# RAMAN SPECTRA OF $As_x Se_{100-x}$ and $As_{40}Se_{60}$ GLASSES DOPED WITH METALS

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Chalcogenide glasses in the system $As_x Se_{100-x}$, as well as $As_{40}Se_{60}$ and $As_{50}Se_{50}$ glasses doped with metals (Bi, Ge, Cd, Ag, Sn, Mn, Dy and Sm) were investigated by Raman spectroscopy. The Raman spectra of $As_x Se_{100-x}$ with $0 \leq x \leq 10$ suggest that the majority building units are Se chains and $Se_8$ closed rings. At higher As contents, new structural units are formed from As and Se atoms. The Raman profiles for $x > 50$ are characterized by the presence of strong narrow bands indicating an advanced ordering in the structure of these glassy materials. The doped samples with small amount of metals, $0.1 - 1.0$ at.%, do not show significant modification of their short-range order, with the exception of the 0.5 at.% Dy-doped sample. For the sample $As_{50}Se_{50}+7.5$ at.% Sn, there is direct evidence for the formation of new Sn-based structural units, such as $Sn(Se_{1/2})_4$ tetrahedra.

*Keywords*: Chalcogenide glassy, Rare-earth ions, Raman spectroscopy

## 1. Introduction

Chalcogenide glasses are widely used in technological applications such as infrared optical elements, acousto-optic and all-optical switching devices, holography recording media etc. Information on the short-range order structure of chalcogenide glasses is particularly valuable in order to establish useful correlations between their structural and macroscopic properties. To this aim, infrared and Raman spectroscopic techniques are powerful tools for probing the structural properties of chalcogenide materials [1,2]. Recently, the analysis of Raman spectra of binary arsenic sulfide chalcogenide glasses, $As_x S_{100-x}$, evidenced the presence of phase separation effects for $x < 25$ [3] and the occurrence of intrinsic nanoscale phase separation for $x = 40$ [4, 5]. In our previous work [6], it was shown that doping of $As_2 S_3$ with 0.5 at.% Mn leads to the appearance of additional narrow bands in the corresponding Raman spectra in the frequency region 130-220 $cm^{-1}$, and they were associated with the formation of new sulphur-containing structural units: as e.g. MnS clusters.

In this work, we present a structural investigation by Raman spectroscopy of chalcogenide glasses in the system $As_x Se_{100-x}$, and of $As_{40}Se_{60}$ and $As_{50}Se_{50}$ glasses doped with metals (Bi, Ge, Cd, Ag, Sn, Mn, Dy and Sm). The obtained results are discussed in the framework of the molecular structure model for chalcogenide glasses and are compared with literature data.

## 2. Experimental

Chalcogenide glasses $As_x Se_{100-x}$ ($x=0, 5, 10, 40, 50, 60$) were synthesised by using elements (As, Se) of 6N purity, which were melted in evacuated ($p \sim 10^{-5}$ Torr) and sealed silica ampoules at $800 \div 850$ $^{o}$C for 8 hours and subsequently quenched in cold water. The prepared bulk glasses were

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cut into plates of 2÷3 mm in thickness with a low speed diamond saw, and polished to yield samples with high quality flat surfaces suitable for optical measurements. Raman spectra were measured on a Fourier-transform Raman spectrometer (Bruker RFS100) in the back-scattering geometry with a resolution of 2 cm$^{-1}$. The 1064.4 nm excitation line of a Nd-Y laser was used, leading to Raman spectra free of luminescence background.

## 3. Results and discussion

### 3.1. X-ray diffraction patterns

It was established from the X-ray diffraction investigation that the position and intensity of the first sharp diffraction peak (FSDP) is changed as a result doping of the $As_2Se_3$ glass by tin. The quasi-distance calculated from the position of FSDP is 4.32 Å for pure $As_2Se_3$ glass and increases up to is 4.547 Å for $As_2Se_3$+3.5 at.% Sn[6]. The metals Dy, Pr, Sm, Ho, Er and Nd enter the host glass as $3^+$ ions, and, due to charge and large ion dimensions, induce deformations in the host matrix. The disordered layers of the glass structure are locally distorted by insertion of the metal atoms that bond to selenium. A high covalencey of the Me-Se bond gives rise to strong directional bonds and the layers become more rigid while high metal ionicity diminishes the stiffness of the layers. The Sm and Dy atoms with higher electronegativity produce a shift of the interlayer distance towards a lower value, i.e. rare-earth atoms play the role of network modifiers that smooth the disordered $As_2Se_3$ layers allowing for a better packing at a smaller thickness. The impurity therefore strongly influences the network of the host glass as regarding both the short-range and medium-range order, and we may expect a significant influence on the Raman spectra of chalcogenide glasses doped with metals.

