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MEDIUM-RANGE ORDERING EFFECTS IN PSEUDO-BINARY VITREOUS As_2S_3-Sb_2S_3 STUDIED WITH CONVENTIONAL XRD ANALYSIS

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In the present work, the medium-range ordering (MRO) effects in pseudo-binary vitreous As_2S_3-Sb_2S_3 are studied with conventional x-ray diffraction measurements. It is found that Sb atoms essentially affect on the MRO scale determined by structural correlation length *L*. As a result, the packing factor of layer configurations *p* increases with increasing Sb content in the amorphous alloys studied, this effect being enhanced after γ-irradiation.

Key words: chalcogenide glasses, medium-range order, x-ray diffraction, first sharp diffraction peak, structural correlation length, As_2S_3-Sb_2S_3.

Two scales can be recognized in the structure of glasses [1]. The first one is quite short and well defined with a relatively good approximation and documented as *short-range ordering* (SRO). The other scale is more complicated to be determined due to longer distances (20–50 Å and/or more) and it documented by many researchers as *medium-range ordering* (MRO). Sometimes, the latter can be also shifted to the *extended-range ordering* (ERO), but the origin of extended structural correlations in the network glasses has been unknown yet.

In the present study, we focus our attention on the MRO scale, the structural correlation length of which *L* can be estimated on the basis of full width at half maximum (FWHM) of the first sharp diffraction peak (FSDP) in x-ray diffraction (XRD) analysis:

$$L = 2\pi / \Delta Q_{FSDP}, \quad (1)$$

where ΔQ_{FSDP} is the FWHM of the FSDP in [$Å^{-1}$], calculated from β_{FSDP} measured in [deg.] using the relationship between the scattering vector Q [$Å^{-1}$] and Bragg angle θ [deg.] in the form of $Q = 4\pi \sin\theta / \lambda$ (λ is the x-ray wavelengths).

Also, information on the MRO structural motif can be obtained from the packing factor of amorphous layer configurations $p = D_S/d_S$, where D_S is an average thickness of the domain built by packing a number of disordered layers determined with the formula [2]:

$$D_S = \{K\lambda/\beta_{FSDP}\cos\Theta_{FSDP}\}\cdot\{360/2\pi\}, \quad (2)$$

where K = 0,9 is the Debye-Scherrer constant, λ is the x-ray wavelengths, Θ_{FSDP} is the position of the FSDP and d_S is the interlayer distance ($d_S = \lambda/2\sin\Theta_{FSDP}$).

The glasses from pseudo-binary $(As_2S_3)_x(Sb_2S_3)_{1-x}$ (x = 0,9, 0,8, 0,7) system are chosen for analysis in order to find the effect of Sb addition into a glass-forming network on the MRO structural correlations. The experimental measurements of the FSDP profiles in the range of 10° < 2Θ < 30° were carried out using conventional HZG-4a x-ray diffractometer (Cu K_α-radiation) with 0,05° step. The samples were tested in the rotation regime. The FSDP parameters, position $2\Theta_{FSDP}$ and FWHM β_{FSDP}, were estimated with accuracy of ±0,1°. To verify Sb-effect, the same glasses were also studied after irradiation by high-energy ^{60}Co γ-quanta with average energy of 1,25 MeV and accumulated dose of 1,23 MGy.

The main physical properties of the investigated alloys are summarized in table 1. One can see the strong compositional dependence of the glass transition temperature T_g, optical band gap energy E_g, crystallization temperature T_c, and microhardness H for $(As_2S_3)_x(Sb_2S_3)_{1-x}$ glasses. It is noticeable that with increasing of Sb content the values of T_g and H increase and the values of E_g and T_c decrease.

Table 1

Physical properties of glasses in $(As_2S_3)_x(Sb_2S_3)_{1-x}$ system [3-5]

Glass composition			*Physical properties*					
X	$1-x$	Chemical formula	T_g, K [4]	T_g^*, K [4]	E_g, eV [3]	E_g, eV [4]	T_c, K [4]	H, GPa [5]
1,00	0,00	$As_{40}S_{60}$	487	487,0	2,23	2,15		1,32
0,90	0,10	$As_{36}Sb_4S_{60}$						1,32
0,80	0,20	$As_{32}Sb_8S_{60}$			2,14			1,36
0,75	0,25	$As_{30}Sb_{10}S_{60}$	485	490,0	2,12	1,97		
0,70	0,30	$As_{28}Sb_{12}S_{60}$						
0,60	0,40	$As_{24}Sb_{16}S_{60}$			2,05			1,42
0,50	0,50	$As_{20}Sb_{20}S_{60}$	487	491,0	2,00	1,90	584	1,45
0,40	0,60	$As_{16}Sb_{24}S_{60}$			1,90			1,50
0,25	0,75	$As_{10}Sb_{30}S_{60}$	491	492,5	1,86	1,80	532	
0,20	0,80	$As_8Sb_{32}S_{60}$			1,85			1,50
0,10	0,90	$As_4Sb_{36}S_{60}$	493	495,5		1,61	516	
0,00	1,00	$Sb_{40}S_{60}$			1,73			1,59

