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STRUCTURAL COMPRESS OF VITREOUS As_2S_3 INDUCED BY γ-IRRADIATION

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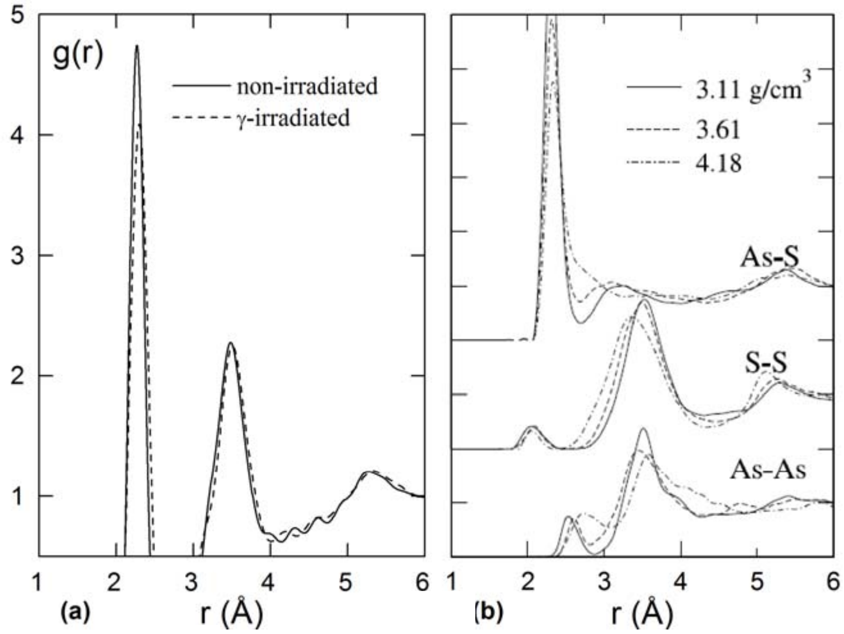
It is observed that recently studied impacts of γ-irradiation and hydrostatic pressure on the local structure of vitreous As_2S_3 are correlated and interconnected. The both effects result in decreasing amplitude of the first sharp diffraction peak and increasing As–As coordination number. On the basis of this correlation it is suggested that radiation-induced internal compression of structural network of the glass takes place upon γ-irradiation the most probably due to switching of shorter As–S bonds into longer As–As ones.

Key words: chalcogenide glasses, structure, x-ray diffraction, hydrostatic pressure, first sharp diffraction peak, radiation modification, As_2S_3.

Recently [1], atomic- and void-species nanostructures for non-irradiated and γ-irradiated As_2S_3 glass were studied by using conventional x-ray diffraction (XRD), high-energy synchrotron XRD, and extended x-ray absorption fine structure (EXAFS) spectroscopy techniques. The obtained experimental results showed that γ-induced structural modification of g-As_2S_3 leads to the significant changes in nanoscale atomic and void topology of the glass network. The largest effect was found [1] on the pair distribution functions $g(r)$ [fig. 1, *a*]. Namely, the first peak $g(r_1)$ corresponding to As–S correlations at r = 2,27 Å shifts to larger r and becomes lower and broader results in increasing average coordination number N. The change in coordination number was supported by EXAFS data showing increase partial coordination number around As atoms, but the nearest-neighbor distance in the first coordination shell 2,28 Å (As–S) remains unchanged upon irradiation from fitting of the EXAFS spectra. Finally, it was suggested in [1] that the changes in the nearest-neighbor distances could be considered as insufficient, taking into account the EXAFS measurements. Although, it can be connected with the EXAFS experiments carried out at room temperature [1], while to obtain more accurate information regarding bond distances EXAFS experiments at low temperature (30–40 K) are needed [2, 3]. The second peak around 3,48 Å exhibits very slight decrease in the $g(r_2)$ intensity and also shift in the peak position to larger r upon irradiation. The second coordination shell in the EXAFS spectra was not resolved for g-As_2S_3 [1] and, consequently, the changes in the position of the second peak $g(r_2)$ can not be compared with EXAFS data. It is also established in [1] that amplitude of the first sharp diffraction peak (FSDP) decreases upon irradiation.



a *b*

Fig. 1. The partial distribution functions $g(r)$ upon γ-irradiation (*a*) [1] and hydrostatic pressure (*b*) [4] for vitreous As_2S_3. The densities at 3,61 and 4,18 g/cm^3 correspond to the calculated effect of pressure at 2 and 6 GPa, respectively [4]

