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ON THE ORIGIN OF NANOVOIDS IN BINARY CHALCOGENIDE GLASSES STUDIED BY FSDP-RELATED XRD, PALS AND MONTE-CARLO SIMULATION

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In the present work the origin of nanovoids in typical binary As_2Se_3 and As_2S_3 glasses has firstly been analyzed using combination of experimental methods, such as X-ray diffraction modified in respect to the first sharp diffraction peak (FSDP-related XRD) and positron annihilation lifetime spectroscopy (PALS), along with theoretical modelling based on Monte-Carlo procedure. It has been established a good agreement between experimental and theoretical results obtained. It is supposed that the approach proposed to characterize nano-scale void species structure in the investigated binary glass compositions can also be used for ternary network glasses within $As_2S(Se)_3$-based sub-systems.

Key words: Chalcogenide glasses, X-ray diffraction, Positron annihilation lifetime spectroscopy, Monte-Carlo simulation.

Although chalcogenide glasses (ChG) are widely used in modern optoelectronics, their structural features need still more understanding. The atomic-species structure is typically taken as the main determinant for ChG' properties, while the void-species one is so far not investigated.

The idea to study nanovoids in glasses has firstly been proposed during computer modeling of glass network within Monte-Carlo procedure [1], but it was not accepted entirely owing to absence of corresponding experimental confirmations.

Further, S.R. Elliott [2,3], interpreting the nature of the first sharp diffraction peak (FSDP) in AX_2-type glasses, has assumed the importance of knowledge about nanovoids for glass structure to be understood.

At the same time, for As_2Se_3 glass, K.O. Jensen et al. [4] have demonstrated that positron annihilation lifetime spectroscopy (PALS) can also be used as experimental tool to study void-species structure of ChG, but the origin of voids for glass has been accepted in full similarity to respective crystal.

Thus, this work is focused to study the origin of nanovoids in typical binary As_2Se_3 and As_2S_3 glasses using combination of experimental methods, such as FSDP-related XRD and PALS, along with theoretical modelling based on Monte-Carlo procedure.

The investigated samples were prepared by a standard melt-quenching procedure [5]. Ampoules synthesized were quenched in water. Before experimental measurements samples were polished to the ~1,5 mm thickness disks of optical quality and annealed near 20-30 K below glass transition temperature T_g.

FSDP-related XRD patterns were obtained by HZG-4a powder diffractometer with Cu K_α-radiation in the range of $10 \le 2\theta \le 40°$ with a step of 0,05° and an integration time of 70 sec per point. The sample was measured in the regime of "rotation" with speed of 2 rotations per sec. The 2θ error in determining the FSDP position was ± 0,01°. The program CSD (Crystal Structure Determination) „Full profile powder data reduction" V.5.11 was used for data processing. The FSDP parameters such as the interlayer separation, quasi-periodic in nature with an effective periodicity, R, and correlation length, L, over which quasi-periodic real-space density fluctuations take place, were calculated within model [16]:

$$R \approx 2\pi / Q_1, \quad (1)$$

$$L \approx 2\pi / \Delta Q_1, \quad (2)$$

where the magnitude of the scattering vector Q_1 (= $4\pi\sin\theta / \lambda$) corresponds to the position of the FSDP and ΔQ_1 is the full width at half maximum (FWHM) of the FSDP.

The PALS experiment was performed using an ORTEC spectrometer with ^{22}Na source described in details in [6]. The PALS data were mathematically processed with LT computer program [7]. The best PALS results within two-state positron trapping model [8] were corresponded to two-component fitting procedure, giving τ_1, τ_2, I_1 and I_2 values (where τ_1 – reduced bulk lifetime, τ_2 – defect-related lifetime, associated with nanovoid volume, I_1 and I_2 – corresponding lifetime intensities ($I_1 + I_2 = 1$, and I_2 values testify about concentration of nanovoids in glass matrix).

In order to obtain nanovoid radius distribution in the based glass forming network of the investigated ChG, the Monte-Carlo procedure possibilities were used previously reported in [1].

FSDP-related XRD. Fig. 1 shows the XRD pattern for g-As_2Se_3 and Table 1 demonstrates the CSD program treatment of the obtained XRD data and calculated FSDP parameters. The FSDP for g-As_2Se_3 is around 2θ=17,67° corresponding to the scattering vector $Q_1 \cong 1{,}252$ Å^{-1}. The magnitude of FWHM of the FSDP is equal to 4,88° or $\Delta Q_1 \cong 0{,}347$ Å^{-1}. The interlayer separation with an effective periodicity, R (the atom-void distance in terms of Elliott's void-based model [2]), and correlation length, L, calculated according to Eqs. (1–2), are found nearby 5.016 Å and 18.1 Å, respectively. It means that periodicity of $R \cong 5{,}016$ Å is necessary to give the FSDP at the observed value of $Q_1 \cong 1{,}252$ Å^{-1} and this real-space quasi-periodicity takes place along the correlation length of $L \cong 18{,}1$ Å.

