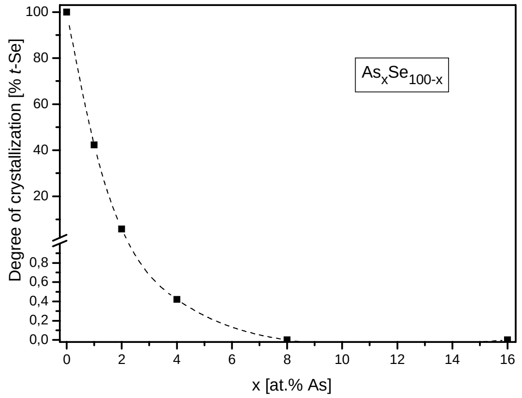

Fig. 8. Degree of crystallization of As_xSe_{100-x} system after StepScan DSC run (average heating rate 0.9 $^oC/min$). Degree of crystallization was recalculated to selenium content for each chemical composition. Dashed line is guide to the eye.

These results are in agreement with ones mentioned above. As it is evident, the behavior of $As_{16}Se_{84}$ differs from other compositions studied because its cross-linked structure is more compact and thus has no tendency to crystallize.

4. Conclusions

The As_xSe_{100-x} glassy system (x = 0, 1, 2, 4, 8 and 16 at.%) was studied by means of novel calorimetric method StepScan DSC and Raman spectroscopy.

Comparing both Raman spectra of glassy selenium and monoclinic selenium (Se_8) we have been able to decide unambiguously that the most intensive vibrational mode at 252 cm^{-1} belongs to the vibration of Se_8 rings. Satellite band at approx. 262 cm^{-1} originates very probably from vibration of Se_8 fragments (*cis*-conformation of selenium chains).

As for thermal properties it was found that the glass transition temperature increases almost monotonically with increasing arsenic content. The isobaric heat capacity change at glass transition, ΔC_p, remains practically constant in the compositional range x = 0 - 8 at.% As, but decreases of about 20 % for $As_{16}Se_{84}$ glass.

The tendency of selenium to crystallize from undercooled melts of As-Se system decreases markedly and vanishes completely for arsenic content higher than 8 at.%, as a consequence of increasing cross-linking of selenium chains by arsenic atoms.

As it is evident, the behavior of $As_{16}Se_{84}$ differs from other compositions studied. The Raman band at 273 cm^{-1}, attributed to the vibration of -Se-Se- bridges between $AsSe_3$ pyramidal units, indicates sufficiently high arsenic content to cross-link the selenium matrix. The fact, that isobaric heat capacity change at the glass transition of $As_{16}Se_{84}$ drops down of about 20 %, compared to the systems with lower arsenic content, means that structure of both glass and undercooled melt are close each other more then in the case of selenium more rich glasses.

Stemming from thermal properties and Raman spectra we can conclude that the structure of studied glasses can be described as heterogeneous system containing selenium chains more or less bridged by As atoms, and molecules of Se_8. As arsenic content increases up to the eutectic composition (20 at.% As), the heterogeneous glassy network, as well as undercooled melt contains sufficiently high concentration of cross-linked selenium chains to avoid selenium crystallization.

Acknowledgements

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