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Structural relaxation of $GeSe_2$ chalcogenide glass studied with use of the radial distribution function

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The short- and medium-range orders of $GeSe_2$ chalcogenide glass were studied by using the radial distribution function. The effect of the annealing temperature on the short-range order structure of this glass was investigated. The short-range order structure of as-prepared and annealed $GeSe_2$ chalcogenide glass is regular tetrahedron (edge and corner sharing $GeSe_4$ tetrahedra). The medium-range order of the $GeSe_2$ chalcogenide glass is chemical order associated with topological order. The topological structure of the medium-range order can be described by the Phillips model. The basic structure unit does not change after annealing. Most changes observed in the diffraction patterns may be interpreted in the framework of structural relaxation during which a system tends to attain a metastable equilibrium state. This relaxation can be described by an α process.

I. INTRODUCTION

In recent years there has been a great deal of interest in the study of chalcogenide glasses from the viewpoints of physics as well as device technology. These glasses are used as switching devices and memory elements and optoelectronic device materials, etc.[1-3] The structural studies of these materials are very important for better understanding the transport mechanism.[4-6]

Chalcogenide glasses of Ge-Se alloys are interesting materials for infrared optics. They have a large range of transparency from 0.6 to 30 μm and good mechanical properties, such as hardness, adhesion, low internal stress, and water resistance. From this point of view, the Ge-Se system is very attractive, since it allows the formation of glasses in the range 0.0–42 at. % germanium.[7-9]

Two models have been proposed for $GeSe_2$ chalcogenide glass. These two models have similar features in local order but differ in intermediate-range order as well as the nature of like-atom bonds and phase separation.[10] The first model is a chemically ordered covalent random-network model (CRN), which consists of randomly bonded $GeSe_{4/2}$ tetrahedra linked to form a three-dimensional network.[11] In this model, the presence of like-atom bonds (Ge-Ge and Se-Se) or phase separation is attributed to defects. In the second model, the raft model, proposed by Phillips,[12] the network is also presumed to consist predominantly with $GeSe_{4/2}$ tetrahedra, but these units are covalently bonded together in layers similar to those of crystalline $GeSe_2$. Each layer consists of parallel chains of corner-sharing tetrahedra, cross linked with pairs of edge-sharing tetrahedra. In the raft model, layers are terminated by Se-Se dimmers parallel to the chains.

Chalcogenide glasses prepared by rapid melt quenching are thermodynamically "unstable" in the as-quenched state. Thus, annealing between room and glass-transition temperatures is accompanied by dramatic changes of some physical properties.[13-17] These changes result from the changes in the atomic-scale structure and are referred to as structural relaxation. According to Götze,[18] the atoms of supercooled liquids relaxed with two manners, α and β relaxation. Götze indicates the existence of a crossover temperature, T_{cr}, located above the glass-transition temperature, T_g, where the transport properties change from those typical for a strongly coupled liquid to those characteristic for a glass. Near T_{cr} the α process is specified by Debye-Waller factor anomalies, power-law divergences of the relaxation scale, and a crossover from α-scale universality to decoupling of the various relaxation processes. The β process is characterized by a complete absence of correlations between spatial and temporal motion and unconventional scaling laws. This phenomenon may be directly studied by the radial distribution function (RDF).

In the present work, the short- and medium-range order of $GeSe_2$ chalcogenide glass has been studied in terms of the radial distribution function on the basis of the data obtained by diffraction of x rays. The effect of annealing temperature on the short- and medium-range order of this glass has been investigated. The sample annealing at different temperatures was carried out under a vacuum of 0.001 Pa ($\approx 10^{-5}$ Torr) for 2 h. In the x-ray investigation a Cu target has been used. Although a Cu target has a limited value of the wave vector ($K_{max} = 81.4$ nm^{-1}), it has a good resolution in the region of small diffraction angles (the prepeak region). The details of the sample preparation and the experimental technique have been reported earlier in a previous work.[19]

