

REVERSE MONTE CARLO MODELING OF Ge-As-Te CHALCOGENIDE GLASS
SYSTEM

by

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ABSTRACT

REVERSE MONTE CARLO MODELING OF Ge-As-Te CHALCOGENIDE GLASS SYSTEM

Chalcogenide glasses are well known for their wide technological applications due to their optical, structural and electrical properties. Their wide-ranging applications can be stated as infrared optical fibers, optical elements, switching and memory devices because of their low phonon energy and optical losses, good thermal and chemical stability and infrared transparency. In this thesis, three dimensional structures of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with total metal contents (Ge+As) of 30, 40, 50, and 70 at.% were generated by employing reverse Monte Carlo modeling based on high energy x-ray diffraction data from the literature. Short- and intermediate-range structural characteristics are elucidated based on these models. Structural parameters involving coordination numbers, partial structure factors, partial pair distribution functions, bond angle distributions and ring size distributions are obtained and evaluated to reveal the atomic structures of these materials. It was found that Ge, As, and Te atoms were 4, 3, and 2, coordinated respectively, independent of chemical composition. Increasing metal (Ge+As) content in the system resulted in the appearance of first sharp diffraction peak (FSDP) in the structure factors that indicate the presence of intermediate-range order in the system. Ring size distributions for glasses with low metal contents ($3x=30$ and 40) revealed a very narrow distribution whereas increasing metal content resulted in much wider ring size distributions that might be correlated with the development of intermediate range order.

ÖZET

Ge-As-Te KALKOJEN CAM SİSTEMİNİN REVERSE MONTE CARLO YÖNTEMİ İLE MODELLENMESİ

Kalkojen camlar optik, yapısal ve elektriksel özelliklerinden dolayı geniş teknolojik uygulamaları ile bilinmektedir. Düşük fonon enerjisi, optik kayıpları, iyi termal ve kimyasal stabilite ve kızılötesi şeffaflık özellikleri nedeniyle bu camların geniş kapsamlı uygulamaları kızılötesi fiber optikler, optik elemanlar, anahtarlama ve bellek aygıtları olarak belirtilebilir. Bu tezde toplam metal içeriği (Ge + As) 30, 40, 50 ve 70 olan $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ camların üç boyutlu yapıları, literatürden alınan yüksek enerjili x-ışını kırınım verilerine dayanan ters Monte Carlo modellemesi kullanılarak oluşturulmuştur. Kısa ve orta ölçekli yapısal özellikler bu modellere dayanarak açıklanmaktadır. Koordinasyon sayıları, kısmi yapı faktörleri, kısmi çift dağılım fonksiyonları, bağ açısı dağılımlarını ve halka boyutu dağılımlarını içeren yapısal parametreler elde edilmiş ve bu camların atomik yapılarını ortaya çıkarmak için değerlendirilmiştir. Kimyasal bileşimden bağımsız olarak Ge, As ve Te atomları sırasıyla 4, 3 ve 2 koordineli olarak bulunmuştur. Orta ölçekli düzenin var olduğunu gösteren yapısal faktörde, sistemde artan metal (Ge + As) içeriği ilk keskin kırılma pikinin (FSDP) oluşmasıyla sonuçlanmıştır. Artan metal içeriği orta ölçekteki düzenin gelişimiyle ilişkili olabilecek çok daha geniş halka dağılımı gösterirken, düşük metal içerikli ($3x = 30$ ve 40) kalkojen camlar için halka boyutu dağılımları çok dar bir dağılım göstermiştir.

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LIST OF SYMBOLS

$g_{ij}(r)$	Partial Pair Distribution Function
$G(r)$	Atomic Pair-Distribution Function
$pjMAT$	Projection Magic-Angle-Turning
R_{ij}	Nearest Neighbor Distance
$S(Q)$	X-ray Structure Factor
$S_{ij}(Q)$	Partial Structure Factor
T_c	Crystallization Temperature of Chalcogenide Glass
Te	Tellurium
T_g	Glass Transition Temperature of Chalcogenide Glass
T_m	Melting Temperature of Chalcogenide Glass

LIST OF ACRONYMS/ABBREVIATIONS

As	Arsenic
BAD	Bond Angle Distributions
ChGs	Chalcogenide Glasses
CN	Coordination Number
CSA	Chemical Shift Anisotropies
CONM	Chemically Ordered Network Model
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
DVD-RAM	Digital Versatile Disc-Random Access Memory
EXAFS	Extended X-ray Absorption Fine Structure Spectroscopy
FSDP	First Sharp Diffraction Peak
GAT	Ge-As-Te
Ge	Germanium
GST	Ge ₂ Sb ₂ Te ₅
GCT	Ge ₁ Cu ₂ Te ₃
IR	Infrared
MRO	Medium Range Order
MRO	Medium Range Order
MCN	Mean Coordination Number
MIR	Mid-Infrared
ND	Neutron-Diffraction
PCRAM	Phase Change Random Access Memory
PCM	Phase Change Memory
PDF	Pair Distribution Functions
SEM	Scanning Electron Microscopy
S	Sulphur
Sb	Antimony
Se	Selenide
RMC	Reverse Monte Carlo

SRO	Short Range Order
VIS	Visible Spectrum
XRD	X Ray Diffraction

1. INTRODUCTION

Chalcogenide glasses have recently been investigated and developed rapidly due to their important properties and wide-ranging applications. They have been of unique importance as optical materials or photonic devices and therefore the chalcogenide glasses have been studied for more than fifty years [1]. There are several chalcogens of III-V group elements used to produce optical fibers. Studies for glasses based on chalcogenide of Arsenic (As) and Germanium (Ge) have the most important results. Wide transparency range, low optical losses, stability to atmospheric moisture and high non-linearity of optical properties, a strong resistance toward resistance can be counted as the properties of chalcogenide glasses. Therefore, when this properties are considered, chalcogenide of As and Ge have a very significant place in production of optical fibers [2].

Reverse Monte Carlo (RMC) Modeling is a general method of structural modeling of intermediate and extended-range scale in vitrified materials and three-dimensional atomic configurations can be figured out by using experimental data. Experimental data is the cornerstone of RMC modeling [3, 4]. RMC modeling is a very effective method to acquire three-dimensional structural information for complex systems. In this modeling technique, the density and cut-off (nearest neighbor coordination) values of the materials are very crucial and required parameters. RMC modeling uses experimental data such as high energy x-ray and neutron diffraction to obtain reliable three-dimensional structure of materials. With RMC simulations, atomic configurations, partial pair distributions, pair distribution factors and bond-angle distributions can be determined [5].

1.1. History of Chalcogenide Glasses

The research of oxygen free glasses published in an early time in 1870 [6]. After that, Wood in 1902 and Meier in 1910 searched the optical features of vitrified selenium [6]. The investigation of chalcogenide glasses began by R.Frierichs for As_2S_3 , arsenic trisulphide, as an optoelectronics material in infra-red region of the electromagnetic spectrum between 1950 and 1953 [7]. Improvements about the glasses of optoelectronic materials were carried

on by W.A. Fraser and J. Jerger in 1953 [7]. In 1960, electrical properties of chalcogenide glasses were investigated by S. Ovshinsky and A.D Pearson in the beginning of 1960, these studies showed their amorphous semiconductor properties and switching behaviors [7]. Investigations have been carried out because of notable properties of chalcogenide glasses and their many important applications such as optical switches, optical amplifiers, infrared lasers, bio-sensors, remote sensing, medical treatment, environmental protection and military applications [6, 8, 9].

1.2. Structural Characteristics and Properties of Chalcogenide Glasses

Chalcogenide glasses primarily have covalent bonds. In terms of $8N$ binding rule, the 4-coordinated germanium (Ge) form tetrahedral units that is $[\text{GeX}_4]$ and 3-coordinated arsenic (As) form trigonal units that is $[\text{AsX}_3]$ where X is the chalcogen (Te, Se, or S). As_2S_3 , As_2Se_3 , GeS_2 and GeSe_2 are some examples of chalcogenide glasses [2]. The structure of glassy As_2S_3 , As_2Se_3 is a layered two dimensional network and this structure consists of $[\text{AsS}_{3/2}]$ and $[\text{AsSe}_{3/2}]$ trigonal pyramids. Within the layer atoms are connected with strong covalent bonds while Van der Waals bonds are formed between layers [2, 10].

When chalcogenide glasses are compared with oxide glasses, it is observed that chalcogenide glasses have much weaker mechanical toughness and thermal stability. On the other hand, they have superior features such as their wide transparency range from the visible region up to the mid infrared region, higher thermal expansion, low optical losses, high optical non-linearity, their low phonon energies ($300\text{-}350\text{ cm}^{-1}$), high refractive index (2-3.2) and tendency to crystallization. By using chalcogenide optical fibers lots of technical problems in optics and opto electronics can be avoided because of low optical losses of chalcogenide glasses [2, 10, 11]. Chalcogenide glasses can be used in numberless potential optical fiber applications such as fiber amplifiers, lasers, modal filters etc. because of their great transmission capacity in longer wavelengths in the infrared region than silica and fluoride glasses [11, 12]. Due to these outstanding characteristic properties, they will be preferred to use in various areas [1, 2, 3].

There are different phases of chalcogenide glasses such as liquid and vapor phase. The chalcogenide glasses with different phases can be obtained by different techniques;

cooling of melt, sol-gel [10], chemical vapor deposition, evaporation and sputtering [13] are most known methods.

The synthesis of chalcogenide glasses should be executed in sealed evacuated quartz ampoules because of their tendency to oxidation and hydrolysis. Different synthesis conditions should be taken into account. Glass compositions, glass-forming region and glass forming ability directly affect these conditions [7]. Therefore, preparation temperature of the glasses with different element such as As and Ge should be within limits or ranges. The range should be 700-750 °C for glasses including As and should be under 900-950 °C for glasses including Ge. Additionally, quartz ampoules' structure deforms at the temperature of 1200-1250 °C, thus this temperature should be the limit of synthesis [7].

When it comes to the properties of chalcogenide glasses, it can be said that optical properties and thermal properties of chalcogenide glasses provide them to be excellent glasses in the IR region. Chalcogenide glasses perform a transmission from VIS up to MIR [14]. First, optical properties of chalcogenide glasses have played a tremendous role in IR due to the extended transparency range. Much absorption are occurred by vibrational transitions. These IR vibrations are performed by impurities in the glass, and basic structural vibrations which is caused glass' infrared cut-off (shortcut), or multi phonon edge [6].

Remarkable interest and investigation in chalcogenide glasses have occurred due to their outstanding transparency in IR and rheological features. One of the most important properties of chalcogenide glasses is also mentioned that the transparency of them is extended and wide range in the IR so that it can be attracted a great deal of attention and interest. Second, thermal properties of chalcogenide glasses are another one of the most significant features. Because of the wide transparency range in IR, this type of glasses plays an important role in infrared sensing applications. However, it is often preferred to use fibers or molded lenses as specific optics for the model of optical sensor. Thus, the important thing is the rheological properties of chalcogenide glasses. As a crucial and leading reason in determination of composition of chalcogenide glass for use in IR utilization, crystallization or devitrification resistance can be performed by Differential Scanning Calorimetry (DSC). By means of DSC, the glass transition (T_g), crystallization (T_x) and melting(T_m) temperature are determined. The difference between T_x and T_g explains the glass stability that means if

the difference between T_g and T_x is large, the crystallisation of glass is probably less during processes such as synthesis and molding. On the other hand, the aim is to maximize the difference between T_g and T_x for glass components with crystallization temperature [6].

Chalcogenide glasses have the unique properties for use in non-linear, IR and optical waveguide optics. When chalcogenide glasses are compared to oxide glasses, the inter-atomic of ChGs are weaker than oxide glasses. Thus, red shift is exhibited by their band gap in light's electromagnetic spectrum. The atomic weight of constituent elements of chalcogenide glasses are heavy, thus the vibrational energy of bond is low and chalcogenide glasses are low phonon materials [15].

1.3. Technological Applications of Chalcogenide Glasses

Chalcogenide glasses have been promising materials for wide applications for recent years. The key features of chalcogenide glasses can be high refractive index (2-3.2), low phonon energy ($300\text{-}350\text{cm}^{-1}$), high nonlinearity, high photosensitivity, and perfect transmission in infrared region (up to wavelength $\lambda=12\text{-}15\mu\text{m}$). These glasses due to their important properties can be used in various areas such as civil, medical, and military applications, including infrared lenses, photonic integrated circuits, infrared detectors, lasers, planar optics that requires IR transmission. Chalcogenide glasses due to their high excellent transmission property in longer wavelengths in the IR than chalcogenide including Silica (Si) and Fluoride (F) glasses [2].

Tellurium containing chalcogenide glasses have been technologically very important materials because of their wide range of applications in many areas, such as rewritable optical data storage and in non-volatile electronic memory applications [11, 16]. Since chalcogenide glass fibers transmit in the IR region, there are numerous potential applications in the civil, medical and military areas. Chalcogenide fibers are well-suited for chemical-sensor applications, such as fiber-optic chemical sensor systems for quantitative remote detection and identification as well as detecting chemicals in mixtures.

Applications areas can be divided into two devices: active and passive photonic devices [12]. These applications can be included in laser power delivery with high power

CO and CO₂ lasers, chemical sensing for quantitative remote detection and identification, imaging, thermal imaging and hyper spectral imaging, scanning near field microscopy/spectroscopy, IR sources/lasers, amplifiers and optical switches, rare earth doped fibers by pumping with the appropriate energy [17].

