

FSDP-related correlations in chalcogenide glasses

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A first sharp diffraction peak (FSDP) is the most sensitive characteristic to medium range order in non-crystalline solids with speculative origin up to now. The compositional trends in the FSDP position and full width at half maximum are tested on the example of pseudo-binary $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ and $\text{Sb}_2\text{S}_3\text{-GeS}_2$ systems of chalcogenide glasses. The FSDP-related correlations are found for the investigated materials and considered in terms of packing factor of amorphous layers and experimental density of glass.

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1. Introduction

A first sharp diffraction peak (FSDP) is still a subject for discussion, although its connection with medium-range order in topologically disordered solids like network glasses is generally concluded by many researchers [1-9]. Speculative statements to the origin of the FSDP in terms of different models (e.g. Philips, 1981 [10], Moss and Price, 1985 [11], Wright et al., 1985 [12], Cervinka, 1987 [13], Fowler and Elliott, 1987 [14], Elliott, 1991-1995 [15,16]) compel us to seek correlations between the FSDP parameters and physical properties of materials, even in the case when we consider that Elliott's void-based approach for the FSDP [15,16] is the most suitable for its description as chemically order pre-peak in a structure factor due to ordering of interstitial voids around cation-centered structural units. It should be noted here that namely Elliott's model explains adequately well known anomalous temperature and pressure dependences of the FSDP intensity in chalcogenide glasses.

The present work is aimed to find possible FSDP-related correlations in amorphous chalcogenides on the example of glasses from pseudo-binary $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ and $\text{Sb}_2\text{S}_3\text{-GeS}_2$ systems with pyramidal $\text{Sb}(\text{As})\text{S}_{3/2}$ and tetrahedral $\text{GeS}_{4/2}$ structural units.

2. Experimental

The bulk glassy samples of $(\text{Sb}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ ($x = 0.1, 0.2, 0.3$) and $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ ($x = 0.1, 0.3, 0.5$) systems were prepared by a standard melt-quenching procedure [17]. The FSDP patterns in the range of $10^\circ < 2\theta < 30^\circ$ were obtained using conventional HZG-4a X-ray diffractometer (Cu $K\alpha$ -radiation) with 0.05° step. The samples were tested in the rotation regime. The FSDP parameters, position $2\theta_{\text{FSDP}}$ and full width at half maximum (FWHM) β_{FSDP} , were estimated with accuracy of $\pm 0.1^\circ$.

3. Results and discussion

Fig. 1 shows the XRD patterns obtained in the FSDP region for the investigated glasses from $(\text{Sb}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ and $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ systems. The FSDP position $2\theta_{\text{FSDP}}$, FWHM β_{FSDP} , average thickness of the domain built by packing a number of disordered layer configurations estimated with the Scherrer's formula [18,19] $D_s (= \{K\lambda/\beta_{\text{FSDP}}\cos\theta_{\text{FSDP}}\} \cdot \{360/2\pi\})$, where $K = 0.9$ is the Debye-Scherrer constant, λ is the X-ray wavelengths), and interlayer distance $d_s (= \lambda/2\sin\theta_{\text{FSDP}})$ are presented in Table 1 along with the data of experimental density ρ taken from literature [20,21].

One can see that practically all FSDP parameters reported here are compositionally dependent. In order to analyze these characteristics we consider the dependences of the FSDP position versus FWHM (see Fig. 2) and compositional trends of the calculated packing factor $p (= D_s/d_s)$ and experimental density ρ (see Fig. 3). In respect to the later, the correlation seems to be expected as the packing factor increases the density should be also increased, whereas former correlation between the position and FWHM was not predicted before experimental observations. As a result, it can be concluded that with addition of antimony sulphide content (Sb_2S_3) into to the glass matrix of good glass-formers such as As_2S_3 and GeS_2 , peak FSDP becomes narrower and shifts to the higher angles with simultaneous increase in the packing of amorphous layers and density.

It is interesting the fact that the correlations observed are found in the both $\text{AsS}_{3/2}$ -based pyramidal and $\text{GeS}_{4/2}$ -based tetrahedral networks. It indicates obviously about a common nature of the medium-range ordering in amorphous chalcogenides, the objective to be studied step by step for other chalcogenide systems such as ternary non-stoichiometric ones with more complicated structure than that for pseudo-binary stoichiometric glasses investigated.