II. RESULTS

The DSC thermogram of $GeSe_2$ chalcogenide glass carried out at a heating rate of 10 K/min is shown in Fig. 1. The DSC thermogram is a typical amorphous-crystalline transition one (the exothermic peak). From the DSC thermogram, the glass-transition temperature, T_g, the crystallization onset temperature, T_c, and the crystalliza-

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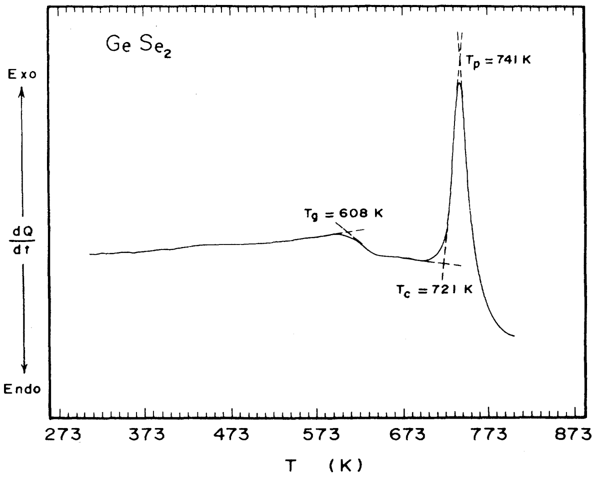

FIG. 1. The DSC thermogram of $GeSe_2$ chalcogenide glass carried out at heating rate 10 K/min.

tion peak temperature, T_p, of $GeSe_2$ chalcogenide glass are 608, 721, and 741 K, respectively. The annealing temperatures ($T_{ann}=373$, 473, and 573 K) are selected between the room temperature and the glass-transition temperature, T_g.

The scattered intensity was calculated as a function of the wave vector (K). In this study, the minimum value of K is 2.8 nm^{-1} and the maximum value of K is 66.8 nm^{-1}. The measured intensity has been corrected from background, polarization, and Compton modified scattering to obtain the coherent intensity, $I_{coh}(K)$.[19-24] The interference function, $I(K)$, has been calculated using the following equation:[19,25,26]

$$I(K)=\{I_{coh}(K)-\langle f^2\rangle+\langle f\rangle^2\}/\langle f\rangle^2 . \quad (1)$$

Here, $\langle f\rangle=X_{Se}f_{Se}(K)+X_{Ge}f_{Ge}(K)$ and $\langle f^2\rangle=X_{Se}f_{Se}^2(K)+X_{Ge}f_{Ge}^2(K)$, where $f_{Se}(K)$ and $f_{Ge}(K)$ are the atomic scattering factors for Se and Ge electrons whereas X_{Se} and X_{Ge} are the atomic concentrations of Se and Ge, respectively. Figure 2 shows $I(K)$ for $GeSe_2$ chalcogenide glass, as-prepared and annealed samples, as a function of K.

The Kaplow correction[27,28] has been applied on $I(K)$ before the calculation of the reduced RDF, $G(r)$. $G(r)$ was obtained as a function of the distance, r, by using the following equation:[19,25]

$$G(r)=4\pi r\{\rho(r)-\rho_0\}$$
$$=2/\pi\int_0^{K_{max}}K\{I(K)-1\}\sin(Kr)dK , \quad (2)$$

where ρ_0 is the average atomic density of $GeSe_2$ chalcogenide glass and $\rho(r)$ is the atomic density.