The applications of chalcogenide glasses are associated with the optimization of the performance of these materials. However when telluride glasses are compared to sulphide or selenide counterparts, a major obstacle is that binary and ternary telluride glasses usually display poor glass-forming tendency [18].

In addition to these applications of chalcogenide glasses, application of optical fibers is very useful and effective to solve some medical and technical diagnostics problems. Supply of laser power through optical fibers can be made efficient solution for these problems. Some examples of actual applications of optical fibers from chalcogenide glasses can be infrared pyrometry, transmission of IR images, analytical IR spectroscopy, power fiber optics, systems for telecommunication and non-linear optics [2].

Chalcogenide glasses' transmission range is between 2-18 μm and this wide transmission range provides chalcogenide glasses a very important and popular position for its usage as biological sensors [6]. The glass should have a low phonon energy to transmit in the infrared. There are two parameters which affect this phonon energy; bond strengths and molecular weights of the glass components. Low phonon energy can be provided by heavy elements such as sulphur, selenium or tellurium forming chalcogenide glasses. On the other hand, there is also a disadvantage for low phonon glasses. As the IR transmission range increases, thermal and mechanical properties of chalcogenide glasses decrease. To form the most functional glass structure, this approach should be followed [6]. For example, chalcogenide glasses containing Te/I have wide transmission range to 20 μm . For these glasses, it is shown that containing more Te element in glass structure can often cause unstable to devitrification. Because of this reason, smaller quantity of Te element can be stabilized by bonding Se and As elements to form $\text{Te}_2\text{As}_3\text{Se}_5$. This composition formed is a very stable glass displaying excellent properties such as wide optical range from 2 to 18 μm , good mechanical and thermal properties and resistance to devitrification. In addition to Te element, As containing chalcogenide glasses are generally available to use in many areas.

However, Arsenic is toxic and one should be careful in designing As-containing glasses for biological applications [6].

In addition to these applications, there is also another usage of chalcogenide glasses containing tellurium such as space exploration [6]. An important way to extend the IR transmission range for space applications is to use chalcogenide glasses containing Tellurium which is the heaviest chalcogen element [19].

Chalcogenide glasses are used widely in imaging and sensing applications. Night-vision devices and recognition systems have been developed such as night-vision cameras for military applications employing chalcogenide glasses. In terms of infrared sensing applications, the surveillance of chemical reactions, biological methods and biomedical sensing are some of the examples [6].

1.4. Literature Survey of Chalcogenide Glasses

The amorphous nature of glassy alloys of $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ ($x=0, 10, 20, 30, 40, 50$) prepared by melt quenching technique was investigated by x-ray diffraction and optical transmission spectra of thin films obtained in the range 400–2400 nm were obtained. In this study, the effect of addition of Te on the optical properties of $\text{Ge}_{10}\text{Se}_{90}$ was studied [33]. In conclusion, decrease in Te content leads to formation of a structure with higher degree of disorder. The optical band gap was found to decrease with the increasing Te content. The absorption coefficient and refractive index decreased with the increasing wavelength. The refractive index first decreased (up to 30 at.%) and thereafter increased with Te content [20].

In a recent study, the short and intermediate- range structural characteristics of the telluride glasses $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ were investigated using high energy x-ray diffraction. The structure was shown to be more coherent with the high metallicity of Te compared to other chalcogens (including S or Se). The structural order at 0.5 nm or higher have been found to be significantly weaker in the chalcogenide glass containing excessive Te. In $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glass system, chemical order in the nearest-neighbour Ge/As-Ge/As bonding environment existed in Te deficiency. In this examination, FSDP position seemed to

decrease with decreasing of Te atoms between $37.5 \leq 3x \leq 70$, it did not change both with $25 \leq 3x \leq 35$ and the width of FSDP increase weakly with the increase of metallicity. FSDP is located at around $1 \text{ \AA}^{-1}$ with $55 \leq 3x \leq 70$. Finally, it was observed that the structural evolution with composition was more coherent with changing molar volume and T_g of the $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses [18].

Dai *et al.* examined the effect of CuI on the formation and properties of the amorphous materials and their compositional dependence. The glass forming region of $\text{Ge}_{20}\text{Te}_{80-x}(\text{CuI})_x$ chalcogenide glass prepared by traditional melt-quenching method was searched ($x=5, 10, 20, 30$ at%) [21]. The X-ray diffraction patterns of $\text{Ge}_{20}\text{Te}_{80-x}(\text{CuI})_x$ ($x = 5, 10, 20, 30$ at.%) glass samples was performed. As a result of this study, X-ray diffraction showed that the glass samples under this study were amorphous and the addition of CuI up to 30 mol% did not cause appearance of any sharp peaks.

Sun *et al.* investigated the local structure of the GeTe_4 based tellurium (Te) glasses modified by heavy metal and metallic iodide with the help of the Raman Spectroscopy [22]. As the ZnI_2 content was increased from 0 to 15 mol% (no more content of ZnI_2 was added), the amplitude of 159 cm^{-1} band decreased and the intensity of 275 cm^{-1} band increased. It is interesting to note that as many as 30 mol% AgI was added into GeTe_4 glasses and the amplitude of 159 cm^{-1} band first decreased and then increased with increasing content of AgI. It was construed as that the addition of iodine efficiently opened up Te–Te bonds and decreased the intensity of 159 cm^{-1} Te–Te vibrations. In conclusion of this experiment, the addition of glass modifiers to GeTe_4 glass structure caused the disorganization of the glass network by break up Ge-Te and Te-Te bonds [22].

Asokan *et al.* studied the amorphous structure of $\text{Ge}_{15}\text{Te}_{85-x}\text{Si}_x$ glass with X-ray diffraction ($0 \leq x \leq 9$). The X-ray diffraction patterns of three structure of $\text{Ge}_{15}\text{Te}_{85-x}\text{Si}_x$ glasses was figured out ($x=2, 5, 6$). As a result, the addition of Si content caused an increase in network connectivity and stiffness of the covalently bonded network [23].

Vergel *et al.* examined the optical functions of chalcogenide glasses $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$, $\text{Ge}_{10}\text{As}_{30}\text{Te}_{60}$, $\text{Ge}_{10}\text{As}_{40}\text{Te}_{50}$, $\text{Ge}_{10}\text{As}_{50}\text{Te}_{40}$, and $\text{Ge}_{10}\text{As}_{60}\text{Te}_{30}$, $\text{Ge}_{20}\text{As}_{20}\text{Te}_{60}$ from Ge-As-Te characterized by spectroscopic ellipsometry in spectral range (300nm - 20 μm). In conclusion

of this study, refractive index clearly decreased with decreasing content of tellurium in the glasses while band gap shows opposite tendency and decreasing content of tellurium in Ge–As–Te glasses led to lower refractive indices values in IR and higher band gap values [24].

In recent study of chalcogenide glass, Mohamed *et al.* studied the effect of composition on the structure and optical parameters of $\text{Ge}_x\text{Se}_{50}\text{Te}_{50-x}$ ($x=0, 5, 15, 20, 35$ at %) thin films prepared by thermal evaporation technique utilizing the optical transmittance and reflectance spectra. The existence of some crystalline peaks was due to Te and Se phases and the number of these peaks decreased as Ge content increased. Optical parameters such as energy gap increased with increasing Ge content [25].

Piarristeguy *et al.* investigated the structure of $\text{Ge}_x\text{Te}_{100-x}$ co-evaporated films with compositions in the range $10 < x < 50$. EXAFS and X-ray diffraction measurements of them are used and analyzed in RMC modeling. Both materials were prepared by melt-quenching and co-evaporation methods. More than 95% Ge atoms proved that the total coordination number of Ge atoms equals to 4.0. In RMCV modeling, the cut-off values of Ge-Te and Te-Te were $2.35 \text{ \AA}^\circ$ and $2.5 \text{ \AA}^\circ$. The Ge-Ge cut-off was $3.5 \text{ \AA}^\circ$ when neighbors for Ge atoms were not allowed and the cut-off of Ge atom was 2.25 when Ge atoms had the nearest neighbor Ge atoms. The First Sharp Diffraction Peak (FSDP) occurred when k_{FSDP} was $1.0\text{--}1.1 \text{ \AA}^{-1}$ with intermediate range order (IRO). The partial structure factors $S_{ij}(k)$ were related to the FSDP ($k_{\text{FSDP}}=1.0 \text{ \AA}^{-1}$) and the first principal peak ($k_{\text{FSDP}}=1.95 \text{ \AA}^{-1}$). All partial contributions for Ge-Ge, Ge-Te and Te-Te were figured out and it was concluded that mostly Ge-Ge and Ge-Te contributed to the FSDP. For these two contributions, it can be concluded that Ge content plays an important role in FSDP. The homopolar bonds were Ge-Ge and Te-Te atoms in the system however Ge-Ge bonds did not occur in the percentage of $x=12.0$. One of the most important point for this study was that when Ge content was almost 22%, the first homopolar Ge-Ge bonds was observed and another significant result was that Ge content was almost 35-35% when there was an quickly increase in the width of $g_{\text{GeGe}}(r)$ whereas the height of $g_{\text{GeGe}}(r)$ decreased [26].

Lippens *et al.* examined the characterization of the local structure in Ge-As-Te glasses with EXAFS data. In this research, the local structure of the Ge and As atoms in $\text{Ge}_{0.1}\text{As}_x\text{Te}_{100-x}$ within the range $x=0.15, 0.20, 0.46, 0.54$) was examined by EXAFS data.

Due to the atomic numbers of Ge and As closely, it was not clear to observe simulations of these two atoms [Figure1]. In this system, As-Te, As-X, Ge-Te and Ge-X bonds, where x means Ge or As, can be taken into consideration for the analysis of EXAFS data. The total coordination number of Ge atom was 4 and the total coordination number of As atoms was 3.0 and 8-N rule was observed for all the compositions. The Ge atoms were bonded 3 Te atoms and one Ge/As atoms and therefore the coordination number of Ge atoms totally equaled to 4.0 (tetrahedral structure). On the other hand, the results obtained show that the average number of Ge-Te bonds around Ge atoms equal to 3.5 (it can be possible to observe GeTe_4 structures) for $x=0.15$. The total coordination number of Ge-Te bonds was 3.0 and does not change within the range $x=0.2-0.54$. The coordination number of As atoms to Te atoms varied from $x=0.15$ to $x=0.54$. This caused chemical disorder around As atoms and the coordination number of As-X bonds showed an increase while x was increasing. It can be concluded that the coordination number of Ge to the Te atoms does not importantly depend on As content. The reason of chemical disorder was the existence of both As and Ge or the absence of Te in the environment when x was increasing (As content was increasing) [27].

Wang *et al.* aimed to analyze the physical and chemical properties of the Ge-Te-AgI chalcogenide glass with differential thermal analysis and x-ray diffraction methods. Thermal characteristics of the $(100-x)(\text{GeTe}_{4.3})-x\text{AgI}$ chalcogenide glasses were investigated and it was found that the compound at $x=15$ had the maximum value of $\Delta T/^\circ\text{C}$ (107). The addition of AgI can cause less Te-Te homopolar bonds so that the stability of the chalcogenide glass can increase. As a conclusion, if the AgI can be added, stability of Ge-Te-AgI chalcogenide glasses will decrease due to formation of Ag-Te or Ag-Te-Te bonds. These chalcogenide glasses have good thermal properties at the differences between T_x (the onset crystallization temperature) and T_g (glass transition temperature) equals to 107°C [28].

Raoux *et al.* studied the structure of $\text{As}_x\text{Te}_{100-x}$ chalcogenide glasses by differential x-ray anomalous scattering and x-ray absorption spectroscopy about their local structure in 1993 and the structural parameters such as coordination number and interatomic distances were found according to As K and Te K edges. For the $\text{As}_{60}\text{Te}_{40}$ composition, the CN of As atoms was 3.1 (CN for As-As was 2.1 with $2.47 \text{ \AA}$ and CN for As-Te was 1.0 with $2.67 \text{ \AA}$) and Te atoms were twofold coordinated (CN for Te-As was 1.7 with $2.66 \text{ \AA}$ and CN for Te-

Te was 0.3 with 2.81 Å). For the As₅₀Te₅₀ composition, As atoms had three neighbors (CN for As-As was 1.6 with 2.47 Å and CN for As-Te was 1.4 with 2.66 Å) and Te atoms were twofold coordinated (CN for Te-As was 1.6 with 2.66 Å and CN for Te-Te was 0.4 with 2.80 Å). For the As₄₀Te₆₀ composition, As atoms had three neighbors (CN for As-As was 0.8 with 2.47 Å and CN for As-Te was 2.2 with 2.66 Å) and the CN of Te atoms was 2.4 (CN for Te-As was 1.5 with 2.67 Å and CN for Te-Te was 0.9 with 2.80 Å). For the As₃₀Te₇₀ composition, the CN of As atoms was 2.9 (CN for As-As was 0.5 with 2.47 Å and CN for As-Te was 2.4 with 2.66 Å) and the CN of Te atoms was 2.5 (CN for Te-As was 1.1 with 2.67 Å and CN for Te-Te was 1.4 with 2.79 Å). For the As₂₀Te₈₀ composition, the CN of As atoms was 3.0 (CN for As-As was 0.2 with 2.48 Å and CN for As-Te was 2.8 with 2.65 Å). In a conclusion, chemical disorder was observed in As_xTe_{100-x} chalcogenide glasses and the coordination number of Te atoms increased suddenly from 2 to 2.4 at As₄₀Te₆₀ [29].

