

## X-RAY ABSORPTION NEAR EDGE STRUCTURE OF $\text{As}_2\text{Se}_3$ AND $\text{As}_4\text{Se}_4$ THIN AMORPHOUS FILMS

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X-ray absorption spectroscopy has been used to get information on the structure of chalcogenide glasses. The data analysis was focused on the near edge X-ray absorption spectrum. The experimental As and Se K-edge absorption spectra of thin films of  $\text{As}_2\text{Se}_3$  and  $\text{As}_4\text{Se}_4$  have been measured in Beijing synchrotron at the beam line, using a double crystal monochromator with Si (111) crystals. The near-edge absorption curves were resolved in two components: the strong white line at the energy threshold and the first oscillatory part following the white line at approximately 7-8 eV above the K-edge, which undergoes changes in shape and position as a function of the modifications in the atomic structure induced by the change of composition. The XANES characteristic for the two types of films allows to conclude that the local disorder around As and Se is different. The non-stoichiometric composition,  $\text{As}_4\text{Se}_4$ , exhibits more disorder than the stoichiometric one.

### 1. Introduction

Chalcogenide and especially  $\text{As}_2\text{Se}_3$  are important glasses due to their potential applications in optoelectronics, holography, non-linear optics and so on [1-10]. Recently, the As (S, Se) glasses were utilized as core materials, for efficient fiber amplifiers as they exhibit high refractive index and very low phonon energy maxims due to strong covalent bonding [11]

In spite of the numerous studies the  $\text{As}_2\text{Se}_3$  glass and amorphous films based on this composition is incompletely known [12-21]. The studies of the structural and electronic properties of the arsenic chalcogenides are of particular importance since electrical and optical properties are strongly influenced by short-range order around the metal atom [22] One of the most powerful method for obtaining information on the structure and structural modifications induced by light and other radiations in chalcogenides is the X-ray absorption spectroscopy [23].

Pfeiffer, Rehr and Sayers ([24] investigated the atomic scale ordering of  $\text{As}_2\text{S}_3$  glass on the basis of X-ray absorption near-edge structure. A detailed analysis of the experimental data was carried out in conjunction with an XANES cluster calculation and an interpretation of the near-edge structure of a-  $\text{As}_2\text{S}_3$  has been developed. Nevertheless the authors do not give a definite conclusion on the atomic-scale ordering in  $\text{As}_2\text{S}_3$  glass.

Jinn-lung Wang et al. [25] investigated the structural properties of As-Se-S glass system by X-ray absorption spectroscopy. The results suggest that arsenic be in trivalent state while selenium is in divalent state. The homopolar bonding (As-As) is increasingly eliminated with increasing replacement of selenium by sulfur in ternary glasses. A more detailed analysis of the electron transitions giving rise to the bound levels in  $\text{As}_2\text{Se}_3$  was carried out relying on the electronic band structure calculations for crystalline  $\text{As}_2\text{Se}_3$  [26]

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Recently, it was demonstrated that As near K-edge region is very sensitive to details of the local atomic structure in arsenic chalcogenide during light irradiation [27-29].

We report in this paper the results obtained in the study of two amorphous films:  $\text{As}_2\text{Se}_3$  and  $\text{As}_4\text{Se}_4$  using X-ray absorption spectroscopy.

## 2. Experimental

X-ray absorption measurements have been performed at beam lines in Beijing Synchrotron Radiation Facilities (BSRF) operating at 30-50 mA and 2.2 GeV at room temperature. The 4W1B beamline is an unfocussed monochromatic X-ray beam with 4 mrad of horizontal acceptance. The X-rays were monochromatized by a fixed exit Si double crystal monochromator. The features of the 4W1B beam line are: an energy range of 3.5-2.2 keV, an energy resolution of  $\Delta E=1\div 3$  eV at  $E=10$  keV, a Bragg angle range of  $5\div 70^\circ$ . The crystals Si(111), Si(200), Si(311) can be alternatively used. A nickel foil was used as a standard sample. The absorption coefficients of As and Se K-edge were determined using a Si(111) double-crystal monochromator. The X-ray intensities of the incident and transmitted beams were monitored by ionization chambers. Detuning the monochromator rejected harmonics.

A focal spot with a size of  $1.5 \text{ mm} \times 1.0 \text{ mm}^2$  thickness was expected at 18.665 m from the light source.

The X-ray absorption edge of As and Se were measured in the range 11700-12900 eV and 12550-13650 eV, respectively.