$G(r)$ was calculated numerically from the above equation for a range of K from 0 to 81.4 nm^{-1}. A reasonable extrapolation of $I(K)$ for small values of K (<2.8 nm^{-1}) has made with a negligible effect on $G(r)$ because of the small values of $K\{I(K)-1\}$.[19,22] Extrapolating $I(K)$ for large K values (>66.8 nm^{-1}) produces an error on the third peak of $G(r)$. This error is irrelevant as this study is only concerned with the first two peaks of $G(r)$.[19,29,30]

Figure 3 shows $G(r)$ for as-prepared and annealed $GeSe_2$ chalcogenide glass as a function of r. RDF(r) can be written as follows:[25]

$$\mathrm{RDF}(r)=4\pi r^2\rho(r)=rG(r)+4\pi r^2\rho_0 . \quad (3)$$

ρ_0 can be determined by two different methods, either experimentally from the weight density or from the slope of the linear part of $G(r)$. The value of ρ_0 determined experimentally for as-prepared sample is 34.8 atom/nm^3. The values of the average atomic density for as-prepared and annealed samples calculated from the results of reduced radial distribution function, ρ_0^{cal}, are listed in Table I. Figure 4 shows RDF(r) for as-prepared and annealed $GeSe_2$ chalcogenide glass as a function of r.

III. DISCUSSION

The x-ray diffraction of the as-prepared and annealed samples of $GeSe_2$ chalcogenide glass proved that the as-prepared and the heat-treated samples (annealed) are in amorphous state over the temperature range of the study.

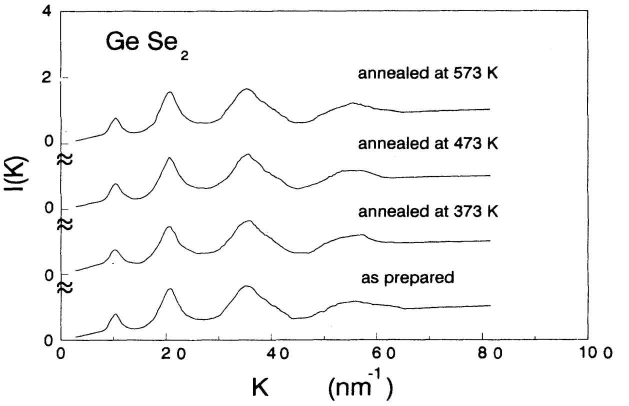

FIG. 2. The interference function, $I(K)$ vs K for as-prepared and annealed $GeSe_2$ chalcogenide glass.

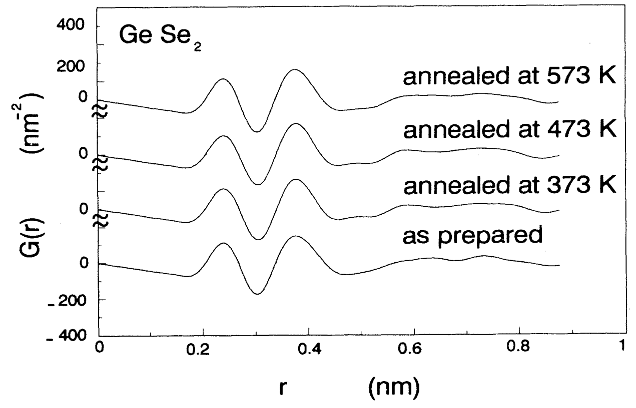

FIG. 3. The reduced radial distribution function, $G(r)$, vs r for as-prepared and annealed $GeSe_2$ chalcogenide glass.

TABLE I. The effect of the annealing temperature on the parameters of $G(r)$ and $\mathrm{RDF}(r)$ for $GeSe_2$ chalcogenide glass.

	Annealing temperature (K)				
	As-prepared				
	This work	From Ref.	373	473	573
r_1 (nm)	0.240	0.240[a]	0.239	0.242	0.240
r_2 (nm)	0.376	0.380[a]	0.378	0.376	0.376
(r_2/r_1)	1.567	1.580[a]	1.582	1.554	1.566
Θ (deg)	103.2	104.7[a]	104.5	102.0	103.1
FWHM_1 (nm)	0.050		0.052	0.058	0.050
FWHM_2 (nm)	0.076		0.066	0.070	0.070
ρ_0^{cal} (at./nm^3)	34.87	34.43[b]	34.91	34.86	34.83
d_s (nm)	0.380	0.386[c]	0.380	0.380	0.380
N_1	3.554	3.640[d]	3.562	3.510	3.455
N_2	10.158		9.983	9.968	9.567
α_W	−0.999	−1.047[d]	−1.004	−0.974	−0.943

[a] References 41 and 42.
[b] Reference 43.
[c] References 45 and 46.
[d] Reference 48.