Ramesh *et al.* examined the structure of chalcogenide glasses containing Ge-As-Te with Differential Scanning Calorimetric (DSC) and XRD. Ge_{7.5}As_xTe_{92.5-x} in GFR I region where 15 < x < 20 and Ge_{7.5}As_xTe_{92.5-x} in GFR II region where 35 < x < 60 was investigated. As a result, the intensity of the chalcogenide glasses prepared by melt quenched and melt spun was examined for both XRD and DSC spectra of the samples. Generally, when As and Ge atoms was added to the system, the interaction between atoms was increased and the bonds become strong, therefore the glass transition temperature (T_g) showed an increase. In general, it was understood that Ge was 4-coordinated atom, As atom had 3 neighbors and Te was 2-coordinated atom. In conclusion, chalcogenide glasses was prepared more adequately by twin roller melt spinning method that helps to investigate 2 glass forming region (GFR I & GFR II). When x became 40 for Ge_{7.5}As_xTe_{92.5-x}, the separation of two glass region was appeared [30].

Derrick *et al.* investigated the structural characteristic of two dimensional ¹²⁵Te *pj*MAT NMR spectroscopy of As_xTe_{100-x} glasses prepared by melting mixtures of the unalloyed metal elements. It was explained that Te atoms existed in the three different types in this study. Te^{III} atoms had 3 coordinated and Te^{II} had 2 fold coordinated atom. It was showed that the As atoms bonded to 3 Te atoms with 2.65-2.82 Å distances in the As₂Te₃ crystal and each Te atoms bonded to 3 As atoms (2 As atoms at 2.74 Å and 1 As atoms at 2.99 Å for Te^{II}, 2 As atoms at 2.95 Å and 1 As atoms at 2.65 Å for Te^I, 2 As atoms at 2.82

Å and 1 As atoms at 2.76 Å for Te^{III}). With these interatomic interaction distances, Te^I and Te^{II} had the longest interatomic interactions between As-Te at 2.99 Å and 2.95 Å. In conclusion, the model complied with Te^{II} seemly for As_xTe_{100-x} chalcogenide glasses that meant Te obeyed the 8-N rule regardless of the Te content. In addition to that, when As content increased, As-Te-As and Te-Te-As bonds increased however Te-Te-Te fraction tended to decrease [31].

Delaizir *et al.* focused to examine the atomic characterization of chalcogenide glasses containing As-Se-Te because of their large transparency. The As₃Se_{7-x}Te_x (0 ≤ x ≤ 3) and As₂Se_{3-x}Te_x (0 ≤ x ≤ 2.5) chalcogenide glasses was investigated to analyze their atomic structure by different methods such as ⁷⁷Se NMR Raman and Infrared and Wide-angle X-ray Scattering. These chalcogenide glasses were prepared by melting of total 10 g of As-Se-Te elements with high purity (99.999%). In the result of ⁷⁷Se NMR, it was given that the spectra of As₄Se₆ and As₄Se₄Te₂ compositions were similar and Te preferred replacing by Se more than replacing by As because of Te and Se being of the same family in the periodic table, both of them had 2-coordinated atoms. Besides, it was concluded that when Te atoms were added to the As₃Se_{7-x}Te_x and As₂Se_{3-x}Te_x, Se-Se bonds was destroyed and Te-Se bonds was occurred in the infrared and Raman results. When it came to the WAXS results, it was stated that increase in Te content caused to the formation of Se-Te and As-Te bonds. In addition to them, substituting Se atoms by Te atoms in the long wavelength was better to use As-Se-Te than As-Se glasses in the improvement of optical fiber sensors [32].

Ramesh *et al.* studied the effect of metal addition to the Ge-Te chalcogenide glasses. The Cu_xGe₁₅Te_{85-x} and Ag_xGe₁₅Te_{85-x} chalcogenide glasses prepared by the conventional melt-quenching method are compared to analyze glass formation ability in Differential Scanning Calorimetric (DSC). ΔT (the difference between crystallization and glass transition temperature) was determined to measure glass formation ability and it was found that ΔT of Cu_xGe₁₅Te_{85-x} increased up to x=5 and then decreased immediately, resulting high crystallization tendency for high content of Cu. On the other hand, ΔT of Ag_xGe₁₅Te_{85-x} decreased up to x=5 and then increased in a wide range of glass formation. In conclusion, the addition of metal element Ag to Ge-Te increased the structural network connectivity and Ag element entered into Ge-Te matrix and improved the glass-forming ability of Ag-Ge-Te chalcogenide glasses, however addition of Cu metal element was not be interacted with Ge-

Te matrix and caused to block the continuity of the Ge-Te structural network and Cu randomly replaced the Ge sites or it was the micro-inclusion in the Ge-Te matrix [33].

Jedema *et al.* studied the chalcogenide phase-change materials' importance, increasing day by day based on their optical properties. Being in the main of producing rewritable optical discs makes chalcogenide phase-change materials unique in this industry. Furthermore, density functional theory and having a full knowledge about the structural phase change's mechanisms help researchers get the wide point of view for the stability of the crystalline state. Based on this information, the appropriateness of chalcogenide materials (for example Ge-Sb-Te) in two both critical usage areas which are future optical recording media and phase-change random access memories (PCRAM) will be well-defined. There are some stages applied on phase-change layer in order to get the optical writing and erasing fragments on a disc. Firstly, phase change material is melted at approximately 600°C and start forming in the writing bit. Then it is cooled for a very short time as a few nanoseconds. Thus, amorphous state of the material which represents the written bit, forms by being solidified. At the erasing a written bit' stage, the same part of the phase-change layer is heated to only a few hundred degrees but differently for tens of nanoseconds. As a result, the amorphous material reverts into the crystalline state. The phase-change materials' crystalline and amorphous states have different optical properties which can be distinguished from each other by their reflectivity. As the limiting factor to succeed in larger recording speeds, the erasure time is wanted to be reduced in the optical recording industry. New discovered two classes of phase-change materials can provide shorter erasure times based on their fast crystallization speed. These two classes of phase-change materials are called nucleation dominated materials (NDM) and fast-growth materials [34].

Wang *et al.* studied the atomic structure and of ternary $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ chalcogenide glasses with the mean coordination number (MCN equals to 2.5). This research was aimed to investigate the coordination numbers, the bond length and bond angle distributions compared with the results deduced from EXAFS spectroscopy. Eventually, each Ge, As and Se atoms obeyed 8-N rule and all Ge, As and Se atoms have 4, 3 and 2-coordinated, respectively. In addition to these main results, the structure of $\text{GeSe}_{4/2}$ and $\text{AsSe}_{3/2}$ chalcogenide glasses was occurred with the addition of As or Se molecular groups and bond angle distribution of Ge-Se-Ge was found 102.4° [35].

Akola *et al.* aimed is to identify, analyze and shows the differences between the significant elements in the structural properties of phase change materials, especially GeTe, GST-225 and GST-8, 2, 11. In bond angle distribution studies, value of bond cut-off distance was used as 3.2 Å. The bond angle distributions of all three elements, Ge, Sb and Te, were located around 90° and Ge and Sb elements also preferred angles of 180° in a linear configuration. When the ring statistics of amorphous GeTe, Ge₈Sb₂Te₁₁ and Ge₂Sb₂Te₅ (GST-225) were compared, it was said that many four-membered rings and few triangular configurations were observed in three phase change materials. As a result, the structural properties of GST-225 and GST-8, 2, 11 were similar in a striking way, only the small but significant difference between them was that amorphous GST-8, 2, 11 had more Ge-Ge coordination number and higher Ge atoms fraction with tetrahedral coordination. To compare GeTe from other two PCM in ring statistics, the difference was that much lower vacancy volume led to increasing amount of Ge-Ge bonds [36].

Wang *et al.* examined the structural properties of the Te –based chalcogenide glasses synthesized by conventional melt-quenching method and it was concluded from this study that when metal halides increased in Te-based such as PbI₂, CuI, AgI, CdI₂, ZnI₂, the glass transition temperature, outstanding glass-forming ability and greater thermal stability were exhibited more than addition of alkali halides such as KI, CsI in these glass system. In addition to that, relatively poor thermal stability were presented by the addition of Te element [37].

Soyer Uzun *et al.* studied the structural properties of Ge_xAs_xS_{100-2x} chalcogenide glasses by using neutron and x-ray diffraction method between 33.3 ≤ x ≤ 70.0. In this work, it was aimed to clarify the effect of the amount of S atoms and to get the detailed structural information of Ge_xAs_xS_{100-2x}, prepared by melting mixtures of the components, at these x ranges. It was found that Ge and As atoms prefer bonding to S atoms at first. At low and intermediate levels of S-lack, homopolar As-As bonds form and therefore chemical disorder were observed. In addition to them, Ge atoms took place in metal metal bonding when S atoms were insufficient in the system, in one case all As atoms were consumed in homopolar bonding [38].

2. REVERSE MONTE CARLO MODELING (RMC)

Reverse Monte Carlo modeling is an inverse modeling technique that aims to determine the 3D structure of different systems such as glasses, liquids, crystalline and magnetic structures. In this reverse modeling technique, experimental data can be used as an input to modeling program together with the local coordination constraints to obtain 3D structures and to produce a model or a series of models [4].

A basic form of the conventional procedure to understand the molecular structures can be defined as follows [4]:

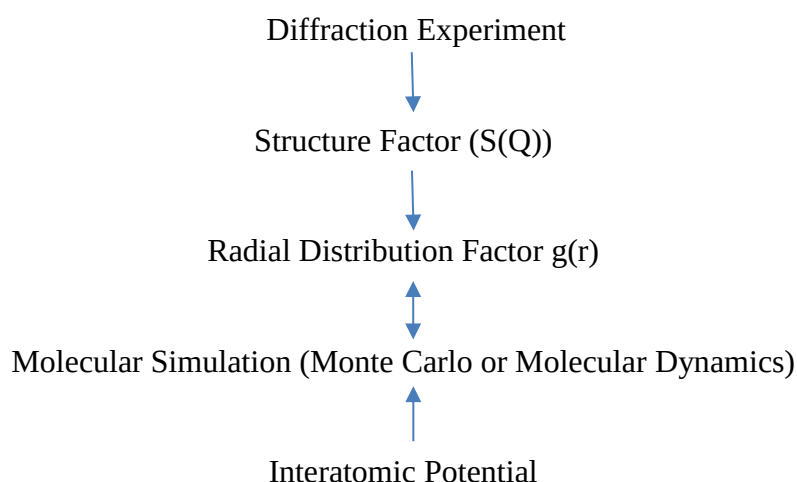


Figure 2.1. Simplified schematic representation of conventional approach for understanding molecular structures.

In Figure 2.1, it can be explained that after implementation of neutron or x-ray diffraction experiment, structure factor, $S(Q)$, is obtained. The structure factor provides Fourier transformed in order to get radial distribution function, $g(r)$. Then, molecular dynamics (MD) or Monte Carlo (MC) simulation methods depending on the algorithm developed by Metropolis *et al.* are used to produce a one dimensional $g(r)$ [39]. After that, the $g(r)$ result obtained from the simulation with the help of an interatomic potential, are comparable with the experimental results [4].

It is very beneficial to compare it with forward modeling to get better explain reverse modeling. As it is seen the interatomic potential in Figure 1, it is used to produce atomic configurations in forward modeling. These arrangements are used to make calculations and find values which are compared with experimental data. Besides, experimental data is the initial point, atomic configurations are occurred and support the experimental data values in inverse modeling [40].

The algorithm for Reverse Monte Carlo modeling can be explained as follows [4]:
The subscripts S and E symbolize simulation and experiment respectively.

- Firstly, an initial configuration can be determined.
- Then, periodic boundary conditions can be applied and radial distribution function $g_s(r)$ can be calculated.
- After that, one particle can be moved randomly to produce a new configuration. The new radial distribution function $g'_s(r)$ can be calculated.
- These findings are comparable with the experimental results, then $g_s(r)$ is transformed to structure factor $S_s(Q)$ using this formula

$$S_s(Q) - 1 = (4\pi\rho/Q) \int_0^\infty r^2 (g_s(r) - 1) \sin Qr \, dr$$

- (i) $S_s(Q)$ for two different configurations are compared with the experimental results using a standard χ^2 test $S_E(Q)$

$$\chi^2 = \sum_{n=i} (S_s(Q)_n - S_E(Q))^2 / \sigma(Q)^2$$

$$\chi'^2 = \sum_{n=i} (S'_s(Q)_n - S_E(Q))^2 / \sigma(Q)^2$$

- (ii) If the value of χ'^2 is smaller than the value of χ^2 , the new configuration is acceptable. On the other hand, it is accepted with a probability that follows a normal distribution with width σ .
- (iii) If the new configuration is acceptable, the new configuration is become for the next stage. If it is not accepted, a new configuration is produced by the

random movement one of the particles and the same steps occur in a following way.

- (iv) Finally, the method is carried out until χ^2 declines to an equilibrium value [4].

Reverse Monte Carlo (RMC) model can express the 3D structure of a system employing experimental data in the simulation environment. One of the advantages of RMC modeling is to measure data sets over different ranges and to be easily modified for simultaneously adjusting to different sets of data. The density and the cut-offs are another important features of RMC modeling. With these restrictions, the algorithm is easily modified and the closest approaches between each atom can be adjusted. These restrictions are short range order, nearest neighbor environment and local coordination constraints [26].