Shimojo et al. [4] studied impact of densification on the local atomic configuration in amorphous As_2S_3 by using ab initio molecular-dynamics (MD) simulations. The partial distribution functions $g(r)$ upon hydrostatic pressure are shown in fig. 1, *b*. The densities at 3,61 and 4,18 g/cm^3 correspond to the calculated effect of pressure at 2 and 6 GPa, respectively, in constant-temperature MD simulations [4]. The main results obtained from pressure-induced effects are (i) significant decreasing intensity of the first peak $g(r_1)$ at $r = 2{,}3$ Å (the first neighbor As–S correlations) without remarkable change in the peak position; (ii) slight decreasing intensity of the second peak $g(r_2)$ at $r = 3{,}55$ Å (the second neighbor S–S correlations) and shift of the peak position to smaller r; (iii) slight decreasing intensity of the second peak $g(r_2)$ at $r = 3{,}5$ Å (the second neighbor As–As correlations) and shift of the peak position to larger r; (iv) increasing As–As coordination number substantially with increasing pressure; (v) decreasing amplitude of the FSDP with increasing pressure and its almost disappearance at the highest density (4,18 g/cm^3) or pressure (6 GPa). Thus, comparative analysis of the γ-irradiation and pressure-induced effects shows that the main features on the $g(r)$ intensities, coordination numbers, and FSDP are in a good agreement. It means that these both effects are correlated and interconnected. This correlation can be originated from radiation-induced structural transformations or covalent chemical bond switching reactions in the glassy network of As_2S_3, well described within the so-called coordination topological defect (CTD) formation concept [5–7], that seems to be similar with internal compression of local atomic structure of glass. Indeed, in the case of vitreous As_2S_3 (v-As_2S_3), as it was shown in [1], the main reaction detected on the $g(r)$ is transformation of As–S into As–As with appearance of under- and overcoordinated negatively and positively charged S_1^- and As_4^+ CTDs. This reaction was previously supported by IR Fourier spectroscopy measurements (see, for example [5]). Because of the bond distance of As–S is around 2,28 Å and bond distance of As–As is around 2,52 Å [4], the reaction of As–S $\rightarrow$ As–As results in transformation of shorter bonds into longer ones and, consequently, increasing internal compression of structural network.

In conclusion, comparative analysis of γ-irradiation and pressure-induced effects on the partial distribution functions $g(r)$ in v-As_2S_3 allows us to identify γ-irradiation-induced internal compression of local atomic structure of the glass. The later can explain the nature of well-known increasing microhardness in v-As_2S_3 with γ-irradiation [8]. Taking into account that radiation-induced changes in microhardness are reversible in the cycles of irradiation-annealing (where sample was annealed at the temperature near glass transition point T_g) [8], it is interesting to see whether impact of γ-irradiation on $g(r)$ is reversible too.

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γ-РАДІАЦІЙНО-ІНДУКОВАНЕ СТИСНЕННЯ СТРУКТУРИ СКЛОПОДІБНОГО As_2S_3

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Простежено кореляцію та взаємозв'язок між уже вивченими впливами γ-опромінення та гідростатичного тиску на локальну структуру склоподібного As_2S_3. Обидва ефекти призводять до зменшення амплітуди першого різкого дифракційного піку та зростання координаційного числа навколо атомів миш'яку (As–As). На підставі цієї кореляції припускається, що під дією γ-опромінення відбувається радіаційно-індуковане внутрішнє стиснення структурної сітки скла, наймовірніше завдяки переключенню коротших зв'язків As–S на довші зв'язки As–As.

Ключові слова: халькогенідні стекла, структура, рентгенівська дифракція, гідростатичний тиск, перший різкий дифракційний пік, радіаційна модифікація, As_2S_3.

γ-РАДИАЦИОННО-ИНДУЦИРОВАННОЕ СЖАТИЕ СТРУКТУРЫ СТЕКЛОВИДНОГО As_2S_3

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Установлено корреляцию и взаимосвязь между уже изученными влияниями γ-облучения и гидростатического давления на локальную структуру стекловидного As_2S_3. Оба эффекта приводят к уменьшению амплитуды первого резкого дифракционного пика и роста координационного числа вокруг атомов мышьяка (As–As). На основании этой корреляции допускается, что под действием γ-облучения происходит радиационно-индуцированное внутреннее сжатие структурной сетки стекла, вероятней всего благодаря переключению более коротких связей As–S на более длинные связи As–As.

Ключевые слова: халькогенидные стекла, структура, рентгеновская дифракция, гидростатическое давление, первый резкий дифракционный пик, радиационная модификация, As_2S_3.

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