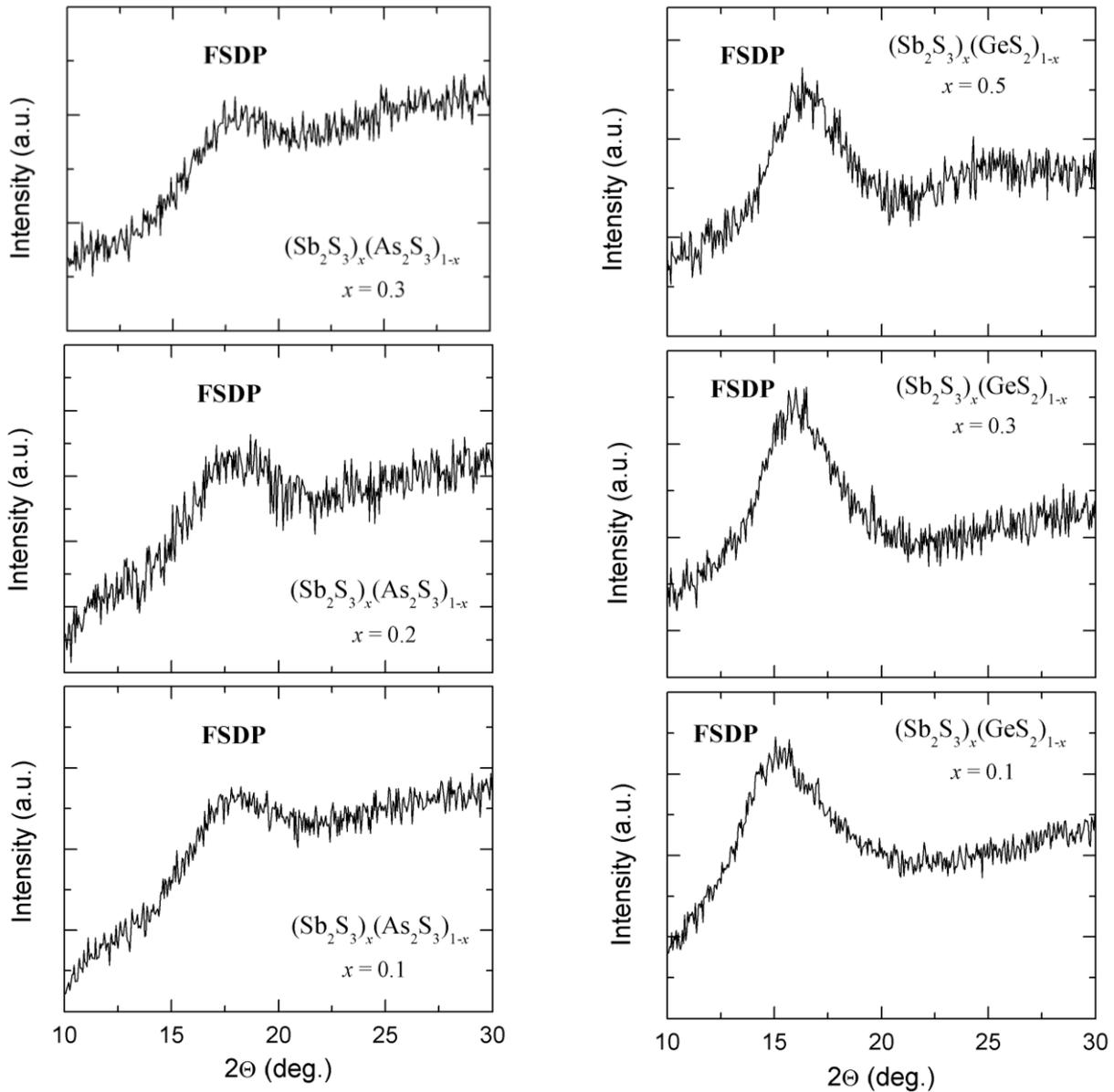


Fig. 1. The FSDP-related XRD patterns ($\text{Cu } K\alpha$ -radiation) for the investigated chalcogenide glasses.