2.1. RMC Modeling of Chalcogenide Glasses

Sen *et al.* investigated the structural atomic characteristics of the $\text{Ge}_x\text{As}_x\text{S}_{100-2x}$ chalcogenide glasses using RMC simulations with the experimental datasets obtained from high energy x-ray and neutron diffraction at $x=18.2$, 25 and 33.3. In RMC modeling, the most important parameters such as the densities of the compositions, the cut-off and connectivity constraints were calculated. The densities of these three glasses, $\text{Ge}_{18.2}\text{As}_{18.2}\text{S}_{63.6}$, $\text{Ge}_{25}\text{As}_{25}\text{S}_{50}$, $\text{Ge}_{33.3}\text{As}_{33.3}\text{S}_{33.3}$, were $0.0379 \text{ \AA}^{-3}$, $0.0371 \text{ \AA}^{-3}$ and $0.0389 \text{ \AA}^{-3}$, respectively. In $\text{Ge}_{18.2}\text{As}_{18.2}\text{S}_{63.6}$, it was observed that Ge atoms were bonded to four S atoms and As were 3-coordinated atoms bonded to three S atoms and it was observed that the system includes both GeS_4 and AsS_3 bonds. Increase in metal contents (x values from 27.5 to 33.3) in the system affected the chemical order in a negative way due to the substitution of Ge/As-S bonds stepwise by metal-metal bonds and when all As atoms consume, Ge atoms prefer bonding to Ge atoms. Two possible cases were considered for $\text{Ge}_{33.3}\text{As}_{33.3}\text{S}_{33.3}$ glass; case I were assumed that all Ge atoms can only bond to As and it could be thought for case 2 that all Ge atoms could favorably bond to Ge atoms. From RMC modeling, the cut-off distances ($\text{\AA}$) of As-As, As-Ge, As-S, Ge-Ge, Ge-S, S-S in $\text{Ge}_{18.2}\text{As}_{18.2}\text{S}_{63.6}$ were 3.30, 3.30, 2.10, 3.30, 2.10 and 3.30, respectively. The coordination constraints of As-S and Ge-S are 3 and 4, and the bond distances of them were both 2.25 for $\text{Ge}_{18.2}\text{As}_{18.2}\text{S}_{63.6}$. From RMC

modeling, the cut-off distances ($\text{\AA}^\circ$) of As-As, As-Ge, As-S, Ge-Ge, Ge-S, S-S in $\text{Ge}_{25}\text{As}_{25}\text{S}_{50}$ are 2.40, 3.00, 3.00, 3.30, 2.10 and 3.3, respectively. The coordination constraints of As-As and Ge-S for $\text{Ge}_{25}\text{As}_{25}\text{S}_{50}$ were 3 and 4, and the bond distances of them were 2.45 and 2.25, respectively. From RMC modeling, the cut-off distances ($\text{\AA}$) of As-As, As-Ge, As-S, Ge-Ge, Ge-S, S-S in $\text{Ge}_{33.3}\text{As}_{33.3}\text{S}_{33.3}$ for case I were 2.45, 2.45, 3.25, 2.45, 2.15 and 3.35, respectively. The coordination constraints of As-As, Ge-As and Ge-S for $\text{Ge}_{33.3}\text{As}_{33.3}\text{S}_{33.3}$ (case I) were 1, 2 and 2, and the bond distances of them were 2.45, 2.45 and 2.25, respectively. From RMC modeling, the cut-off distances ($\text{\AA}$) of As-As, As-Ge, As-S, Ge-Ge, Ge-S, S-S in $\text{Ge}_{33.3}\text{As}_{33.3}\text{S}_{33.3}$ for case II were 2.30, 2.30, 3.25, 2.30, 2.10 and 3.25, respectively. The coordination constraints of As-As, Ge-Ge and Ge-S for $\text{Ge}_{33.3}\text{As}_{33.3}\text{S}_{33.3}$ (case II) were 3, 2 and 2, and the bond distances of them were 2.45, 2.45 and 2.25, respectively. Additionally, FSDP positions were observed approximately at $1.13 \text{ \AA}^{-1}$ when x equaled to 18, it was located at around $1.04 \text{ \AA}^{-1}$ when x equals to 25 and around $0.96 \text{ \AA}^{-1}$ when x equaled to 33. In addition to that, the coherence length λ of intermediate-range order were calculated by dividing 2π to $\Delta\theta_{\text{FSDP}}$ and these values were approximately $18\text{-}19 \text{ \AA}^\circ$ at $x=18$, about $23\text{-}24 \text{ \AA}^\circ$ at $x=25$ and approximately $21 \text{ \AA}^\circ$ at $x=33$. In a conclusion that more homogeneous spatial distribution of metal atoms in $\text{Ge}_{25}\text{As}_{25}\text{S}_{50}$ glass were observed and therefore case I was expressed to be more consistent with the experimental results than case II [5]. In addition to that, more content of S atoms caused more homogeneous Ge-As bonds such as metal bonding and GeS_2 and As-rich clusters were disrupted.

Fabian *et al.* examined a neutron diffraction structural study on newly synthesized 4-component chalcogenide specimens with composition ($\text{Ge}_{20}\text{As}_{20}\text{Se}_{50}\text{Te}_{10}$ and $\text{Ge}_{27}\text{As}_{13}\text{Se}_{50}\text{Te}_{10}$) [40]. Interatomic distances, $r_{ij}(\text{\AA})$ and coordination numbers, CN_{ij} obtained from RMC simulations calculated. As a result, Ge-Ge, Ge-Se and As-Te distribution were quite similar to each other; both first and second neighbor distances were been at the same distance within limit of error, at $2.42 \pm 0.02 \text{ \AA}$ and at $3.78 \pm 0.05 \text{ \AA}$, respectively [42].

Moharram studied the structural information of $\text{Ge}_{20}\text{Se}_{80}$ chalcogenide glass prepared by melt-quenching method using RMC simulation of X-ray diffraction data between 0.28 and $6.87 \text{ \AA}^{-1}$. It was concluded from RMC simulations that the partial coordination numbers of Ge-Ge, Ge-Se, Se-Ge and Se-Se were found as 0.03, 4.04, 1.01 and 2.26,

respectively. The total coordination number of Ge atoms was 4.07 and CN of Se was 3.27. In addition to the coordination number results, bond angle distribution functions were obtained for $\text{Ge}_{20}\text{Se}_{80}$. The main achievements were found that a main peak was observed at 104.2° and a small peak appeared at 60° for $\Phi_{\text{Se-Ge-Se}}(\theta)$. Furthermore, a main peak was observed at 60° and a small peak appeared at 104.2° for $\Phi_{\text{Se-Se-Se}}(\theta)$ and the existence of a $\Phi_{\text{Se-Se-Se}}(\theta)$ at 104.2° help pave the way inter-tetrahedral units. Wide angle distribution for $\Phi_{\text{Ge-Ge-Ge}}(\theta)$ was observed between 50° and 150° that was explained by existing pairs of tetrahedral units connected by corner or edge and the FSDP appeared in the total structure factors because of both Ge-Ge and Se-Se bonds [43].

Sun *et al.* investigated the atomic configurations and chemical structure of the chalcogenide glass of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) under 18, 22 and 33 GPa. It was mentioned that there were two types of framework structure of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) amorphous state, one part was the cubic framework (c-amorphous) and the other one is t-amorphous was the trigonal structure (t-amorphous). As a result, it was understood that increase in pressure caused the formation of homopolar bonds and the amorphization results from the formation of homopolar Ge/Sb and Te bonds. In addition to that, sharp peaks were observed around at 90° and 172° at 18 GPa in bond angle distributions. When the pressure was increasing to 22 GPa, wide peak positioning around 88° for Ge and Te and 84° for Sb were obtained in this combination. Furthermore, the c-amorphous were observed as trigonal framework and wide angle distribution were observed from approximately 60° to 130° when the pressure was higher than 33 GPa [44].

Fabian *et al.* examined the atomic properties of $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{40}\text{Se}_{50}\text{Te}_{10}$ glass synthesized by conventional melt-quenching method using RMC simulations with the datasets of neutron and high-energy XRD. From the results of 3-D atomic configuration of RMC simulations, the coordination numbers and bond-angle distributions were determined. There were some critical parameters used in RMC program, such as densities, cut-off and connectivity constraints. The densities of $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{40}\text{Se}_{50}\text{Te}_{10}$ were found 0.03 and 0.035 atoms/cm³, respectively. It was given that the cut-off values obtained from $G(r)$ functions were $2.2\text{\AA}$ for As-Se, $2.45\text{\AA}$ for As-Te and Se-Te, $3.1\text{\AA}$ for As-As, Se-Se and Te-Te. When it comes to the average coordination numbers of As and Se atoms, CN (AsSe) equaled to 2.6 ± 0.1 and CN (SeAs) is 1.8 ± 0.1 . In addition to them, it was revealed that it was

not observed any difference of structural network in the substitution of Se by Te atoms for the binary system. It was found from RMC simulations that the bond-angle distribution of $\Phi(\text{As-Se-As})$ and $\Phi(\text{Se-As-Se})$ equaled to $95 \pm 5^\circ$ for the average triple bond-angle structure [45].

Vazquez *et al.* investigated the chalcogenide glass of $\text{Ge}_{0.14}\text{As}_{0.43}\text{Te}_{0.43}$ prepared by quenching the molten mixture of the elements in 1988. It was aimed to examine the atomic configurations using by Metropolis-Monte Carlo random method, the most appropriate to simulate the structural characteristic properties of the alloy. It was taken into consideration that there were two types of Ge atoms; $\text{Ge}(\text{Ge}(4))$ that was 4-coordinated and $\text{Ge}(\text{Ge}(3))$ that was 3-coordinated. Consequently, both $\text{Ge}(\text{Ge}(4))$ and $\text{Ge}(\text{Ge}(3))$ were present in the system and the mean value of Ge-Ge, Ge-As, Ge-Te, As-As, As-Te, Te-Te bond lengths hypothetically calculated for this model are 0.253 nm, 0.247nm, 0.259nm, 0.256nm, 0.261nm and 0.262nm, respectively [46].

The most vital property of GCT chalcogenide glass was to have higher simulated reflectance of a-GCT than c-GCT when it was compared to other phase-change materials. Chen *et al.* investigated the bonding rule of other crucial chalcogenide glass $\text{Ge}_1\text{Cu}_2\text{Te}_3$ (GCT) using molecular dynamics. Compared to the thermal stability of GCT and GST in the way of atomic and electronic structural properties, the atomic structures of crystalline and amorphous phases in GST both appeared similar, octahedral 4-fold rings were observed for both. In GCT, however, large difference, leading to transit between crystalline and amorphous phases difficulty, was observed between local structures of both phases. It was explained that the Cu triangle cluster was found in GCT chalcogenide amorphous glass system prepared by melt-quenching method. In a conclusion, important chemical disorder was disclosed by large amounts of Cu-Cu and Ge-Ge homopolar bonds in a-GCT and mean coordination number for each element is stated as 4.36. In addition to these results, bond angle distributions were observed in two different phases; tetrahedral structure for c-GCT (crystalline GCT) and wide BAD (100° for Ge, 105° for Cu, 107° for Te), which was close to the tetrahedral, in a-GCT (amorphous GCT) system were found [47].

One of the most important properties of the chalcogenide glasses was underlined in this study that they had fast phase transition between crystalline and amorphous phases

because of an umbrella flip of the Ge atom to tetrahedral from octahedral coordination near the blank location and fast crystallization of the amorphous phase can contribute energy storage to help the next fast crystallization. In this research, Chen *et al.* aimed to analyze the rational mechanism for the crystalline and amorphous phase transition in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) prepared by using RMC refinements allied with density functional theory. Using of molecular dynamics simulation of crystallization led to very time consuming and this method cannot be applied for large models of materials. Rational model, however, was very useful to determine the significant structural properties of transformation at larger scale. As a result, it was observed that FSDP located at $2.68 \text{ \AA}^\circ$ and four-membered rings played an important role for the structural properties of the GST in amorphous phase determined by RMC simulation with density functional theory to the empirical electron diffraction data. When the ring statistics were calculated, it was observed that four-membered rings were occurred frequently in this model (RMC + DFT), Ge-Te-Sb-Te (4) with one Ge-Te-Ge-Te and one Sb-Sb-Te-Te [48].

Ligero *et al.* studied and examined the atomic structural model of $\text{Ge}_x\text{As}_{0.20}\text{Te}_{0.80-x}$ (when x equals to 0.05, 0.10) chalcogenide glasses obtained by melt-quench method. In this research, Metropolis Monte Carlo method was used to analyze these chalcogenide glass system. It was found that average bonding distances ($\text{\AA}^\circ$) of Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te for $\text{Ge}_{0.05}\text{As}_{0.20}\text{Te}_{0.75}$ are 2.46, 2.69, 2.65, 2.61, 2.63 and $2.67 \text{ \AA}^\circ$, respectively. It was determined that average bonding distances ($\text{\AA}^\circ$) of Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te for $\text{Ge}_{0.10}\text{As}_{0.20}\text{Te}_{0.70}$ are 2.53, 2.66, 2.63, 2.55, 2.67 and $2.70 \text{ \AA}^\circ$, respectively. In terms of angle bonding angles (degrees), it was given in this article that 107.5° for Ge, 107.3° for As and 108.2° for Te atoms in $\text{Ge}_{0.05}\text{As}_{0.20}\text{Te}_{0.75}$ chalcogenide glass and 110.2° for Ge, 113.3° for As and 109.2° for Te atoms in $\text{Ge}_{0.10}\text{As}_{0.20}\text{Te}_{0.70}$ chalcogenide glass [49].

