

On the correlation between FSDP and PALS parameters in As–Se chalcogenide glasses

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Abstract

Correlation between nanovoids sizes obtained from the first sharp diffraction peak and positron annihilation lifetime spectroscopy data is found for As-rich glasses in $\text{As}_x\text{Se}_{100-x}$ system ($x = 40, 50, 55, 64$). The results reported in this work confirm suggestion of K. Jensen *et al.* [Microvoids in chalcogenide glasses studied by positron annihilation, *J. Non-Cryst. Solids* **170**, 57 (1994)] that the positron annihilation lifetime spectroscopy could be a sensitive tool to test the void-based model for the first sharp diffraction peak of covalent chalcogenide glasses.

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1. INTRODUCTION

In 1994, Jensen with co-workers [1] assumed that the positron annihilation lifetime spectroscopy (PALS) could be a sensitive tool to test the void-based model. This model was proposed by Wright *et al.* [2] on the basis of the characteristics of the first sharp diffraction peak (FSDP) of covalent chalcogenide glasses and developed later by Elliott [3]. Indeed, on the one hand, the positron lifetime τ (in ns) is related to the open volume V (positron traps) through the expression [1]

$$\tau \cong 0.240 + 0.0013 \cdot V, \quad (1)$$

which was determined on the basis of theoretical calculations for crystalline As_2Se_3 . On the other hand, in the framework of the void-based model, it was found for As_2Se_3 glass that the position of the FSDP Q_1 and diameter of nanovoids D_v can be linked by the relation [4]

$$Q_1 = 2.3\pi/D_v. \quad (2)$$

Thus, both the FSDP and PALS may provide related information about nanovoids in the real glass structure as this was demonstrated for stoichiometric $g\text{-As}_2\text{Se}_3$ in [4].

As–Se glasses have been studied with PALS by Alekseeva *et al.* [5]. In the present work we perform x-ray diffraction (XRD) measurements of $\text{As}_x\text{Se}_{100-x}$ ($x = 40, 50, 55, 64$). The aim is the examination of nanovoid parameters obtained from FSDP and PALS data in As–Se chalcogenide glasses within a wide composition range.

2. EXPERIMENTAL

As–Se bulk glasses were prepared by conventional melt-quenching method. Before experimental measurements the samples were polished to optical quality.

High-energy synchrotron XRD measurements were performed at the experimental station BW5 at

HASYLAB, DESY (Hamburg, Germany). The samples were investigated in transmission geometry. The energy of radiation was 99.9996 keV, which corresponds to the wavelength of ~ 0.124 Å. XRD diffraction curves were measured between 0.5 and 18 Å $^{-1}$. Raw data were corrected for detector dead-time, polarization, absorption and variation of detector solid angle [6].

Experimental intensities measured in arbitrary units were converted into the coherent scattering intensities per atom in electronic units using Krogh-Moe-Norman method [7,8]. Compton scattering was corrected using the values given by Cromer and Mann [9]. Then, Faber-Ziman [10] total structure factors were calculated.

3. RESULTS AND DISCUSSION

Figure 1 shows parts of the experimental structure factors $S(Q)$ for $\text{As}_x\text{Se}_{100-x}$ glasses in the FSDP range. The FSDP position shifts to the lower Q values and its intensity increases remarkably with increasing As concentration. The same behaviour of the FSDP parameters in arsenic selenide glasses has also been observed by Bychkov *et al.* [11].

The FSDP intensity I_1 on the structure factors $S(Q)$ was determined as a ratio of the peak maximum $S(Q)_{\text{max}}$ to the minimum value on the tail of the peak $S(Q)_{\text{min}}$ from its high- Q part (i.e. $I_1 = S(Q)_{\text{max}}/S(Q)_{\text{min}}$) as it has been done in Ref. 12.

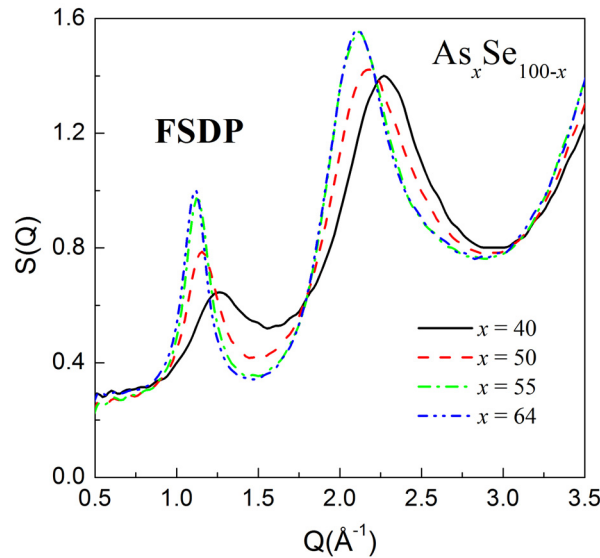


Fig. 1. The experimental structure factors $S(Q)$ for $\text{As}_x\text{Se}_{100-x}$ glasses in the FSDP range.