Note. 1) The glass compositions in the glass-forming region ($0<x<0,62$ [6]) are marked by bold.
2) The T_g^* values are obtained using the relation: $T_g^*=520,8-15,72\,E_g$ [4].

Structural study of $(As_2S_3)_x(Sb_2S_3)_{1-x}$ (x = 0,9, 0,8, 0,7) alloys demonstrates the strong Sb-effect on the MRO scale. Figure 1 shows the FSDP-related XRD patterns for the investigated glasses in non-irradiated and γ-irradiated states. The MRO parameters β_{FSDP}, L, D_S, d_S, and $p = D_S/d_S$ are gathered in table 2.

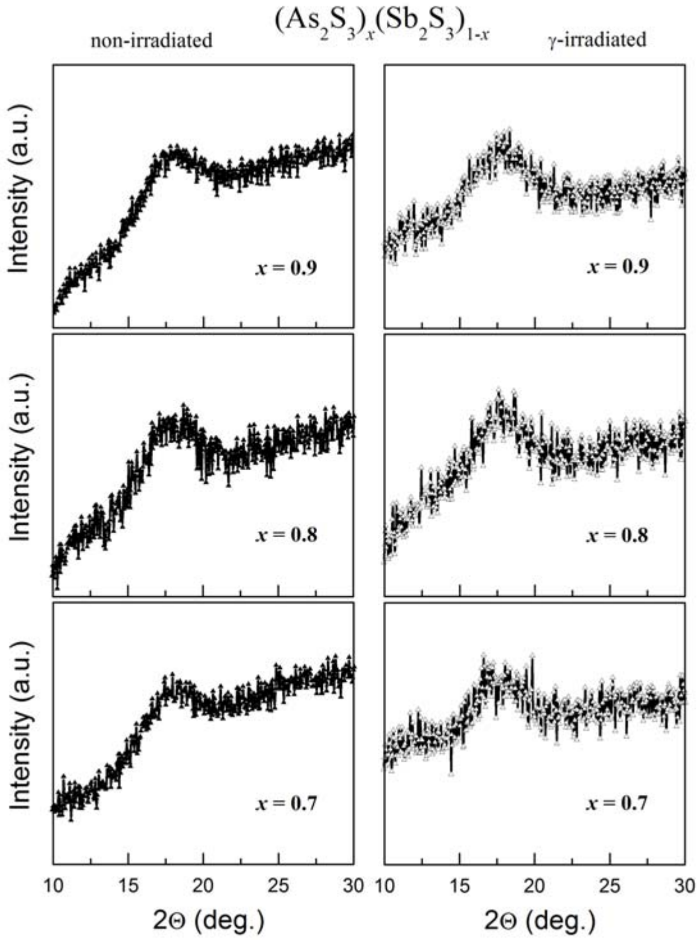

Fig. 1. The FSDP-related XRD patterns for $(As_2S_3)_x(Sb_2S_3)_{1-x}$ glasses (x = 0,9, 0,8, 0,7) in non-irradiated (closed symbols) and γ-irradiated (open symbols) states

Table 2

The MRO parameters for $(As_2S_3)_x(Sb_2S_3)_{1-x}$ glasses (x = 0,9, 0,8, 0,7) in non-irradiated (non-irrad.) and γ-irradiated (irrad.) states

MRO parameters (± 0,1)	$(As_2S_3)_x(Sb_2S_3)_{1-x}$					
	x = 0,9		x = 0,8		x = 0,7	
	Sample conditions					
	non-irrad.	irrad.	non-irrad.	irrad.	non-irrad.	irrad.
β_{FSDP} (°)	5,6	5,0	4,6	4,0	4,3	3,6
L (Å)	15,7	17,4	19,0	22,4	20,3	24,2
D_S (Å)	14,4	16,1	17,5	20,1	18,7	22,4
d_S (Å)	5,1	5,1	5,1	5,0	5,0	5,1
$p = D_S/d_S$	2,92	3,16	3,43	4,02	3,74	4,39

It is established that impact of Sb is mainly due to increase MRO structural correlation length L and packing factor of amorphous layer configurations p, it enhancing after irradiation. In order to estimate percentage of the medium-range ordering effects observed we calculate the radiation-induced change in the packing factor $\Delta p/p$ in percents (fig. 2). The effect is found to be increased from 12,1 to 17,4 % when the molar fraction of As_2S_3 x in $(As_2S_3)_x(Sb_2S_3)_{1-x}$ system changes from 0,9 to 0,7.