A. Short-range order

Figure 3 shows the variation of the reduced radial distribution function, $G(r)$, with r for as-prepared and annealed samples of $GeSe_2$ chalcogenide glass. The position of the first peaks, r_1, the position of the second peaks, r_2, and the (r_2/r_1) ratios deduced from $G(r)$, Fig. 3, are listed in Table I. The position of the first peak, r_1, gives a value for the nearest-neighbor bond length (Se-Ge) and the position of the second peak, r_2, gives a value for the next-nearest-neighbor distance.[19,31] The value of (r_2/r_1) ratio is equal to the average value of (c/a) ratio in the tetrahedron structure.[19,31] For as-prepared and annealed samples, the values of (r_2/r_1) ratios are approximately constant. The average value of (r_2/r_1) ratios is 1.567 ± 0.010 which is the typical value of the corner as well as edge-sharing tetrahedron structure. The tetrahedron short-range order structure of the atom distribution in amorphous Ge systems can be described with the covalent random network model[11] (CRN), or the chain crossing model (CCM).[12] In CCM, the Se chain structure is maintained, but the fourfold, tetrahedrally coordinated Ge atoms act as chain crossing. In this model, Ge atoms are not allowed to bond to one another.[11,32–35] The layer model (raft model) suggested by Phillips has used the CCM to interpret the layer structure in glasses.[12,30] The Mössbauer work on $GeSe_2$ chalcogenide glass by Boolchand *et al.*[36] is more consistent with a raft model. In addition, results from Raman spectroscopy[37] as well as pressure and optical measurements[38] and laser recrystallization studies[39] of $GeSe_2$ chalcogenide glass have been used to support and extend Phillips layer model. Therefore, the Phillips layer model will be used in this study.

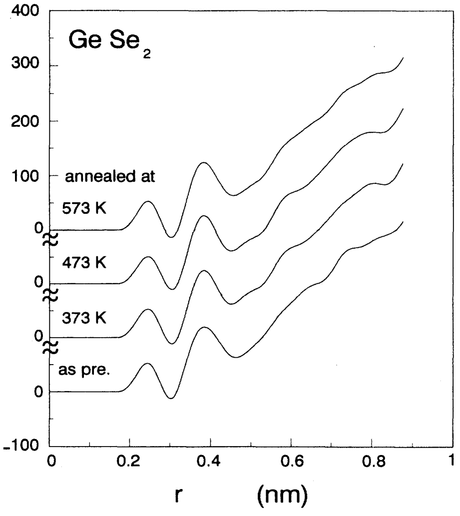

FIG. 4. The radial distribution function, $\mathrm{RDF}(r)$, vs r for as-prepared and annealed $GeSe_2$ chalcogenide glass.

The bond angle, Θ, can be calculated as[19,31]

$$\Theta = 2\sin^{-1}\left\{\frac{r_2}{2r_1}\right\} . \tag{4}$$

The bond angle values for the as-prepared and annealed samples are listed in Table I. The annealing temperatures exhibit no significant change in the bond angles. The average value of the bond angle is 103.20°±0.89° which is the ideal value of bond angle for perfect tetrahedral coordination.