Table 1. The data of the FSDP position $2\theta_{\text{FSDP}}$, full width at half maximum (FWHM) β_{FSDP} , average thickness of the domain built by packing a number of disordered layer configurations D_s , interlayer distance d_s and experimental density ρ for the investigated chalcogenide glasses.

| x | $2\theta_{\text{FSDP}}$ (deg.) | β_{FSDP} (deg.) | D_s (Å) | d_s (Å) | ρ (g/cm ³) |
|--|--------------------------------|------------------------------|----------------|---------------|-----------------------------|
| $(\text{Sb}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ | | | | | |
| 0.3 | 17.8 ± 0.1 | 4.3 ± 0.1 | 18.7 ± 0.1 | 5.0 ± 0.1 | 3.53 ± 0.01 [20] |
| 0.2 | 17.5 ± 0.1 | 4.6 ± 0.1 | 17.5 ± 0.1 | 5.1 ± 0.1 | 3.42 ± 0.01 [20] |
| 0.1 | 17.3 ± 0.1 | 5.6 ± 0.1 | 14.4 ± 0.1 | 5.1 ± 0.1 | 3.31 ± 0.01 [20] |
| $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ | | | | | |
| 0.5 | 16.4 ± 0.1 | 3.8 ± 0.1 | 21.2 ± 0.1 | 5.4 ± 0.1 | 3.65 ± 0.01 [21] |
| 0.3 | 16.0 ± 0.1 | 4.3 ± 0.1 | 18.7 ± 0.1 | 5.6 ± 0.1 | 3.35 ± 0.01 [21] |
| 0.1 | 15.2 ± 0.1 | 5.4 ± 0.1 | 14.9 ± 0.1 | 5.8 ± 0.1 | 2.95 ± 0.01 [21] |

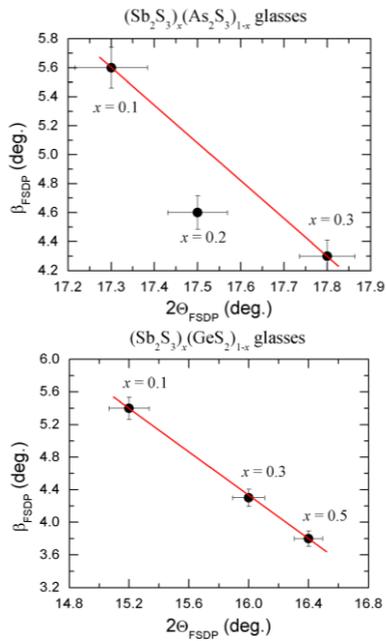


Fig. 2. The full width at half maximum (FWHM) of the FSDP (β_{FSDP}) versus the position of the FSDP ($2\theta_{\text{FSDP}}$) for the investigated chalcogenide glasses.

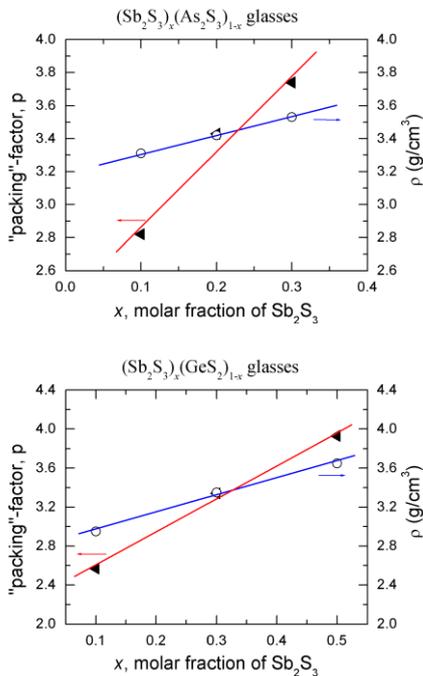


Fig. 3. The calculated "packing"-factor (p) and experimental density (ρ) as a function of composition x for the investigated chalcogenide glasses.

4. Conclusions

In summary, we report here that the correlations between the FSDP position and FWHM are found for chalcogenide glasses from pseudo-binary stoichiometric $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ and $\text{Sb}_2\text{S}_3\text{-GeS}_2$ systems to be agreed with the compositional trends of the calculated packing factor and

experimental density of glass. The results obtained can probably indicate on the modification of medium range ordering in the investigated glasses by antimony sulphide Sb_2S_3 with a common nature for pyramidal based network within $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ cut-section and mixed pyramidal-tetrahedral based network within $\text{Sb}_2\text{S}_3\text{-GeS}_2$ one.

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