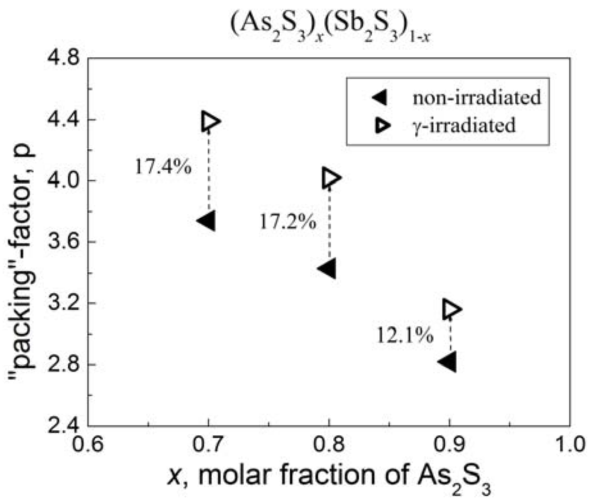

Fig. 2. The "packing"-factor p calculated for $(As_2S_3)_x(Sb_2S_3)_{1-x}$ glasses (x = 0,9, 0,8, 0,7) in non-irradiated (closed symbols) and γ-irradiated (open symbols) states (the dashed arrows indicate the relative radiation-induced change in the packing factor $\Delta p/p$ in percents)

In conclusion, by studying the medium-range ordering effects in pseudo-binary vitreous As_2S_3-Sb_2S_3 with conventional XRD measurements, it is found that Sb atoms essentially affect on the MRO scale determined by the structural correlation length *L*. As a result, the packing factor of amorphous layer configurations *p* increases with increasing Sb content in the alloys studied, the effect is enhanced after γ-irradiation of the samples.

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ЕФЕКТИ СЕРЕДНЬОГО ПОРЯДКУ В ПСЕВДОБІНАРНИХ СКЛОПОДІБНИХ СПЛАВАХ СИСТЕМИ As_2S_3-Sb_2S_3: АНАЛІЗ МЕТОДОМ ТРАДИЦІЙНОЇ РЕНТГЕНІВСЬКОЇ ДИФРАКЦІЇ

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Вивчено ефекти середнього порядку (СП) в псевдобінарних склоподібних сплавах системи As_2S_3-Sb_2S_3 за допомогою методу традиційної рентгенівської дифракції. З’ясовано, що атоми Sb суттєво впливають на шкалу СП, яка визначається структурною кореляційною довжиною *L*. Тому з підвищенням вмісту Sb в досліджуваних сплавах зростає фактор упаковки аморфних шаруватих конфігурацій *p*, причому більш інтенсивно після γ-опромінення зразків.

Ключові слова: халькогенідні стекла, середній порядок, рентгенівська дифракція, перший різкий дифракційний пік, структурна кореляційна довжина As_2S_3-Sb_2S_3.

ЭФФЕКТЫ СРЕДНЕГО ПОРЯДКА В ПСЕВДОБИНАРНЫХ СТЕКЛОВИДНЫХ СПЛАВАХ СИСТЕМЫ AS_2S_3-SB_2S_3: АНАЛИЗ МЕТОДОМ ТРАДИЦИОННОЙ РЕНТГЕНОВСКОЙ ДИФРАКЦИИ

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Изучены эффекты среднего порядка (СП) в псевдобинарных стекловидных сплавах системы As_2S_3-Sb_2S_3 с помощью метода традиционной рентгеновской дифракции. Установлено, что атомы Sb существенно влияют на шкалу СП, которая определяется структурной корреляционной длиной *L*. Поэтому при повышении содержания Sb в исследуемых сплавах растет фактор упаковки аморфных слоистых конфигураций *p*, причем более интенсивно после γ-облучения образцов.

Ключевые слова: халькогенидные стекла, средний порядок, рентгеновская дифракция, первый резкий дифракционный пик, структурная корреляционная длина As_2S_3-Sb_2S_3.

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