Fig. 2 shows the XRD pattern for g-As_2S_3 and Table 2 demonstrates the CSD program treatment of the obtained XRD data and calculated FSDP parameters. The FSDP for g-As_2S_3 is around 2θ =17,84°, $Q_1 \cong 1{,}264$ Å^{-1} that is a good agreement with literature data. The magnitude of FWHM of the FSDP is equal to 3,88° or $\Delta Q_1 \cong 0{,}276$ Å^{-1}. The interlayer separation with an effective periodicity or repetitive distance, R and structural correlation length, L are obtained to be equal 4,968 Å and 22,8 Å.

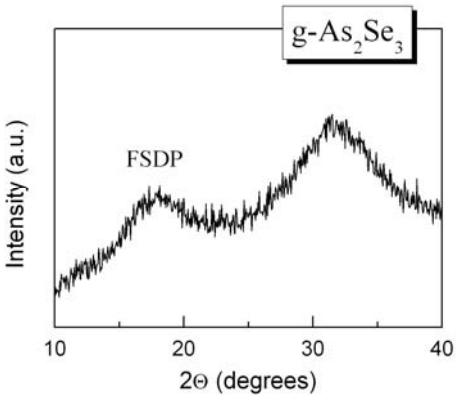

Fig. 1. X-ray diffraction pattern (Cu K_α-radiation) for g-As_2Se_3

Table 1. The FSDP parameters for g-As_2Se_3

2θ (°)	±2θ (°)
17,67	0.01
FWHM (°)	± FWHM (°)
4,88	0,05
Q_1 (Å^{-1})	ΔQ_1 (Å^{-1})
1,252	0,347
R (Å)	L (Å)
5,016	18,1

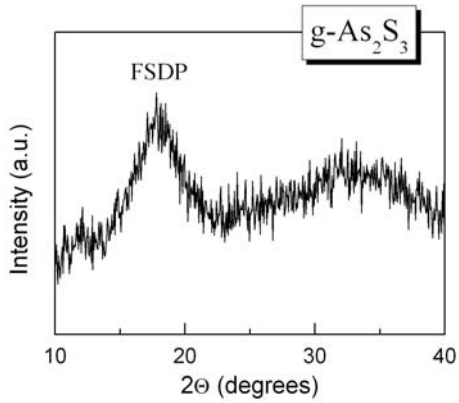

Fig. 2. X-ray diffraction pattern (Cu K_α-radiation) for g-As_2S_3

Table 2. The FSDP parameters for g-As_2S_3

2θ (°)	±2θ (°)
17.84	0,01
FWHM (°)	± FWHM (°)
3,88	0,05
Q_1 (Å^{-1})	ΔQ_1 (Å^{-1})
1,264	0,276
R (Å)	L (Å)
4,968	22,8

Recently [9,10], it has been shown that the analytical equation between the FSDP position, Q_1, and nanovoid diameter, D, for layer-like As_2Se_3-type ChG can be presented in the form of expression:

$$Q_1 = 2{,}3\times\pi/D. \quad (3)$$

In this way, the nanovoid volume, V, in the spherical approximation, calculated using Eq. (3), is found to be equal 100,5 Å^3 for g-As_2Se_3 and 97,4 Å^3 for g-As_2S_3.

PALS. By using two-state positron trapping model [8], the most real PALS characteristics with the optimal *FIT* range are obtained to be equal $\tau_1\approx0{,}20$ ns, $\tau_2\approx0{,}37$ ns, $I_2\approx0{,}60$ for g-As_2Se_3 and $\tau_1\approx0{,}19$ ns, $\tau_2\approx0{,}37$ ns, $I_2\approx0{,}615$ for g-As_2S_3.

According to K.O. Jensen with co-workers [4], the defect related positron lifetime τ (in ns) and vacancy volume V (in Å^3) are interconnected in the terms of expression:

$$\tau \cong 0{,}240 + 0{,}0013\times V. \quad (4)$$

So, the nanovoid volume, V, calculated using Eq. (4), is found to be equal 100 Å^3 for the both g-As_2Se_3 and g-As_2S_3.