Figures 2(a) and 2(b) show the FSDP position Q_1 and positron lifetime of open-volume defect-related component τ_2 [taken from Ref. 5] for $\text{As}_x\text{Se}_{100-x}$ glasses as functions of cation (As) concentration x . Composition dependences of the FSDP and positron lifetime intensities are shown in Figs. 3(a) and 3(b).

Taking into account the fact that the nanovoid size is proportional to the positron lifetime τ_2 [Eq. (1)] and inversely proportional to the FSDP position Q_1 [Eq. (2)], composition dependences plotted in Figs. 2(a) and 2(b) indicate an increase of nanovoids in $\text{As}_x\text{Se}_{100-x}$ glasses with increasing As concentration.

The rise of the FSDP intensity [Fig. 3(a)] for $\text{As}_x\text{Se}_{100-x}$ glasses with high As content is explained in the frame of void-based model [2,3] by increasing number of cation-cation correlations. It can be supposed that larger number of these correlations is related to a larger number of nanovoids around cation-centred structural units.

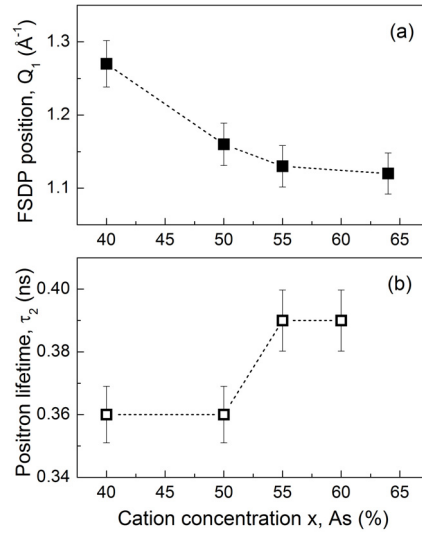


Fig. 2. The FSDP position and positron lifetime for As_xSe_{100-x} glasses as a function of cation concentration x . PALS data are taken from Ref. 5.

No regularity is seen on the composition dependence for the PALS intensity of open-volume defect-related component [Fig. 3(b)]. This can be due to different relation of the FSDP and PALS intensities to the nanovoids in the glass network. The FSDP intensity is related to ordered nanovoids around cation atoms, while the intensity of positron annihilation lifetime is sensitive not only to nanovoids responsible for the FSDP but also to practically all open-volume sites where positrons are trapped. Hence, size of nanovoids obtained from FSDP and PALS data will be correlated, whereas their intensities may show different values as it was observed indeed.

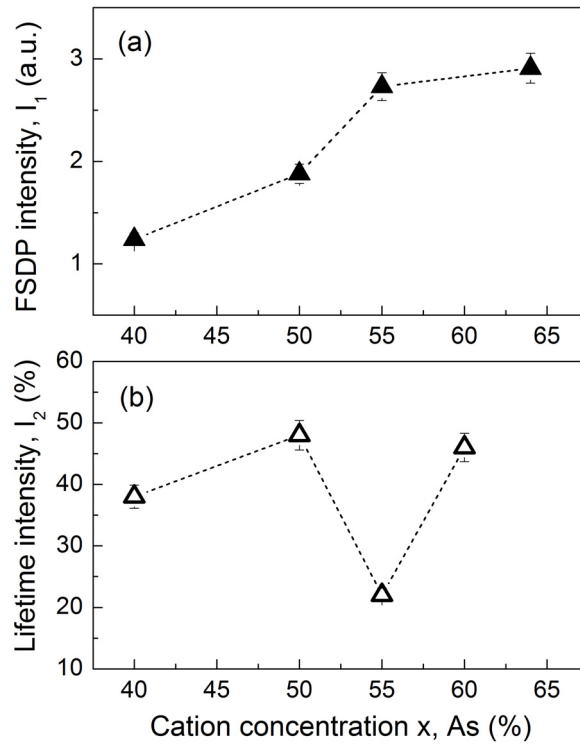


Fig. 3. The FSDP and positron lifetime intensities for As_xSe_{100-x} glasses as a function of cation concentration x . PALS data are taken from Ref. 5.