Fabian *et al.* aimed to investigate the atomic structure of $\text{As}_{40}\text{Se}_{(60-x)}\text{Te}_x$ for $x=0,10$ and 15 with neutron and high energy X-ray diffraction energy methods [50]. The patterns of these two methods were analyzed by RMC technique to gather information about atomic configurations. In RMC model, the components of $\text{As}_{40}\text{Se}_{60}$, $\text{As}_{40}\text{Se}_{50}\text{Te}_{10}$, $\text{As}_{40}\text{Se}_{45}\text{Te}_{15}$ prepared by melt-quenching method were studied with 10.000 atoms and two important constraints were cut-off distances and connectivity constraints in RMC simulation. It was

taken into consideration that the existence of heteropolar bonds had more possibility than the existence of homopolar bonds due to cut-off distances. These cut-off distances were 2.2°Å for As-Se, 2.45°Å for As-Te and Se-Te, 3.1°Å for As-As and Se-Se and Te-Te, respectively. In terms of cut-off values, the approximation was that only the heteropolar bonds was occurred at first since the homopolar bonds was not arised. When it comes to the partial atomic correlation functions ($g(r)$), it was said that first peak of $g_{AsTe}(r)$ was observed at 2.55 and 2.55 Å⁻¹ for $As_{40}Se_{50}Te_{10}$ and $As_{40}Se_{45}Te_{15}$, respectively. Another important issue investigated in this search was about angular distribution θ ($\cos \theta$), and it was calculated that $97 \pm 2^\circ$ for As-Se-As, $99-92 \pm 2^\circ$ for Se-As-Se, $92 \pm 3^\circ$ and $56 \pm 3^\circ$ for Se-Te-Se, $96 \pm 2^\circ$ and $60 \pm 2^\circ$ (close to ideal tetrahedral structure) for Te-As-Se, $92 \pm 3^\circ$ for Te-As-Te. The angular bond distribution θ ($\cos \theta$) for Te-Se-As found that $88 \pm 2^\circ$ for $As_{40}Se_{50}Te_{10}$, $92 \pm 2^\circ$ for $As_{40}Se_{45}Te_{15}$ and $60 \pm 2^\circ$ (close to ideal tetrahedral structure) for both ($As_{40}Se_{50}Te_{10}$ and $As_{40}Se_{45}Te_{15}$). For this reason, it was observed that the difference between these two components is the angle distribution and it is increased from 88° to 92° by addition of Te content. In addition to them, it was found that the atomic network structure was not affected by addition of Te content and approximately 92% of the bonds were heteropolar disclosed in RMC modeling. Finally, a significant observation was concluded that Te atoms substituting Se atoms behave similarly as Se atoms into As-Se glass. The mean coordination number of As atoms was 2.8 Å° surrounding by Se atoms and Se atoms are bonded 1.8 As atoms [50].

Jovari *et al.* aimed to investigate structural model of $GeCu_2Te_3$ chalcogenide glasses with X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS). This chalcogenide glass was prepared by prepared by radio-frequency sputtering a Ge-Cu-Te alloy target. The experimental data obtained from these methods was fitted by simultaneously RMC simulation. The minimum interatomic distances of Ge-Ge, Ge-Cu, Ge-Te, Cu-Cu, Cu-Te, Te-Te are 2.35 Å°, 3.1 Å°, 2.35 Å°, 2.45 Å°, 2.35 Å°, 2.45 Å° in RMC, respectively. In conclusion, Ge, Cu and Te had 4-coordinated atoms in crystalline structure of $GeCu_2Te_3$ and similarly the mean coordination number was close to 4 in amorphous chalcogenide glass $GeCu_2Te_3$. It is shown that both crystalline and amorphous GCT ($GeCu_2Te_3$) glasses met 8-N rule. In this experiment, Ge was 4-coordinated atom, total number of Te atom was 4.10 ± 0.5 and the summation of Te-Te and Te-Ge coordination

numbers were 2.71 ± 0.4 so that more Cu atoms increased the connectivity of the host structure. It was deduced from the result that thermal stability of amorphous GeCu_2Te_3 glass was improved by high average coordination number [51].

Moharram *et al.* investigated the structural information of bulk chalcogenide glass $\text{Ge}_{20}\text{Se}_{80-x}\text{Te}_x$ prepared by melt-quenching technique at which x equaled to 0, 10, 20 and 30. When Te was added to the chalcogenide glass $\text{Ge}_{20}\text{Te}_{80}$ at $x=0$, energy losses were decreased due to the multi-phonon absorption. Densities of Ge, Se and Te atoms were calculated for each x values. Partial pair distributions and partial scattering factors for Ge-Ge, Se-Se, Ge-Se, Se-Te, Ge-Te, Se-Te, Ge-Te, Te-Te were obtained from the RMC simulation for the bulk chalcogenide glass $\text{Ge}_{20}\text{Se}_{80-x}\text{Te}_x$ at $x=0, 10, 20$ and 30 . In RMC simulations, total number of 4000 atoms of $\text{Ge}_{20}\text{Se}_{80-x}\text{Te}_x$ at $x=0, 10, 20$ and 30 were used in RMC simulations. As a conclusion, first sharp diffraction peak was observed at $1.2 \text{ \AA}^{-1}$ for the binary glass. When Te increased (x increased) in the chalcogenide glasses, the intensity of FSDP reduced. It was deduced from partial structure factors that the presence of homopolar bonds such as Ge-Ge, Se-Se and Te-Te caused the peak around the first coordination sphere. The bond angle distribution was calculated from partial pair distribution functions. It was obtained that bond angle function of Se-Ge-Se was observed at 105° which was nearly similar to the tetrahedral angle (109°) and other small peak was close to 60° . The bond angle function of Se-Se-Se was observed around at 109° so that tetrahedral structures was obtained by homopolar bonds [52].

Jovari *et al.* investigated the structure of the $\text{As}_x\text{Te}_{100-x}$ ($20 \leq x \leq 60$) chalcogenide glasses and probe techniques were used for x-ray (XRD) and neutron diffraction (ND) and EXAFS datasets. Experimental datasets were analyzed and modelled simultaneously by RMC simulation method. $\text{As}_{20}\text{Te}_{80}$, $\text{As}_{34}\text{Te}_{66}$, $\text{As}_{40}\text{Te}_{60}$ and $\text{As}_{60}\text{Te}_{40}$ were examined and As-As, As-Te and Te-Te bonds were observed for $20 \leq x \leq 60$. One of the most important outcomes from this study was that As atoms were triple coordinated for all composition range investigated. The other significant result was that when x equaled to 40 or smaller than 40, 40% of Te atoms were threefold coordinated, and when x was greater than 40, the coordination number of Te atoms was two in the alloys. The results showed that when x equaled to 40, average coordination number of As-As was 1.7 ± 0.2 and CN of Te-Te was 1.3 ± 0.1 for $\text{As}_{40}\text{Te}_{60}$. When x equaled to 50 or smaller than 50, Te atoms were mainly 2

coordinated, however the coordination number of Te was approximately 2.31 where x equaled to 60 ($\text{As}_{60}\text{Te}_{40}$). It revealed that Te atom had chemical disordered structure when x value was greater than 50. As a result, 8-N rule was valid for $\text{As}_x\text{Te}_{100-x}$ components when x equaled to 50 or smaller than 50. The last noteworthy conclusion was that the structure of glasses was chemical disordered as homopolar bonds such as As-As and Te-Te existed [53].

Pethes *et al.* analyzed the structure of $\text{Ge}_{20}\text{Sb}_x\text{Se}_{80-x}$ glasses by neutron diffraction, X-ray diffraction and extended X-ray fine structure measurements at $x=5,15,20$. The structural information of $\text{Ge}_{20}\text{Sb}_x\text{Se}_{80-x}$ was found by RMC simulation with experimental data sets fitted simultaneously and the result showed that these glasses generally were chemically ordered structures. Ge-As(Sb)-Se(Te) components followed the 8-N Rule according to Mott rule, so that Ge had 4-coordinated atoms and As(Sb) had 3 nearest neighbors and Se(Te) atoms were 2-coordinated. When it was compared to Ge-Sb-Se glasses with other chalcogenide glasses including three analogous systems such as Ge-As-Se, Ge-As-Te, Ge-Sb-Te, it was more preferable substituting As than Sb and Se than Te for the chemical short-range order. Due to the structure of Ge-As-Te glasses, they were more stable against crystallization. The heteropolar bonds Ge-Se, Ge-Te, As(Sb)-Se, As(Sb)-Te were preferable in the chemically ordered network model (CONM) [54].

Machado *et al.* examined the structure of $\text{Se}_{0.90}\text{S}_{0.10}$ amorphous chalcogenide glass by RMC simulations with data obtaining from XRD and EXAFS. The structural properties were found from RMC simulations. As a result, changing minimum interatomic distances between atoms such as Se-Se, Se-S and S-S made the results better and cut-off values of Se-Se, Se-S and S-S pairs were $2.20\text{\AA}$, $2.20\text{\AA}$, and $2.20\text{\AA}$, respectively. When the concentration was compared, Sulphur's was very low, so that the information about S atoms was less than Se atoms. In addition, the bond angle distribution functions were determined and found 60° for S-Se-S and Se-S-S. For $\theta_{\text{Se-S-Se}}$ and $\theta_{\text{Se-Se-Se}}$, they were found identical and peaks at angles around 101° and 155° . For Se-Se-S, the sharp and longest peak was observed around 54° and the certain peak was observed at 61° [55].

Ratkai *et al.* searched the structure of $\text{Ge}_{20}\text{Te}_{80}$ (test run), $\text{Ge}_{15}\text{Cu}_5\text{Te}_{80}$, $\text{Ge}_{15}\text{Cu}_{10}\text{Te}_{70}$ chalcogenide glasses. The structures of these chalcogenide glasses were investigated by XRD and EXAFS data and the model was fitted simultaneously by RMC simulations and

the structures of these glasses were analyzed from RMC simulations. The cut-off values were 3.7, 2.3, 2.5, 3.1, 2.5 and 2.3 Å for Ge-Ge, Ge-Te, Te-Te, Cu-Ge, Cu-Cu, Cu-Te, respectively. In this research, average coordination numbers for Te-Te, Te-Ge, Ge-Te, Cu-Te, Cu-Cu, Te-Cu and total coordination numbers for each element, Ge, Te and Cu. Total coordination numbers of Te, Ge and Cu elements for $\text{Ge}_{20}\text{Te}_{80}$ are 2.10, 4.02 and 0, respectively. Total coordination numbers of Te, Ge and Cu for $\text{Ge}_{15}\text{Cu}_5\text{Te}_{80}$ are 2.15, 4.03 and 2.37, respectively. In addition, total coordination numbers of Te, Ge and Cu elements for $\text{Ge}_{15}\text{Cu}_8\text{Te}_{77}$ are 2.30, 4.00 and 3.36, respectively. It was taken into consideration that Te and Ge atoms obeyed the 8-N rule for $\text{Ge}_{20}\text{Te}_{80}$. Additionally, total coordination number of Te was importantly higher than 2 for $\text{Ge}_{15}\text{Cu}_8\text{Te}_{77}$. The values of N_{CuCu} for $\text{Ge}_{20}\text{Te}_{80}$, $\text{Ge}_{15}\text{Cu}_5\text{Te}_8$, $\text{Ge}_{15}\text{Cu}_8\text{Te}_{77}$, were 0,0 and 1.63, respectively. It was said that Cu-Cu bonds were more important for $\text{Ge}_{15}\text{Cu}_8\text{Te}_{77}$ having large amount of Cu. In addition to them, Cu in $\text{Ge}_{15}\text{Cu}_5\text{Te}_{80}$ preferred bonding to Te elements (N_{CuTe} equals to 2.37) when it was compared to $\text{Ge}_{20}\text{Te}_{80}$ (N_{CuTe} equals to 0.0) and $\text{Ge}_{15}\text{Cu}_8\text{Te}_{77}$ (N_{CuTe} equals to 1.73) [56].

Kohara *et al.* aimed to investigate three dimensional the atomic structural model of amorphous GeTe and amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ using Reverse Monte Carlo Model with synchrotron-radiation high energy x-ray diffraction data. These glasses enabled to crystallize in a very short time and have a high phase-stability of the amorphous phase. The number of densities of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe are 0.0315 and 0.0337 Å^{-3} , respectively. The total coordination of Ge (Sb) was obtained 3.7 (3.0) from α - $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and 4.1 from α -GeTe. When it came to the bond angle distribution to identify the structural unit and to examine relationship between the atomic configuration and the speed of phase change, it was observed that the peaks of Ge(Sb)-Te and Ge(Sb)-Te-Ge(Sb) in α - $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are occurred at 90° . The peak of Te-Ge-Te in α -GeTe was observed around 109.4° , whereas bond angle between Ge-Te-Ge atoms occurred at 90° and 50° because of the formation of Ge-Ge homopolar bonds. It was found that ring structure of α - $\text{Ge}_2\text{Sb}_2\text{Te}_5$ was even numbered and α -GeTe was odd- and even-numbered both due to the existing Ge-Ge homopolar bonds. The addition of Sb_2Te_3 to GeTe caused not to be occurred the Ge-Ge bonds in α - $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [57, 58].

Yuan *et al.* analyzed ring statistics methods to study the atomic network structures and the connectivity profile of the network. In this research, the two parameters were

crucial to form topological network; nodes (or vertices) linked points in the structure for the atoms and links (or edges) to help pave the way connections between couples of nodes for the bonds. A consecutive connected nodes and links except any overlap was called a path. In addition to them, a ring containing n-links was called n-ring [59].