### 3.2. Raman spectra of $As_xSe_{100-x}$ glasses

The Raman spectra of $As_xSe_{100-x}$ bulk glasses are reported in Figs.1 and 2. For the pure selenium sample, x=0, the spectrum is characterized by a strong band at 238 cm$^{-1}$ which is attributed to the vibrational mode of –Se-Se-Se- chains [2].
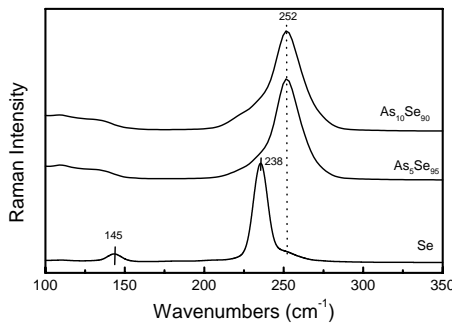


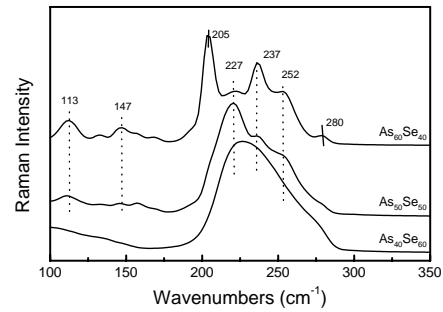Fig. 1. Raman spectra of bulk samples of Se (1), $As_5Se_{95}$ (2), $As_{10}Se_{90}$ (3).

Fig. 2. Raman spectra of bulk samples of $As_{40}Se_{60}$ (4), $As_{50}Se_{50}$ (5), $As_{60}Se_{40}$ (6).

Additional weaker features can be revealed at 252 and 145 cm$^{-1}$ which are assigned to the presence of $Se_8$ rings and to the bending modes of Se units [2,7]. According to Ref.[8], amorphous selenium consists of a mixture of chains ($Se_n$) and rings ($Se_8$) with covalent bonding of the atoms in rings and Wan der Waals weak bonding between the atoms in chains. The average inter-atomic distance is about 2.37 Å. For the selenium rich binary glasses, $0 <x \leq 0.10$, the 252 cm$^{-1}$ band

dominates the corresponding Raman spectra while the 238 cm$^{-1}$ band becomes very weak. This trend is consistent with the progressive breaking of Se-chains by As atoms.

Further increase of the arsenic content in $As_xSe_{100-x}$ bulk glasses causes substantial changes in the Raman spectra (Fig.2). The main band situated at ca. 250 cm$^{-1}$ for x=10 becomes broader and shifts to lower frequency values for x=40. For higher x values, this broad profile splits into several narrow distinct peaks at 205, 227, 237, 252 cm$^{-1}$, which dominate the spectrum of the x=60 sample. These strong narrow peaks evidence the high degree of ordering in these chalcogenide glasses. While the peak situated at 252 cm$^{-1}$ was previously assigned to $Se_8$ rings, the additional features indicate the formation of new structural units consisting of both As and Se atoms. In particular, $As_4S_4$ cages contribute to the 205 cm$^{-1}$ feature, $AsSe_3$ pyramidal units to the 227 cm$^{-1}$ band and $As_4Se_3$ entities to the 237 cm$^{-1}$ band [2]. The additional narrow bands situated in the 100-200 cm$^{-1}$ region confirm the presence of structural units containing As—As bonds. Finally, the narrow band at 280 cm$^{-1}$ which appears as a shoulder in the Raman spectra of the $As_{60}Se_{40}$ sample, can be assigned to the vibrational mode of —Se—Se— bridges between $AsSe_3$ pyramidal units and $As_4Se_4$ or $As_4Se_3$ cages [2].