Figures 4(a) and 4(b) demonstrate the void volume V_{FSDP} calculated from the FSDP data [Eq. (2)] and the void volume V_{PALS} calculated from the PALS data [Eq. (1)] for $\text{As}_x\text{Se}_{100-x}$ glasses as a function of As concentration. A good agreement between nanovoid size determined from the FSDP and PALS data proves the assumption of Jensen *et al.* [1] that the positron annihilation lifetime spectroscopy is a sensitive tool to test the void-based model for the first sharp diffraction peak of covalent chalcogenide glasses.

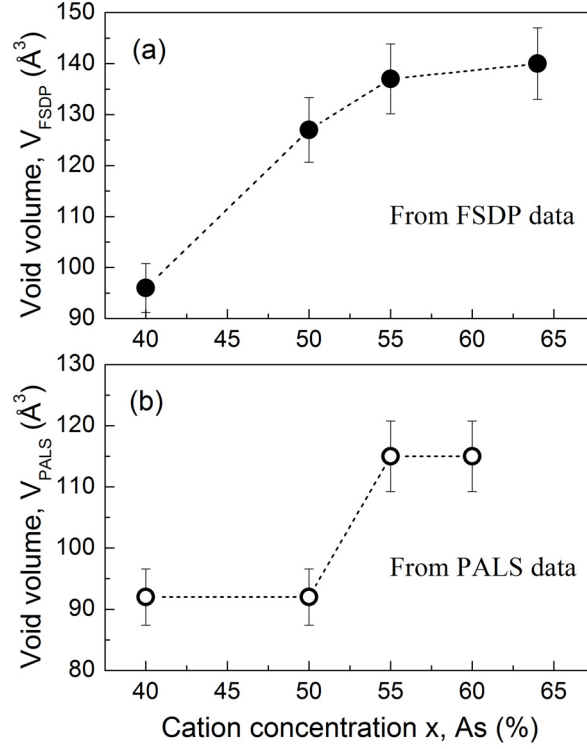


Fig. 4. The void volumes calculated from the FSDP and PALS [5] data with Eqs. (1) and (2) for $\text{As}_x\text{Se}_{100-x}$ glasses as functions of cation concentration x .

4. SUMMARY

The paper reports the correlation between nanovoid size determined from the first sharp diffraction peak and positron annihilation lifetime spectroscopy data for As–Se glasses. The obtained results prove the suggestion of Jensen *et al.* [1] that the positron annihilation lifetime spectroscopy could be a sensitive tool to test the void-based model for the first sharp diffraction peak of covalent chalcogenide glasses.

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REFERENCES

- [1] K.O. Jensen, P.S. Salmon, L.T. Penfold, P.G. Coleman, J. Non-Cryst. Solids **170**, 57 (1994).
- [2] A.C. Wright, R.N. Sinclair, A.J. Leadbetter, J. Non- Cryst. Solids **71**, 295 (1985).
- [3] S.R. Elliott, Phys. Rev. Lett. **67**, 711 (1991).
- [4] T.S. Kavetsky, O.I. Shpotyuk, J. Optoelectron. Adv. Mater. **7**, 2267 (2005).
- [5] O.K. Alekseeva, V.I. Mihajlov, V.P. Shantarovich, Phys. Status Solidi A **48**, K169 (1978).
- [6] H. F. Poulsen, J. Neufeld, H.-B. Neumann, J.R. Schneider, M.D. Zeidler, J. Non-Cryst. Solids **188**, 63 (1995).
- [7] J. Krogh-Moe, Acta Cryst. **9**, 951 (1956).
- [8] N. Norman, Acta Cryst. **10**, 370 (1957).
- [9] D.T. Cromer, J.B. Mann, J. Chem. Phys. **47**, 1892 (1967).
- [10] T.E. Faber, J.M. Ziman, Philos. Mag. **11**, 153 (1965).
- [11] E. Bychkov, C.J. Benmore, D.L. Price, Phys. Rev. B **72**, 172107 (2005).
- [12] H. Hamanaka, S. Minomura, K. Tsuji, J. Non-Cryst. Solids **137&138**, 977 (1991).