Monte-Carlo simulation. The nanovoid distribution results obtained within theoretical modelling by Monte-Carlo simulation procedure [1] are presented in Figs. 3 and 4 for As_2Se_3 and As_2S_3 based glass forming, respectively.

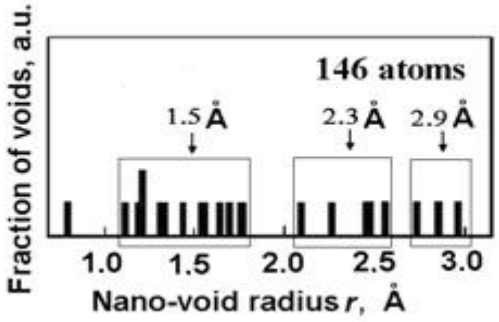

Fig. 3. Nanovoid distribution for layer-biased l46-atoms structural model of g-As_2Se_3

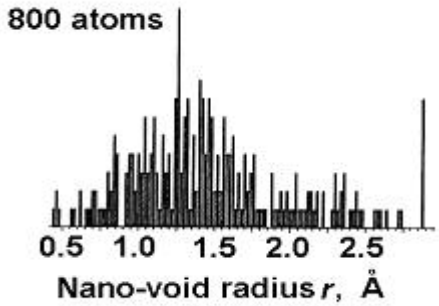

Fig. 4. Nanovoid distribution for layer-biased 800-atoms structural model of g-As_2S_3

It has been found that nanovoid structure of *g*-As_2Se_3 includes at least three types of free-volume nanovoids centered near $r_1\approx1{,}5$, $r_2\approx2{,}3$ and $r_3\approx2{,}9$ Å (Fig. 3). The numerical value of the greatest nanovoids centred near $r_3\approx2{,}9$ Å (Fig. 3) is in full agreement with the experimental results obtained using Eq. (2) for long-lived lifetime component $\tau_2\approx0{,}37$ ns, associated with the nanovoids of $V\approx100$ or $r\approx2{,}88$ Å. From this reason another two types of nanovoids centered near $r_1\approx1{,}5$ and $r_2\approx2{,}3$ Å make contribution into short-lived lifetime component $\tau_1\approx0{,}20$ ns. The nanovoids centred near 2,9 Å can be found for g-As_2S_3 too (Fig. 4).

Finally, we have obtained a good agreement between the results obtained by FSDP-related XRD, PALS and Monte-Carlo simulation (Table 3).

Table 3

The size of nanovoids obtained by FSDP-related XRD, PALS and Monte-Carlo simulation methods

Method	FSDP-related XRD		PALS		Monte-Carlo simulation	
Glass	r (Å)	V (Å^3)	r (Å)	V (Å^3)	r (Å)	V (Å^3)
As_2Se_3	2,885	100,5	2,880	100,0	2,900	102,0
As_2S_3	2,855	97,4	2,880	100,0	2,900	102,0

In conclusion, for the first time, the origin of nanovoids in typical binary As_2Se_3 and As_2S_3 glasses has been analyzed using combination of experimental and theoretical methods such as FSDP-related XRD, PALS and Monte-Carlo simulation. The results obtained by such independent techniques are agreed well. It means that approach proposed to study of nanovoid topology in network binary ChG is quite applicable and one should be used in the case of more structurally complicated ternary ChG compositions.

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ВИВЧЕННЯ ПРИРОДИ НАНОПУСТОТ У БІНАРНИХ ХАЛЬКОГЕНІДНИХ СТЕКЛАХ МЕТОДАМИ РЕНТГЕНІВСЬКОЇ ДИФРАКЦІЇ ІЗ ЗАСТОСУВАННЯМ ДО ПЕРШОГО РІЗКОГО ДИФРАКЦІЙНОГО ПІКУ ПОЗИТРОННОЇ АНІГІЛЯЦІЇ ТА МОНТЕ-КАРЛО МОДЕЛЮВАННЯ

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У статті вперше проаналізовано природу нанопустот в типових бінарних стеклах As_2Se_3 та As_2S_3, з використанням комбінації методів рентгенівської дифракції із застосуванням до першого різкого дифракційного піку позитронної анігіляції та Монте-Карло моделювання. Визначено добру узгоджуваність між отриманими експериментальними та теоретичними результатами. Припускається, що запропонований підхід до характеризації нанорозмірної атомно-дефіцитної структури в досліджуваних бінарних стеклах може бути також використаний для потрійних сіткових стекол на основі $As_2S(Se)_3$ підсистем.

Ключові слова: халькогенідні стекла, рентгенівська дифракція, позитронна анігіляція, Монте-Карло моделювання.

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