The samples were thin As-Se films of different composition deposited on optical glass, by vacuum evaporation, in the Center of Optoelectronics, Chisinau. The thickness of the films is  $\sim 2$  micrometers. No annealing treatment was applied to the thin film samples.

## 3. Results

Fig. 1 and 2 shows the results of the measurements of As K and Se K-absorption edges. The absorption curves exhibit significant details. The As  $K_\alpha$  edge is situated around the theoretical value of 11863 eV. It is characterized by an intense white line, a shoulder on the high-energy side and a small peak at  $\sim 11878$  eV. The spectrum continues with the EXAFS spectrum up to approximately 12400 eV. The Se  $K_\alpha$  edge is situated around the theoretical value of 12652 eV and is characterized by a narrow white line followed by a small peak situated at  $\sim 12667$  eV. Thereafter, for higher energies, the EXAFS spectrum extends up to 13200 eV energy.

The XANES spectra in principle should be characteristic to oxidation states and to the covalence of the metal-ligand bonding.

The region situated near K-edge is shown at a larger scale for both As and Se K-edge measured on both  $\text{As}_2\text{Se}_3$  and  $\text{As}_4\text{Se}_4$  amorphous chalcogenide films. The XANES structure around the Se K-edge is more expressed than that around the As K-edge. One can observe easily that the width of the white line varies as a function of sample composition. The small peak that follows after the white line is more intense in  $\text{As}_2\text{Se}_3$ . A shoulder on the high-energy side of the white line in  $\text{As}_2\text{Se}_3$  film is clearly observed. The second small peak in the spectrum of As K-edge of  $\text{As}_2\text{Se}_3$  film is more expressed if compared with the same spectrum of the  $\text{As}_4\text{Se}_4$  film.

We have carefully analyzed the positions on the energy axis of the peaks characteristic to the K-absorption edges (As and Se) of both amorphous films investigated in this paper. We have deconvoluted the peaks using Lorentz-type curves and calculated their full width at half maximum (FWHM).

The results are given in the Table 1. The differences in positions and widths of the X-ray absorption near edge peaks have been calculated. They are shown in Table 2.

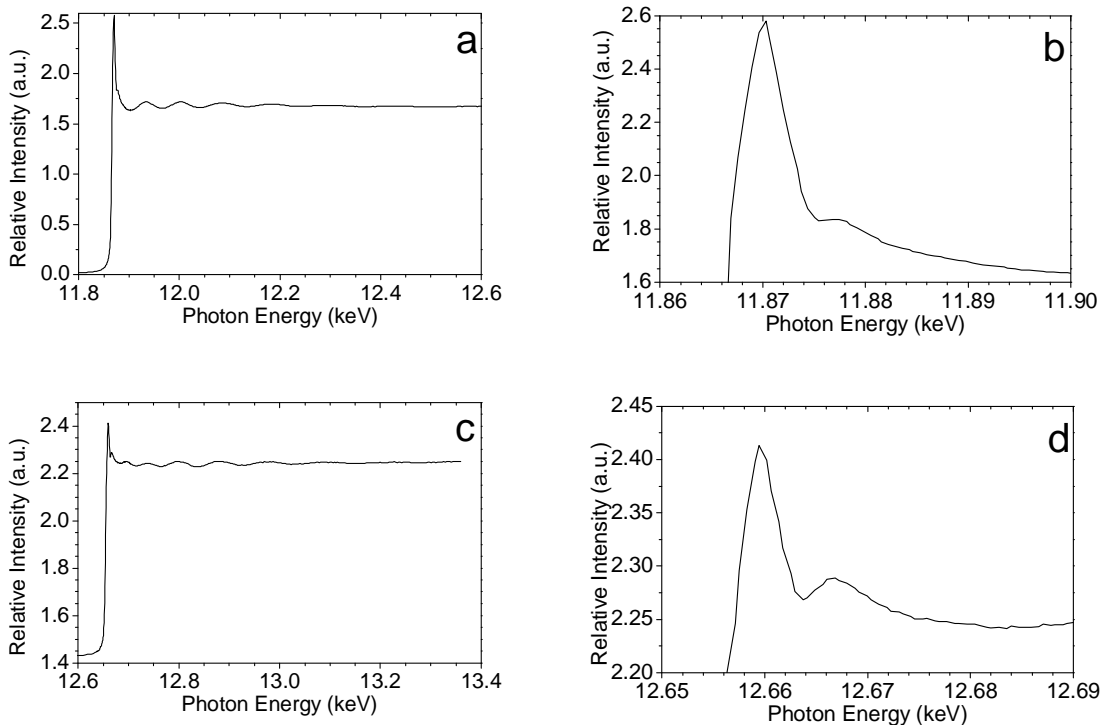


Fig. 1. X-ray absorption spectra of amorphous  $\text{As}_4\text{Se}_4$  films

- a. As K-edge and EXAFS spectrum    b. XANES structure for As K-edge  
 c. Se K-edge and EXAFS spectrum    d. XANES structure for Se K-edge.