Jund *et al.* studied the analysis of topological network of amorphous GeS₂ and SiO₂ glass systems obtained using ring statistics to determine the structural connectivity properties. In this study, it was aimed to obtain the network connectivity profile using the ring statistics at a farther scale than the first or the second coordination shell. 30 nodes as maximum search depth were used for the analysis and over 100 configurations were obtained in the result. It was highlighted that the ring size of GeS₂ was important between 4,6 and 24-29 nodes and the importance of ring size of SiO₂ observed between 8-14 nodes. Two parameters were very significant in this research; they were $P_{\min(n)}$ and $P_{\max(n)}$. The connectivity of the rings with their size was obtained by these two parameters. It was explained that $P_{\min(n)}$ described the shortest ring and $P_{\max(n)}$ meant the longest ring obtained using this node to start the search. As a result, $P_{\min(n)}$ was approximately 1 and it observed for $n \leq 8$ in g-SiO₂ system, thus the rings with equals or smaller than 8 were always the shortest paths for the node at the origin. When $P_{\max(n)}$ was about at 0.5 and the rings equal or smaller than 12 in total number of nodes, it was concluded that Si atoms did not have a connectivity network with the ring size of 4,6 or 8 nodes. In addition to SiO₂ system, $P_{\min(n)}$ of g-GeS₂ did not equal to 0 and when n value was between 12 and 22, the shortest path for the certain node. This result was observed for $P_{\max(n)}$. Generally, the ring size distribution of g-GeS₂ seemed to be very non-uniform between 4-10 nodes and greater than 12 nodes [60].

Opletal *et al.* studied the molecular dynamics model of different five Ge-As-Se chalcogenide glasses ranging from Se poor to Se rich from EXAFS restriction RMC models when mean coordination number equaled to 2.5 value and investigated in terms of their structural variability and behaviors between bonds [61]. Molecular dynamics were used to determine the physical behaviors of atoms or molecules with computer [60]. All configurations Ge_{7.5}As₃₅Se_{57.5}, Ge₁₀As₃₀Se₆₀, Ge_{12.5}As₂₅Se_{62.5}, Ge₁₅As₂₀Se₆₅ and Ge₂₀As₁₀Se₇₀ chalcogenide glasses with increasing Se content were examined and concluded that the average coordination was around 2.5. Additionally, mean coordination As and Se atoms seemed to be unchanged while Ge atoms' increased with increasing Se content. It was

observed that homopolar bonds, increment of non Se bonding, short Se chains, SeAs_2 and AsS_3 bonds occurred for chalcogenide glasses containing Se poor, whereas decrease in non Se bonding observed and substituting it by Ge-Se_4 for chalcogenide glasses containing Se rich [62].

3. RESULTS AND DISCUSSIONS

In this thesis, RMC modeling was performed to build three dimensional structures of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses with Ge+As contents ($3x$) of 30, 40, 50 and 70 at.% based on high energy x-ray diffraction data reported in the literature [18]. The experimental structure factors $S(Q)$ obtained from high energy x-ray diffraction for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses are given in Figure 3.1. The data covers the Q range from 0 to $25 \text{ \AA}^{-1}$. These patterns are used in the simulations. First sharp diffraction peak (FSDP) is an important feature in glass systems that is indicative of intermediate range order present in the system. It is seen from Figure 3.1 that FSDPs with minor intensities (marked with dashed red circle) are clearly observed at around $1 \text{ \AA}^{-1}$ for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=50$ and 70% . $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ ($3x=40$) glass displays a relatively small FSDP feature compared to glasses with $3x=50$ and 70 .

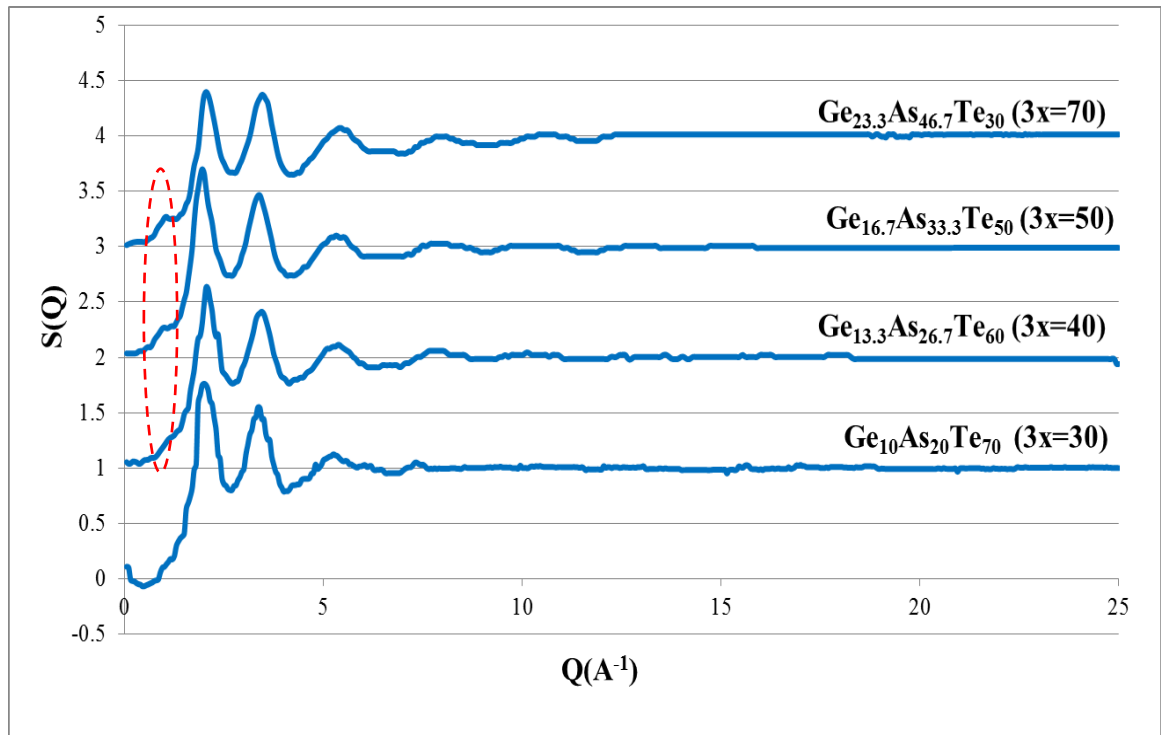


Figure 3.1. X-ray total structure factors $S(Q)$ for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses. Corresponding total metal (Ge+As) content $3x$ is shown alongside each curve [18].

Table 3.1 shows the molar volume and the glass transition data of the glasses studied here [18]. Number densities to be used in simulations are calculated based on the molar volume data and values are found to be $0.030027 \text{ \AA}^{-3}$, $0.03099 \text{ \AA}^{-3}$, $0.032052 \text{ \AA}^{-3}$, $0.034550 \text{ \AA}^{-3}$ for the glasses with $3x=30$, 40, 50 and 70, respectively.

Table 3.1. Composition, molar volume and T_g of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses used in this study [18].

Chemical composition (± 0.1 at. %)	Molar Volume (cm^3)	T_g ($^\circ\text{C}$)
$\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ ($3x=30$)	20.055	130
$\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ ($3x=40$)	19.432	158
$\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ ($3x=50$)	18.788	196
$\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ ($3x=70$)	17.430	285

The RMC models were obtained using cubic cells containing 1000 atoms for all of the glass systems. By using RMCA code, atomic configurations were produced in forward modeling. The coordination constraints that are used to create these configurations are provided in Table 3.2. These configurations are then provided to the simulation environment together with the experimental data to create structural models consistent with the experimental data set in inverse modeling [39, 40].

The nearest neighbor coordination numbers and bond distances that were employed as constraints for these simulations are given in Table 3.2. For $3x=30$, the nearest neighbor coordination numbers were obtained based on Ge and As k-edge extended absorption fine structure spectroscopy (EXAFS) study performed by Lippens [27]. Cut off distances are taken based on the work of Lippens and a previous high energy x-ray diffraction study [18]. As it is seen in Table 2.2, it was taken into consideration that the Ge atoms in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30$, 40 were bonded to three Te atoms. This observation is in agreement with the results from Lippens *et al.*, where they reported that Ge atoms were bonded to three Te atoms [27]. Te-Te coordination number for $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ ($3x=30$) was taken from what is reported in literature for this composition [27]. The decreasing trend in Te-Te coordination numbers in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glass system was quantified in the work of Sen et al before [18]. Te-Te coordination numbers used in these simulations (Table 3.2) are

calculated based on this previous work. It is seen that Te coordination number in the system decreases as the metal content ($3x$) increases in the $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ system [18] and it becomes 0 for the glass composition with $3x=70$.

Table 3.2. Coordination Numbers (C_{ij}), Bond Distances (d_{ij} , in Å) and Cut-Off Distances (in Å) that are used in the RMC simulations for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50$ and 70.

Composition	Coordination Numbers(C_{ij}) and Bond Distances(d_{ij}) (Å)											
	$C_{\text{Ge-Ge}}$	$d_{\text{Ge-Ge}}$	$C_{\text{Ge-As}}$	$d_{\text{Ge-As}}$	$C_{\text{Ge-Te}}$	$d_{\text{Ge-Te}}$	$C_{\text{As-As}}$	$d_{\text{As-As}}$	$C_{\text{As-Te}}$	$d_{\text{As-Te}}$	$C_{\text{Te-Te}}$	$d_{\text{Te-Te}}$
$\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$	-	-	1.0	2.55	3.0	2.7	-	-	2.2	2.7	0.94	2.75
$\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$	-	-	1.0	2.55	3.0	2.7	-	-	1.66	2.7	0.6	2.75
$\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$	-	-	1.0	2.55	1.27	2.7	-	-	1.27	2.7	0.155	2.75
$\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$	-	-	1.42	2.55	2.58	2.7	-	-	-	-	0.0	2.7
Composition	Cut-Off Distances (Å)											
	Ge-Ge		Ge-As		Ge-Te		As-As		As-Te		Te-Te	
$\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$	2.5		2.5		2.65		2.5		2.65		2.7	
$\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$	2.5		2.5		2.65		2.5		2.65		2.7	
$\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$	2.5		2.5		2.65		2.5		2.65		2.7	
$\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$	2.5		2.5		2.65		2.5		2.65		2.7	

The cut-off values (nearest neighbor distances) used in the simulations were 2.5 Å, 2.5 Å, 2.65Å, 2.50 Å, 2.65Å and 2.70 Å for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te atom pairs, respectively. These values are in agreement with the results of Sen et al, where they reported bond distances of 2.5 Å, 2.5 Å, 2.6Å, 2.50 Å, 2.6Å and 2.70Å for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te atom pairs, respectively [18].

RMC simulations were carried out by introducing the experimental structure factors (Figure 3.1) together with the initial configurations into the simulation environments. χ^2 values of 107.6, 61.86, 109.9, and 126.0 were obtained for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50$ and 70, respectively. Figure 3.2-3.5 represents the RMC generated structure factors together with the experimental data. It is seen that the simulations and experimental results are in close agreement with each other.

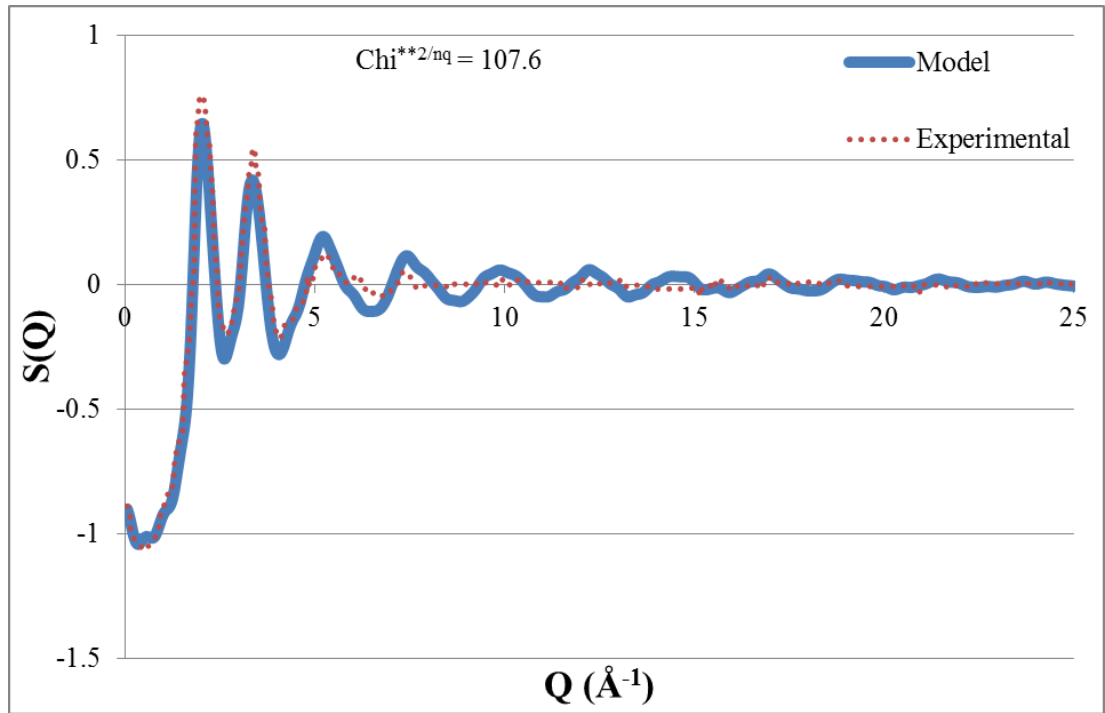


Figure 3.2. Experimental and RMC-generated x-ray total structure factors $S(Q)$ for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30$) glass. Experimental $S(Q)$ [18] is shown in red and RMC simulated $S(Q)$ is given in blue.