### 3.3. Raman spectra of $As_{50}Se_{50}$ and $As_{40}Se_{60}$ glasses doped with metals and rare-earth ions

The Raman spectra of $As_{50}Se_{50}$ glasses doped with metals belonging to the I-V groups of the periodic table (Ag, Cd, Ge, Sn, Bi) are depicted in Fig. 3.
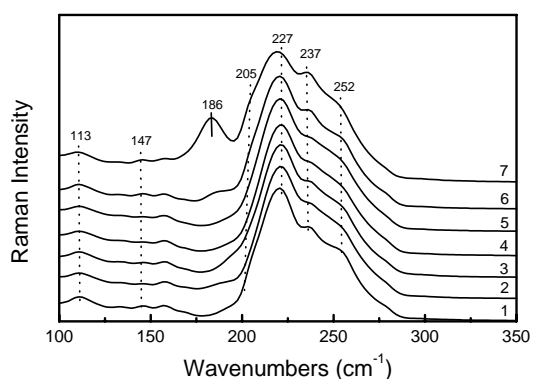


Fig. 3. Raman spectra of bulk samples of $As_{50}Se_{50}$ (1) doped with: 1.0 at.%Bi (2), 1.0 at.%Ge (3), 1.0 at.%Cd (4), 1.0 at.%Ag (5), 1.0 at. % Sn (6), and 7.5 at.%Sn (7).
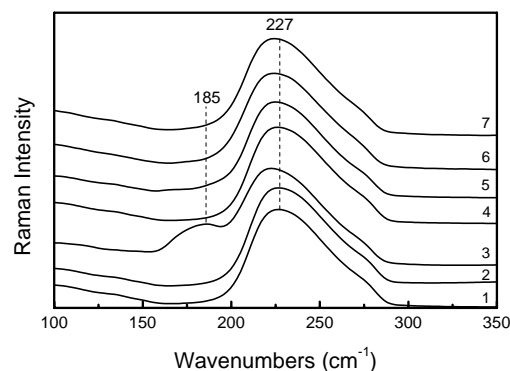
Fig. 4. Raman spectra of bulk samples of $As_{40}Se_{60}$ (1) doped with: 0.1 at.% Dy (2), 0.5 at.% Dy (3), 0.1 at.% Sm (4), 0.5 at. % Sm (5), 0.1 at.% Mn (6), 0.5 at. % Mn (7).

All spectra present their strongest band at 223 cm$^{-1}$, which was assigned to $AsSe_{3/2}$ pyramidal units. In addition, the features associated to $As_4Se_3$ cages, 237 cm$^{-1}$, and to $Se_8$ rings, 252 cm$^{-1}$, are also evident. The introduction of small amounts of metals, around 1.0 at.%, does not alter the corresponding Raman profiles, suggesting that the short-range order structure of the glass matrix is not affected by the foreign metals. For the sample with a higher amount of Sn impurities, 7.5 at.% (curve 7), the Raman spectrum shows an additional strong band situated at ca. 186 cm$^{-1}$. This new feature can be attributed to the formation of $Sn(Se_{1/2})_4$ tetrahedral units. Introduction of Sn additive in the $As_{50}Se_{50}$ host glassy matrix promotes the growth of $Sn(Se_{1/2})_4$ structural units, thus leading to a more As-rich network with the formation of monomeric $As_4Se_4$ cages based on realgar - type structure [10]. This is further confirmed by the enhancement of the intensity at 205 cm$^{-1}$ in the Raman spectrum, which is attributed to $As_4Se_4$ cages.

The Raman spectra of $As_{40}Se_{60}$ glasses doped with different concentrations of rare-earth metal ions (0.1 and 0.5 at.% of Dy and Sm) and transition metal ions (Mn) are presented in Fig. 4.