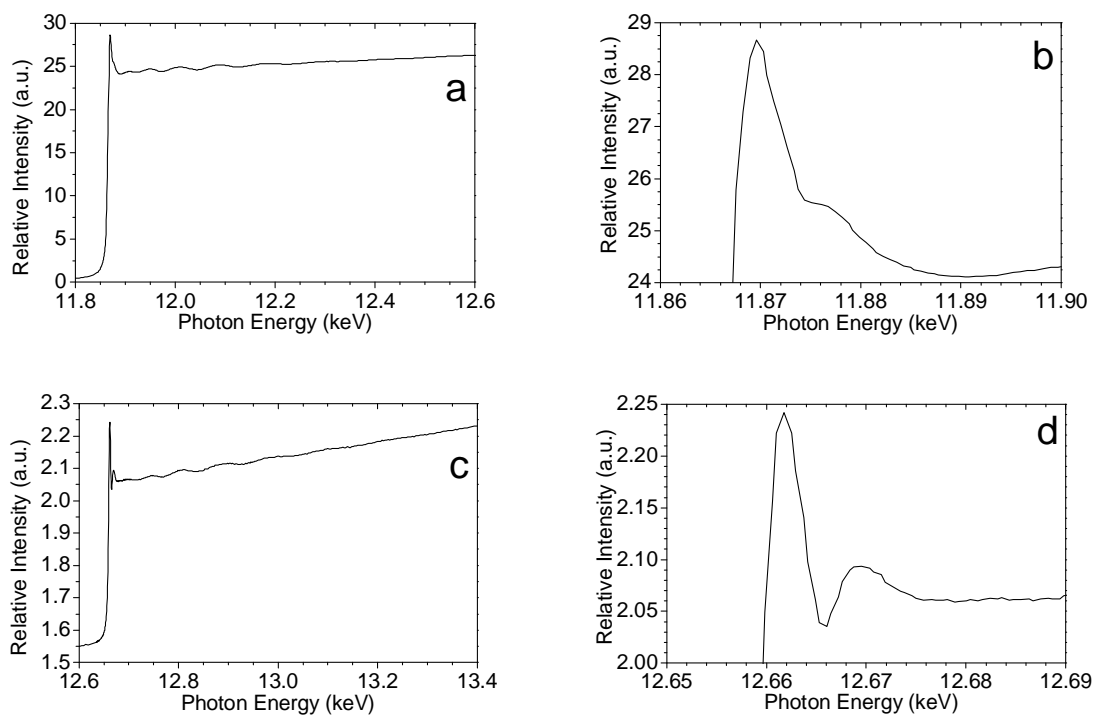


Fig. 2. X-ray absorption structure in amorphous  $\text{As}_2\text{Se}_3$ .

- a. As K-edge and EXAFS spectrum    b. XANES structure for As K-edge  
 c. Se K-edge and EXAFS spectrum    d. XANES structure for Se K-edge.

Table 1. The characterization of the X-ray absorption near edge structure of the As-Se films.

As K-edge				
Thin film	Main peak (white line)		Secondary peak	
	Position (eV)	FWHM (eV)	Position (eV)	FWHM (eV)
As <sub>2</sub> Se <sub>3</sub>	11869.680	5.2497	11877.744	5.2839
As <sub>4</sub> Se <sub>4</sub>	11873.211	4.9649	11877.924	3.9581

Se K-edge				
Thin film	Main peak (white line)		Secondary peak	
	Position(eV)	FWHM(eV)	Position (eV)	FWHM(eV)
As <sub>2</sub> Se <sub>3</sub>	12661.822	2.959	12669.440	4.6558
As <sub>4</sub> Se <sub>4</sub>	12659.629	3.3507	12666.834	5.0584

Table 2. The variation of the parameters of the X-ray absorption peaks in the XANES structure from the stoichiometric (As<sub>2</sub>Se<sub>3</sub>) to non-stoichiometric amorphous film (As<sub>4</sub>Se<sub>4</sub>).