The full width at half maximum of the first peak of $G(r)$, FWHM_1, and for the second peak, FWHM_2, deduced from Fig. 3 are listed in Table I. It is clear that FWHM_2 is greater than FWHM_1. This can be attributed to the thermal vibration of the atoms and the presence of static disorder in the bond length.[19,31,40]

For the as-prepared sample, the values of r_1, r_2, and Θ are in good agreement with those obtained by Lannoo and Benesousson[41] and Poltavtsev and Polzdnayakova.[42] The average atomic density of the as-prepared sample, ρ_0^{cal}, obtained from the slope of the linear part of $G(r)$ is in good agreement with the experimental value carried out in this work and with those obtained by Iytomi, Voshista, and Kalia.[43] The value of ρ_0^{cal} increases by annealing at 373 K. In contrast, it decreases as the annealing temperature increases. The variation of ρ_0^{cal} with the annealing temperature, T_{ann}, can be described by the following empirical formula:

$$\rho_0^{\mathrm{cal}}(\mathrm{atom/nm^{-3}}) = -0.187T_{\mathrm{ann}}(K) + 36.02 . \tag{5}$$

The mean interatomic spacing, d_s, can be calculated from the relation[9,44,45]

$$d_s = (6/\pi\rho_0)^{1/3} . \tag{6}$$

The values of d_s are listed in Table I. For the as-prepared sample, the value of d_s is in good agreement with those obtained by Price *et al.*[45] and Moss and Price.[46]

The area under the peak in the $\mathrm{RDF}(r)$ gives the average coordination number, N. This area can be calculated by fitting the curve with Gaussian function[13,44,47] or by integration of the RDF(r) using the following equation:[9,19,25]

$$N=\int_{r_0}^{r'}4\pi r^2\rho(r)dr \ , \tag{7}$$

where r_0 is a lower limit of r below which $\rho(r)$ is zero and r' is the first minimum of $4\pi r^2\rho(r)$. The deference between the N values calculated by both methods is within the experimental error (about 2%). The same techniques are used to calculate the average coordination number for the first and the second peaks. The average coordination numbers of the first peak, N_1, and the second peak, N_2, are listed in Table I. The deduced value of N_1 for the as-prepared sample is in good agreement with those obtained by Iytomi, Voshista, and Kalia.[48] After annealing, N_1 and N_2 decrease slightly as the annealing temperature increases. The variation of N_1 with the annealing temperature, T_{ann}, can be described by the following empirical formula:

$$N_1=-5.35\times10^{-4}T_{\mathrm{ann}}(K)+3.76 \ . \tag{8}$$

For as-prepared and annealed samples, the value of the average coordination number of the first peak, N_1, is ranged between 3.455 and 3.554. For the as-prepared and annealed (373 and 473 K) samples, the fraction is greater than 0.5 which means that the fourfold coordination is predominant. This results in good evidence for using the chain crossing model[12] (CCM) and also for the 4-2 network[11,25] which means that, in $\mathrm{GeSe_2}$ chalcogenide glass, the Ge atom bonded only with Se atoms (four atoms) and the Ge-Ge bond did not exist in this glass.[11,25,32–35] This interpretation is also in good agreement with the Raman study on $\mathrm{Ge}_x\mathrm{Se}_{1-x}$ chalcogenide glasses obtained by Tronc *et al.*[32] By increasing the annealing temperature, the fraction decreases and has a value less than 0.5, which means that the threefold coordination begins to predominate and the 3-3 network, suggested by Bienenstock,[49] becomes more convenient.

The Warren parameter, α_W, can be calculated from the relation[9,50,51]

$$\alpha_W=1-N_{ij}/X_j(X_jN_j+X_iN_i) \ , \tag{9}$$

where N_{ij} is the average value of the coordination number of the nearest neighbor reduced from the RDF results (N_1), N_j and N_i are the coordination numbers of the major and minor element in the binary alloy, respectively. While X_j and X_i are the concentrations of the major and minor elements in the binary alloy, respectively. The values of α_W for as-prepared and annealed samples are listed in Table I.

The Warren parameter, α_W, is used to discuss the type of order, chemical and/or cluster order. According to Warren,[9,50,51] the values of α_W indicate the type of order as $\alpha_W>0$ for chemical ordering, $\alpha_W<0$ for chemical order associated with clustering, and $\alpha_W=0$ for complete chemical disorder. From the results it is clear that the $\mathrm{GeSe_2}$ chalcogenide glass has a chemical order associated with clustering ($\alpha_W<0$).