As shown, with the exception of the sample doped with 0.5 at.% of Dy, the doping of the base glass with small concentrations of rare-earth ions does not affect the Raman profiles and, consequently, the short-range order structure does not change.
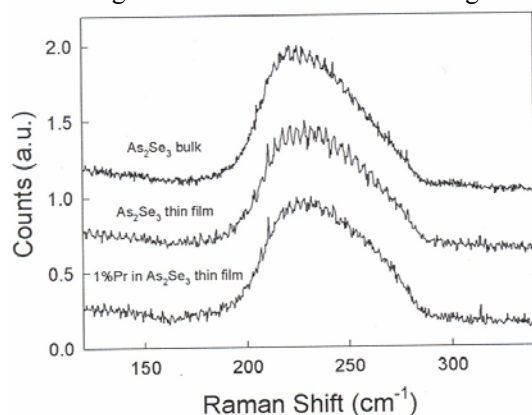


Fig. 5. Raman spectra of $As_{40}Se_{60}$ bulk glass, $As_{40}Se_{60}$ thin film and $As_{40}Se_{60}$+1.0 at.% Pr thin film.
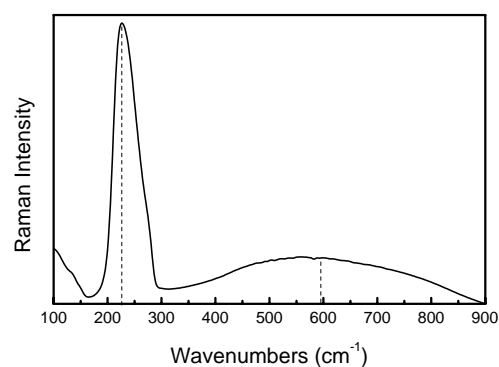
Fig. 6. Raman spectra of bulk samples of $As_{40}Se_{60}$ doped with 0.1 at.% Dy.

The same result was found also in the case of $As_2S_3$ glasses doped with the same amount of rare-earth and Mn ions [6]. In the case of $As_{40}Se_{60}$+0.5 at.% Dy, the Raman spectrum exhibits an additional band located around 185 cm$^{-1}$. This new band can be attributed to the appearance of new structural units like DySe or DySe$_2$. The Raman spectra of bulk glasses of $As_{40}Se_{60}$, thin films, and $As_{40}Se_{60}$+1.0 at.% Pr thin films are similar (Fig. 5). The same Raman spectra of bulk glasses and thin films of $As_{40}Se_{60}$ confirm that the composition during thermal evaporation dose not changes. The existence of these structural units was suggested from a recent X-ray diffraction, and electrical from photoelectrical studies carried out on $As_{40}Se_{60}$ glass doped with rare-earth ions [11]. For the $As_{40}Se_{60}$ glass doped with 0.1 at.% Dy a broad fluorescence band situated in the range 300-900 cm$^{-1}$ with maximum around 600 cm$^{-1}$ was observed (Fig. 6). This finding suggests that optical fibres fabricated from rare-earth doped chalcogenide glasses can be used as Raman amplifiers [11,12]. According to Ref. [12] the Raman optical fibers amplifiers from chalcogenide glasses have a Raman gain 340 times greater than that of silica.

## 4. Summary

Chalcogenide glasses in the system $As_xSe_{100-x}$, $As_{50}Se_{50}$ doped with metals (Bi, Ge, Cd, Ag, Sn), and $As_{40}Se_{60}$ doped with rare-earth ions (Dy and Sm) and Mn were investigated by Raman spectroscopy. For $As_xSe_{100-x}$ glasses, it was found that adding arsenic in pure Se glass, $0<x\leq10$, results in the progressive rupture of –Se-Se-Se- chains while closed Se$_8$ rings constitute the major species in the network structure. Further addition of As causes the formation of new As-Se structural units, like AsSe$_3$ pyramids, As$_4$Se$_3$ and As$_4$Se$_4$ cages. Doping $As_{50}Se_{50}$ glasses with small amount of metal ions, 1 at.%, does not affect the short-range order structure of the host matrix. However, in the sample with higher content of Sn impurities, 7.5 at.%, the formation of $Sn(Se_{1/2})_4$ tetrahedral units occurs. In the case of $As_{40}Se_{60}$ glasses doped with 0.1 or 0.5 at.%, Dy, Sm and Mn the network structure of the host glass is not altered with the exception of the 0.5 at% Dy doped composition. This outstanding behaviour was ascribed to the formation of new structural units, like DySe or DySe$_2$, in agreement with previous results.

**Acknowledgement**

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