Parameter	As K-edge	Se K-edge
	Film(As <sub>4</sub> Se <sub>4</sub> ) – Film(As <sub>2</sub> Se <sub>3</sub> )	Film(As <sub>4</sub> Se <sub>4</sub> ) – Film(As <sub>2</sub> Se <sub>3</sub> )
Main peak position (eV)	0.398	-2.193
Main peak FWHM (eV)	-0.2848	0.3917
Second peak position (eV)	0.180	-2.606
Second peak FWHM (eV)	-1.3258	0.4026

#### 4. Discussion

The fine differences in the XANES spectra of a stoichiometric and non-stoichiometric amorphous As-Se film could be explained by the presence of chemical and structural disorder.

It is remarkable from the Tables 1 and 2 that the peaks in XANES spectrum, measured at the Se K edge, significantly broaden when the stoichiometry is lost, i.e. when the composition changes from As<sub>2</sub>Se<sub>3</sub> to As<sub>4</sub>Se<sub>4</sub>. Oppositely, the XANES peaks of the As K-edge become narrower when one passes from the stoichiometric to non-stoichiometric composition of thin As-Se amorphous film. This specific and very different variation may be related to the state of chemical disorder around the selenium and arsenic atoms. In the crystalline As<sub>2</sub>Se<sub>3</sub> the chemical bonding is exclusively As-Se. As-As and Se-Se direct bonding is lacking.

In the amorphous films it is possible to appear wrong bonds: As-As and Se-Se. In the case of amorphous As<sub>4</sub>Se<sub>4</sub> the concentration of As-As direct bonds increases, while the direct bonds Se-Se practically does not exist. So the chemical disorder implies a fluctuation in the arsenic environment.

The large disorder of selenium positions determines the distortion of the electron charge distribution around selenium and, therefore, the widening of the XANES peaks is produced. In the case of As K-edge one observes a strong narrowing of the peaks when one passes from the stoichiometric to non-stoichiometric film, and this effect could be ascribed to a better and homogeneous arrangement of the arsenic atoms.

Regarding the peak position, the change of composition from stoichiometric to non-stoichiometric one gives rise to a shift of the XANES peaks towards low energies in the case of Se-K-edge, and towards higher energies in the case of As K-edge. This effect can be correlated with the strength of the bonding.

Poborchii et al. [30] remarked that the position of the first oscillation in EXAFS spectrum is directly related to the first order distance in the material. Taking into account the rule  $KR = \text{constant}$  [31] where K is a wave vector corresponding to the onset of EXAFS oscillations and R is the bond

length, this implies that the average bond length becomes longer for shiftings to lower energies. We have compared the shift of the first EXAFS oscillation (the secondary peak in our graphs of the absorption edge) in both  $\text{As}_2\text{Se}_3$  and  $\text{As}_4\text{Se}_4$ . The shifts were referenced to the position of the white line.

For the Se K edge the shift of the secondary peak when one passes from  $\text{As}_2\text{Se}_3$  to  $\text{As}_4\text{Se}_4$  is of -0.413 eV (towards lower energies).

For the As K edge the shift of the secondary peak when one passes from  $\text{As}_2\text{Se}_3$  to  $\text{As}_4\text{Se}_4$  is of -0.218 eV (towards lower energy).

The shift toward lower energies both for Se K and As K edges proves the increase of the bonding length As-Se when the  $\text{As}_2\text{Se}_3$  becomes not stoichiometric (low Se content). This effect can be understood on the basis of an effect of dehybridization of bonds when the stoichiometry is not preserved.

The as-prepared films of  $\text{As}_4\text{Se}_4$  is probably inhomogeneous, consisting of arsenic-rich ( $\text{As}_4\text{Se}_3$  –dimorphite) and selenium-rich regions [28]. Highly stressed As-As bonds are present in  $\text{As}_4\text{Se}_3$  clusters. Selenium linked to arsenic, or even in small clusters, exhibits weaker bondings than in the case of  $\text{As}_2\text{Se}_3$  (where strong As-Se bonds exist) and, as a consequence, its absorption edge will be shifted to lower energies.

## 5. Conclusions

X-ray absorption near edge structure of amorphous thin films of composition  $\text{As}_2\text{Se}_3$  and  $\text{As}_4\text{Se}_4$  has evidenced a different level of atomic-scale ordering in the samples. Selenium sites are more affected by disorder as shown by the strong broadening of the XANES peaks when one passes from the stoichiometric to non-stoichiometric film. The shift of the first EXAFS peak towards lower energies for the Se K-edge and As K-edge, when the film losses its stoichiometry demonstrates the weakening of the selenium-arsenic bond in the film and an increase of the bonding length. A significant dehybridization of the As-Se bonds could be admitted. Future calculations based on cluster approach method will permit to get detailed information on the kind of structural disordering around the arsenic and selenium atoms.

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