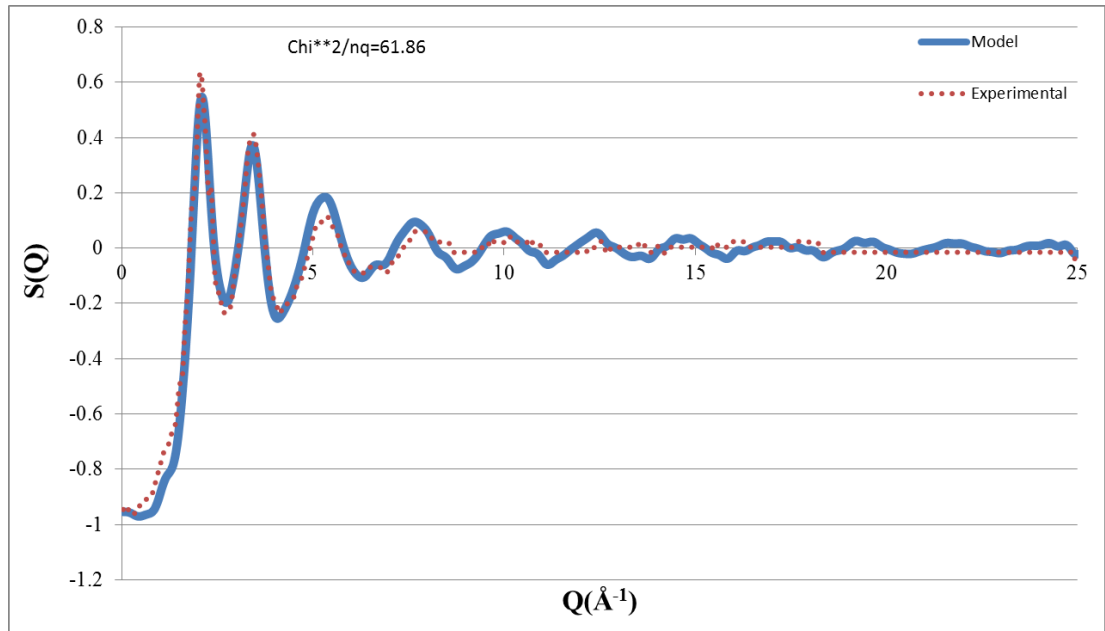


Figure 3.3. Experimental and RMC-generated x-ray total structure factors $S(Q)$ for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=40$) glass. Experimental $S(Q)$ [18] is shown in red and RMC simulated $S(Q)$ is given in blue.

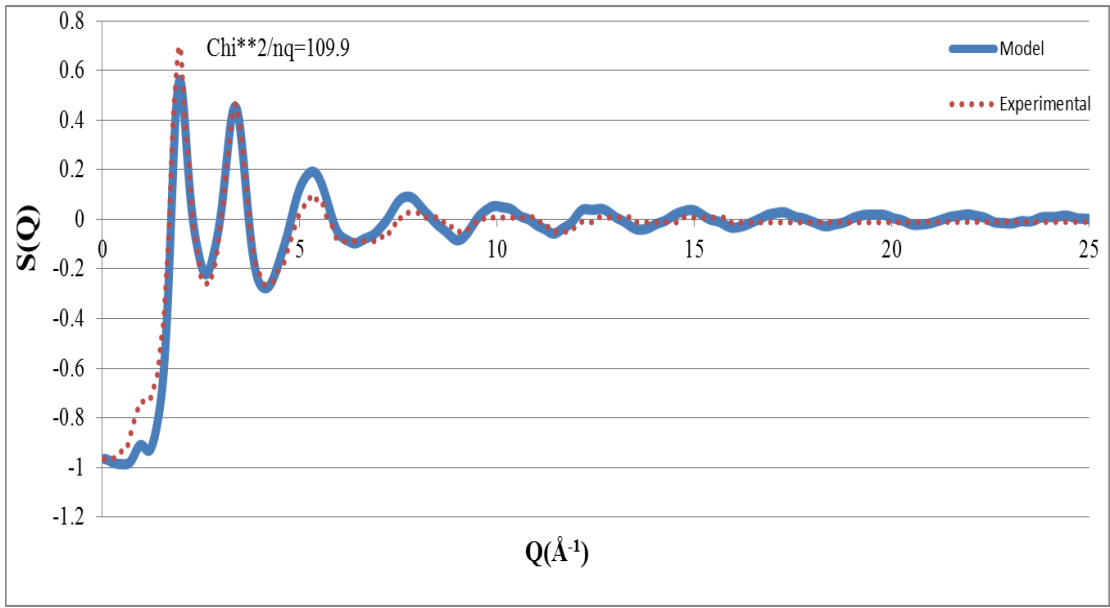


Figure 3.4. Experimental and RMC-generated x-ray total structure factors $S(Q)$ for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=50$) glass. Experimental $S(Q)$ [18] is shown in red and RMC simulated $S(Q)$ is given in blue.

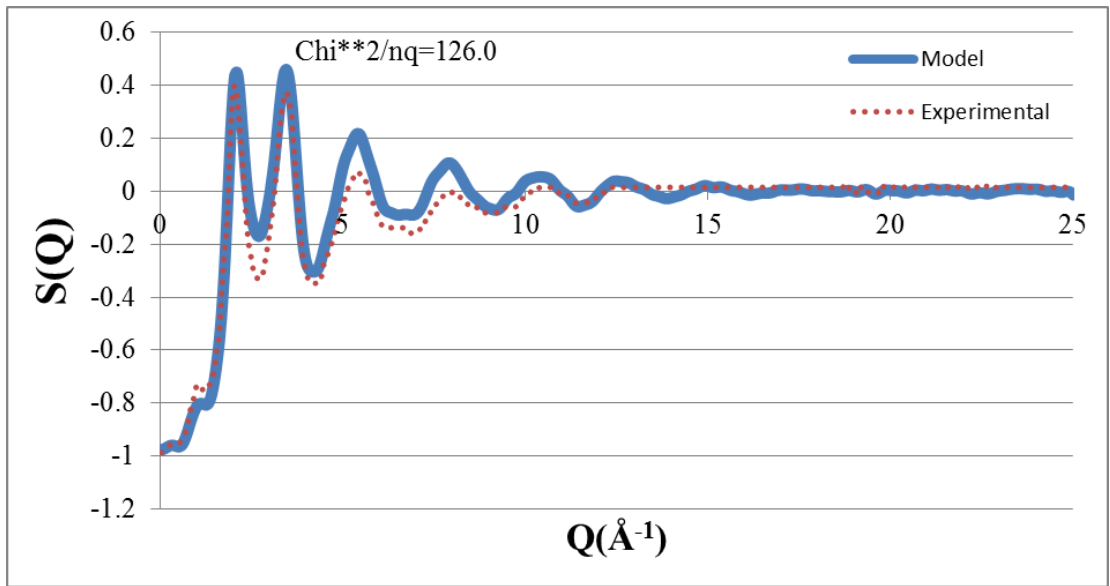


Figure 3.5. Experimental and RMC-generated x-ray total structure factors $S(Q)$ for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=70$) glass. Experimental $S(Q)$ [18] is shown in red and RMC simulated $S(Q)$ is given in blue.

Figure 3.6 represents the three dimensional models obtained for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x= 30, 40, 60$ and 70 . The Ge, As and Te atoms are represented by green, purple and orange spheres, respectively. The three dimensional pictures display random

disordered networks in these systems. Although the configurations are random, the total coordination numbers of Ge, As and Te atoms are seen to be approximately 4, 3 and 2, respectively, indicating that 8-N rule is obeyed in this system. These atomic configurations are used in further analysis to obtain partial structure factors, partial pair distribution functions, coordination numbers, bond angle and ring size distributions in this system.

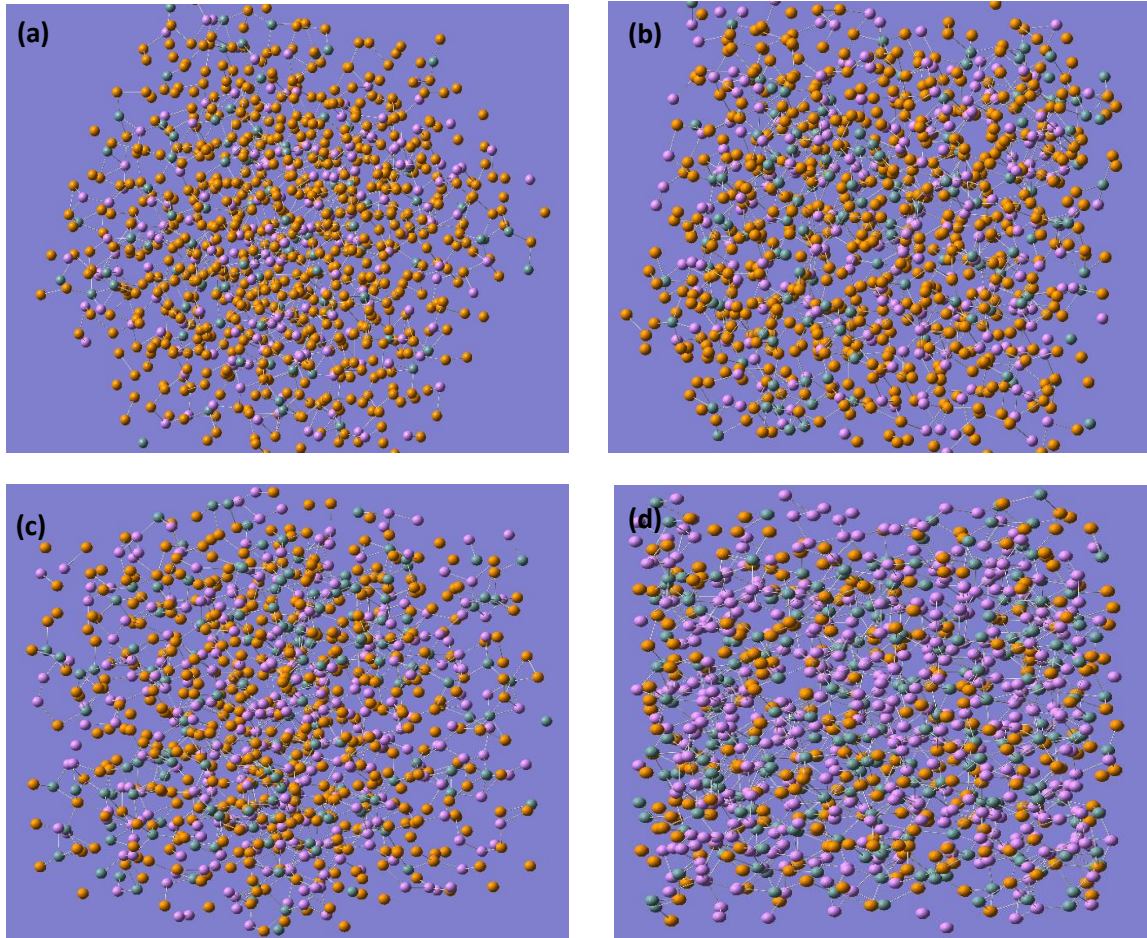


Figure 3.6. Atomic configurations generated by RMC simulations for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with (a) $3x=30$, (b) $3x=40$, (c) $3x=50$ and (d) $3x=70$. Green, purple and orange spheres correspond to Ge, As, and Te atoms, respectively.

3.1. Partial Structure Factors

The first sharp diffraction peak (FSDP) is one of the most characteristic features in the diffraction patterns of network-forming glasses. This feature is indicative of intermediate-range order (about nano-meter length-scale) present in a glass system. It might be difficult to understand the interatomic correlations responsible for this feature especially

in multicomponent glass systems as in this study. The partial structure factors that can be obtained by RMC modeling can be extremely useful for the determination of the interatomic correlations that result in FSDP. Figure 3.7- 3.10 represent the experimental x-ray and the RMC generated total structure factors $S(Q)$, with the six different partial structure factors $S_{ij}(Q)$ for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50$ and 70 . Based on these figures, the interatomic correlations related to FSDP feature are assigned and these correlations are summarized in Table 3.3. It is seen that, FSDP results from metal (Ge and/or As) related correlations in this system consistent with the previous studies (5, 18). Increasing total metal (Ge+As) contents ($3x$) is seen to result in increasing FSDP intensity (Figure 3.1) supporting this argument.

Table 3.3. Interatomic correlations contributing to FSDP for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass system based on Figures 8-11.

Composition	Interatomic correlations contributing to FSDP	Ring Size Distributions
$\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ ($3x=30$)	No FSDP feature	4-10 membered rings
$\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ ($3x=40$)	Ge-Ge, Ge-Te, As-As	4-10 membered rings
$\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ ($3x=50$)	Ge-Ge, Ge-Te, As-As	4-10 & 14-30
$\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ ($3x=70$)	Ge-Ge, Ge-As, As-As	Up to 40 membered nodes

Figure 3.7 presents experimental and RMC-generated structure factors $S(Q)$ together with six partial structure factors $S_{ij}(Q)$ for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30$) glass. An investigation of Figure 3.7 reveals that the experimental and RMC-generated $S(Q)$ data are in good agreement with a χ^2 value around 107.6. As it was noted earlier, FSDP feature was not observed in the total $S(Q)$ of this composition.