B. The medium-range order

Figure 2 indicated that, for as-prepared and annealed samples, the interference function, $I(K)$ has prepeaks at $K=10.42\pm0.12\ \mathrm{nm}^{-1}$. The positions of the prepeak, K_{pre}, are listed in Table II. The presence of the prepeak indicates a strong pointer for the existence of clusters or medium-range order. The origin of this prepeak is due to the fact that many materials have crystalline polyamorphous which have a layer structure with an interlayer separation of order 0.4–0.6 nm. The diffraction from the layers produces the prepeak. The position of the prepeak corresponds well to that of the interlayer Bragg peak seen in crystalline material.[52] Its position in real space, r_{pre}, ($r_{\mathrm{pre}}=2\pi/K_{\mathrm{pre}}$) is listed in Table II. The values of K_{pre} and r_{pre} for as-prepared sample are in good agreement with those obtained by Lin *et al.*[53] These values of r_{pre} are in the range of the medium-range order.[9,17,31] r_{pre} is called the interlayer separation[9,31] or cluster radius.[9,17] The appearance of the medium-range order in this glass can be attributed to the germanium atom.[9,31,54–58] The prepeak has been observed in the germanium chalcogenide glasses (Ge-S and Ge-Se systems) (Refs. 9, 31, and 54–58) and in the arsenic chalcogenide glasses (As-S and As-Se systems).[9,31]

TABLE II. The effect of the annealing temperature on the parameters of the interference function for $\mathrm{GeSe_2}$ chalcogenide glass.

	Annealing temperature (K)				
	As-prepared				
	This work	From Ref.	373	473	573
K_{pre} (nm^{-1})	10.49	10.40[b]	10.20	10.49	10.48
$I(K)_{\mathrm{pre}}$	0.793		0.759	0.746	0.776
r_{pre} (nm)	0.599	0.604[b]	0.616	0.599	0.599
$\mathrm{FWHM_{pre}}$ (nm^{-1})	1.973		2.537	2.255	1.973
R (nm)	3.185		2.476	2.787	3.183
α_{pre} ($10^{-5}\ \mathrm{K}^{-1}$)		4.33[a]	−58.78	5.43	1.27
K_{fp} (nm^{-1})	20.80		20.50	20.52	20.80
$I(K)_{fp}$	1.565		1.473	1.582	1.571
r_{fp} (nm)	0.302		0.306	0.306	0.302

[a] Reference 43.

[b] Reference 53.

For as-prepared and annealed samples, the values of the full width at half maximum of the prepeak, $\mathrm{FWHM}_{\mathrm{pre}}$, are listed in Table II. The value of $\mathrm{FWHM}_{\mathrm{pre}}$ increases by annealing at 373 K, whereas, it decreases as the annealing temperature increases. The variation of $\mathrm{FWHM}_{\mathrm{pre}}$ with the annealing temperature, T_{ann}, can be described by the following empirical formula:

$$\mathrm{FWHM}_{\mathrm{pre}}(\mathrm{nm}^{-1}) = -2.82\times 10^{-3} T_{\mathrm{ann}}(K) + 3.589 \; . \tag{10}$$

The origin of the prepeak must be attributed to the presence of large molecular clusters with a center-to-center spacing $r_c \approx 0.5$ nm. If these clusters are quasiplanar a correlation length, R, normal to planes can be estimated from the prepeak width:[59]

$$R = 2\pi/\Delta K \; , \tag{11}$$

where ΔK is the full width at half maximum of the prepeak, $\mathrm{FWHM}_{\mathrm{pre}}$ (listed in Table II). The values of the correlation length, R, are listed in Table II. The value of R decreases by annealing at 373 K. This could be attributed to the transformation to metastable amorphous phase.[60] The correlation length increases as the annealing temperature increases. This indicates the formation of small clusters restricted to the nearest-neighbor shell, i.e., the cluster size increases. The variation of R with the annealing temperature, T_{ann}, can be described by the following empirical formula:

$$R(\mathrm{nm}) = 3.54\times 10^{-3} T_{\mathrm{ann}}(K) + 1.14 \; . \tag{12}$$

The data of the first sharp peak in the interference function are listed in Table II. According to Busse[17] and Emagi,[60] the variation of the position and the intensity of both the prepeak and the first sharp peak are similar, which indicates that the annealing of $\mathrm{GeSe_2}$ chalcogenide glass causes a chemical order associated with clustering, i.e., topology order. This result is in good agreement with those deduced from the values of Warren parameter. Above room temperature, the prepeak shifts were measured from which the thermal expansion coefficients, α_{pre}, were calculated by[17]

$$\alpha_{\mathrm{pre}} = \{ K_{\mathrm{pre}}^{-1} (dK/dT) \} \; , \tag{13}$$

where K_{pre} is the wave vector at the prepeak position and dK is the variation of the peak position due to variation in the annealing temperature with dT.

The thermal expansion coefficient, α_{pre}, calculated from the shift of the prepeak is listed in Table II. The difference in the calculated values of thermal expansion coefficients can be attributed to the formation of clusters from unlike atoms, indicates that the wave vector (K) must be related to different directions in the local order of the glass.[17] According to these suggestions the $\mathrm{GeSe_2}$ glassy structure might be isotropic and consists of groups of layers randomly oriented. These results are in good agreement with those obtained by Iytomi, Voshista, and Kalia.[43] They suggested that the difference in the value of α_{pre} indicates that there are two characteristic length scales distinguishing the medium-range correlation and the short-range correlation.

The most changes, which are observed in the diffraction patterns after annealing, may be interpreted in the framework of structural relaxation during which a system tends to a metastable equilibrium state.[60] When the temperature rises, it would be possible to break or bend bonds, the atoms are relaxed into the layers but within the layers themselves there would be less ordering. On the other hand, according to Götze, the relaxation of $\mathrm{GeSe_2}$ chalcogenide glass can be described by the α process.[18] The annealing temperature (except at $T_{\mathrm{ann}} = 373$ K) did not have any influence on many parameters such as r_1, K_{pre}, and r_{pre}. This can be attributed to the strong coupling below the crossover temperature, T_{cr}.[18,61,62] Generally, the structure stability of $\mathrm{GeSe_2}$ chalcogenide glass with annealing can be interpreted using the Phillips proposal for the arsenic sulfide.[12,30,63] When heated or annealed, the arsenic sulfide glasses are more resistant to crystallization. Phillips[12,30,63] proposed that there are stocks of layers (or rafts), present in the glass which are not microcrystalline. He described the atomic arrangement in a raft so that it has minimal strain energy.[63]

IV. CONCLUSIONS

From the (r_2/r_1) ratio (1.567 ± 0.010) and the bond angle $(103.2^\circ \pm 0.9^\circ)$ the short-range order structure of the $\mathrm{GeSe_2}$ chalcogenide glass has corner- as well as edge-sharing tetrahedron structure. The structure of the atom distribution in amorphous systems corresponds to the cross chain model (CCM).

From the appearance of the prepeaks in the interference functions, the atom's distribution of the as-prepared and annealed $\mathrm{GeSe_2}$ chalcogenide glass has medium-range order. From the variation of the peaks in the interference function and according to Emagi, the medium-range order of $\mathrm{GeSe_2}$ chalcogenide glass is chemical order associated with topology order. The topological structure of the medium-range order can be described by the Phillips model (raft model).

The basic structure unit does not change after annealing. Most changes observed in the diffraction patterns may be interpreted in the frame of structural relaxation during which a system tends to attain a metastable equilibrium state. This relaxation can be described by an α process.

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