Figure 3.8 illustrates experimental and RMC-generated structure factors together with partial structure factors $S_{ij}(Q)$ for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=40$) glass. An investigation of Figure 3.8 shows that the experimental and modeled $S(Q)$ data are in good agreement with a χ^2 value around 61.86 for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=40$). It is seen in Figure 3.8 that the FSDP in $S(Q)$ has quite low intensity and its position is located about at $1.05 \text{ \AA}^{-1}$. Ge-Ge, As-As and

Ge-Te partial structure factors display peaks at around $1.05 \text{ \AA}^{-1}$ signifying that these atomic pairs are mainly contributing to FSDP for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=40$) chalcogenide glass.

The experimental and RMC generated structure factors together with partial structure factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=50$) glass are given in Figure 3.9. An investigation of Figure 3.9 indicates that the experimental and obtained $S(Q)$ data are in good agreement with a Chi^2 value around 109.9, excluding some small discrepancy at low (Q) values. As it is seen in Figure 3.9, the FSDP position is located about at $0.75 \text{ \AA}^{-1}$. The partial structure factors of Ge-Ge, As-As and Ge-Te bonds displayed peaks at around $0.75 \text{ \AA}^{-1}$, indicating the contribution of Ge-Ge, As-As and Ge-Te pairs to the FSDP for this glass composition.

Figure 3.10 shows the experimental and RMC generated structure factors and partial structure factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=70$) glass. An analysis of Figure 3.10 shows that the experimental and RMC generated total x-ray structure factors $S(Q)$ agree with each other with a Chi^2 value around 126.0. Figure 3.9 clearly indicates that the FSDP for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=70$) glass is located at $0.90 \text{ \AA}^{-1}$. RMC-generated partial structure factors indicate that Ge-Ge and As-As metal bonds contribute significantly to the FSDP of the $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=70$), with a minor contribution from the Ge-As pair as it is seen in Figure 3.10.

To sum up, the experimental and RMC-generated total structure factors are in agreement with the experimental data with Chi^2 values of 107.6, 61.86, 109.9, and 126.0 for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50$ and 70 , respectively. The FSDP feature is not observed for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ with $3x=30$ as it is shown in Figure 8, while FSDP is present for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses with $3x=40, 50$ and 70 (Figures 9-11). It was previously shown by Sen et. al. that there was a relationship between FSDP intensity and the amount of Te in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses such that FSDP intensity increased monotonously with decreasing Te content [18]. This study supports findings of Sen et. al. as partial structure factors obtained from RMC models revealed that metal-including correlations given in Table 3 mainly contributed to the FSDP in this system.

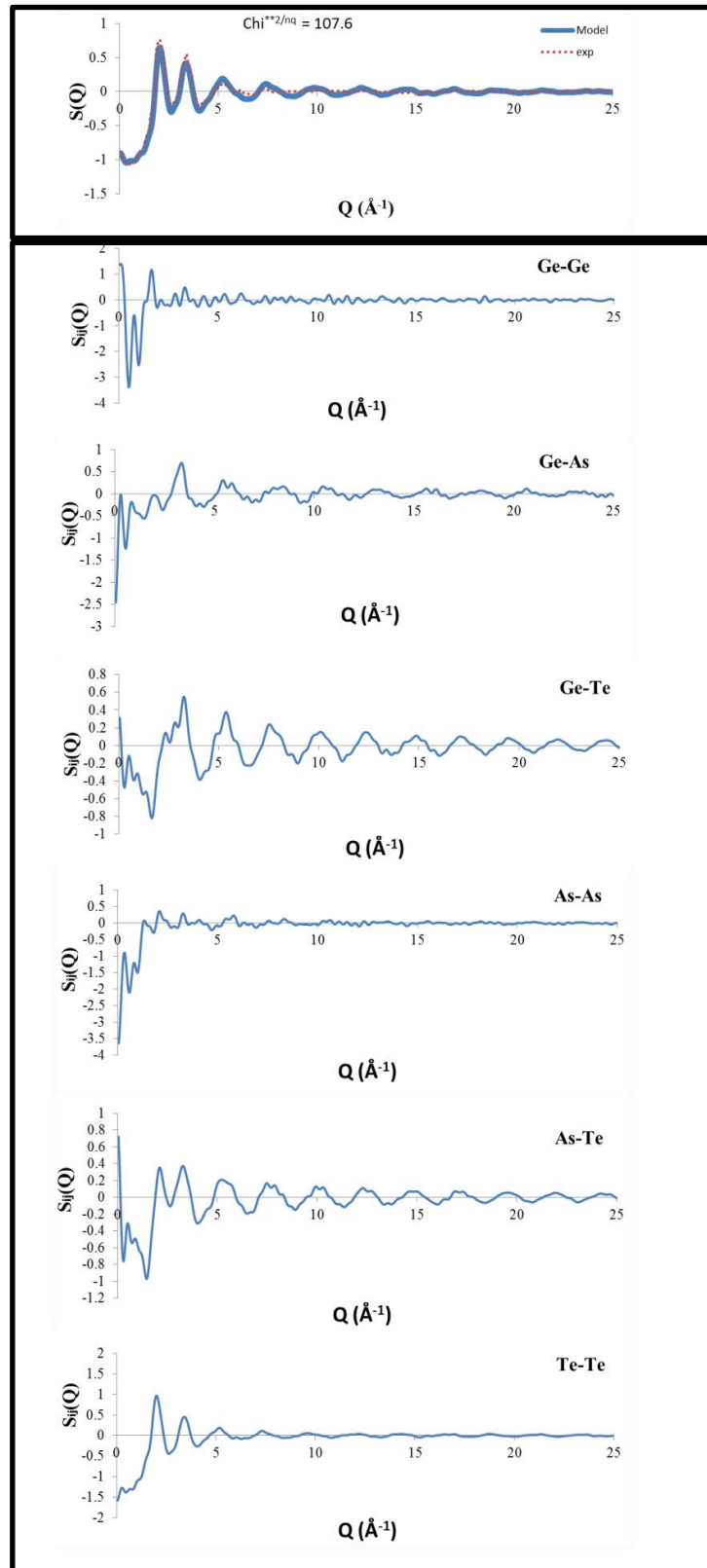


Figure 3.7. Upper panel: Experimental and RMC model structure factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30$) Lower panel: Partial structure factors $S_{ij}(Q)$ obtained from RMC simulations for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te pairs in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30$) chalcogenide glass, respectively.

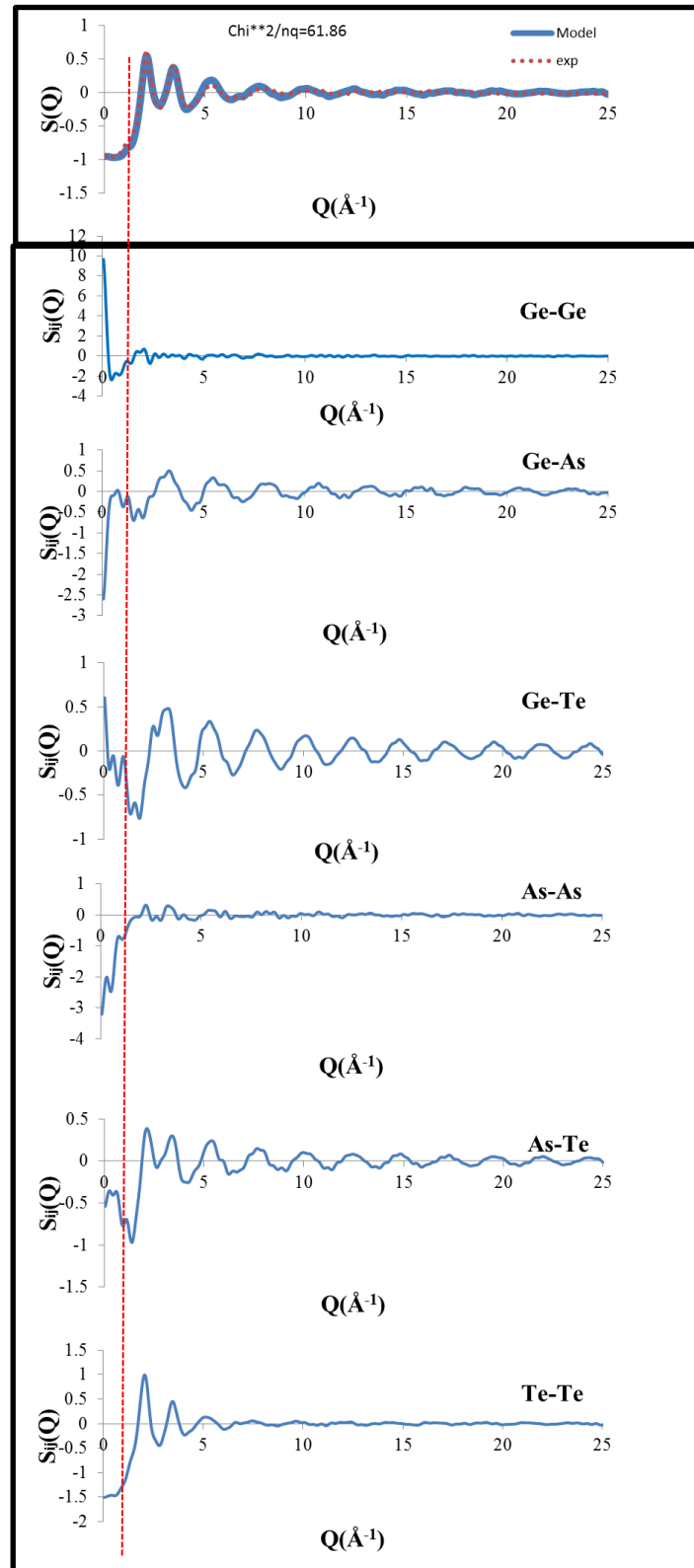


Figure 3.8. Upper panel: Experimental and RMC model structure factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=40$) Lower panel: Partial structure factors $S_{ij}(Q)$ obtained from RMC simulations for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te pairs in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=40$) chalcogenide glass, respectively.

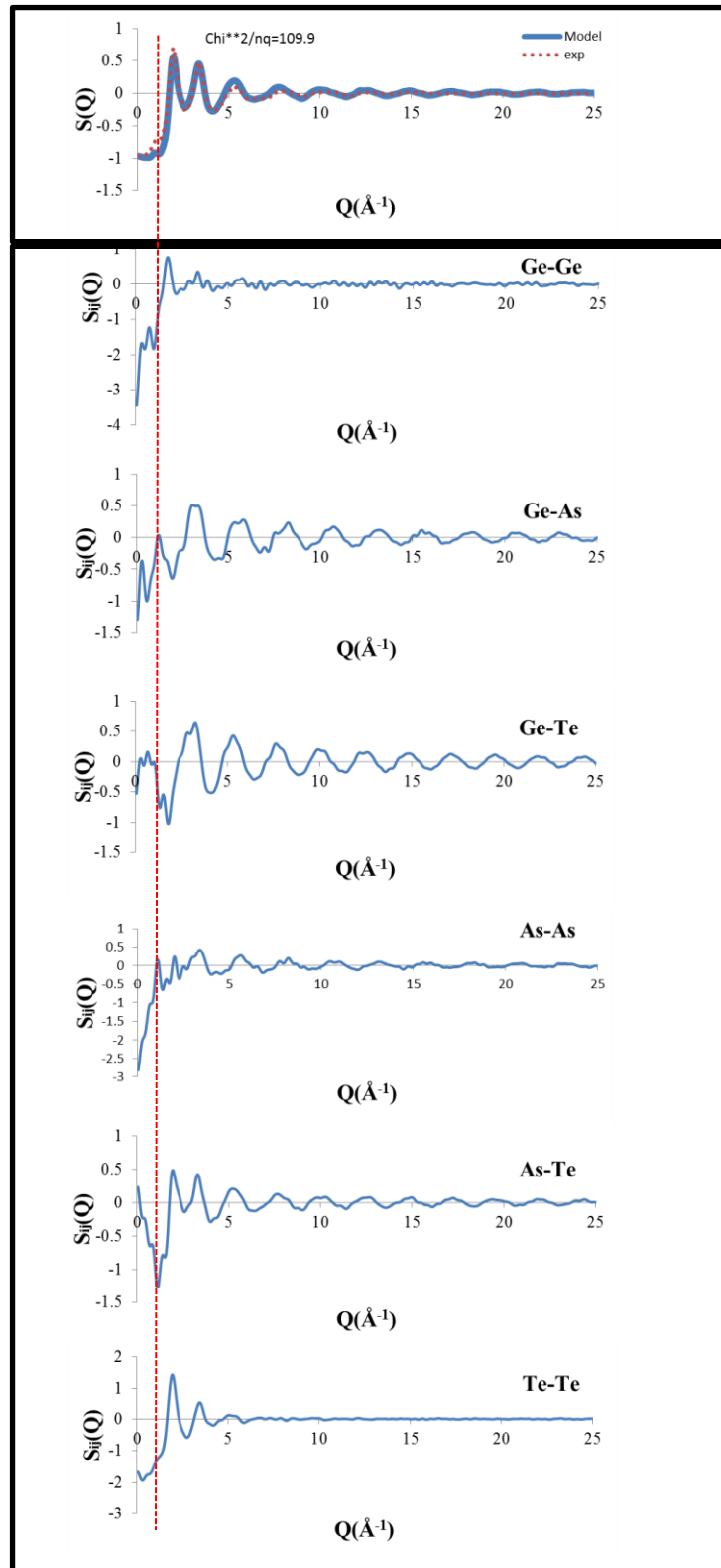


Figure 3.9. Upper panel: Experimental and RMC model structure factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=50$) Lower panel: Partial structure factors $S_{ij}(Q)$ obtained from RMC simulations for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te pairs in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=50$) chalcogenide glass, respectively.

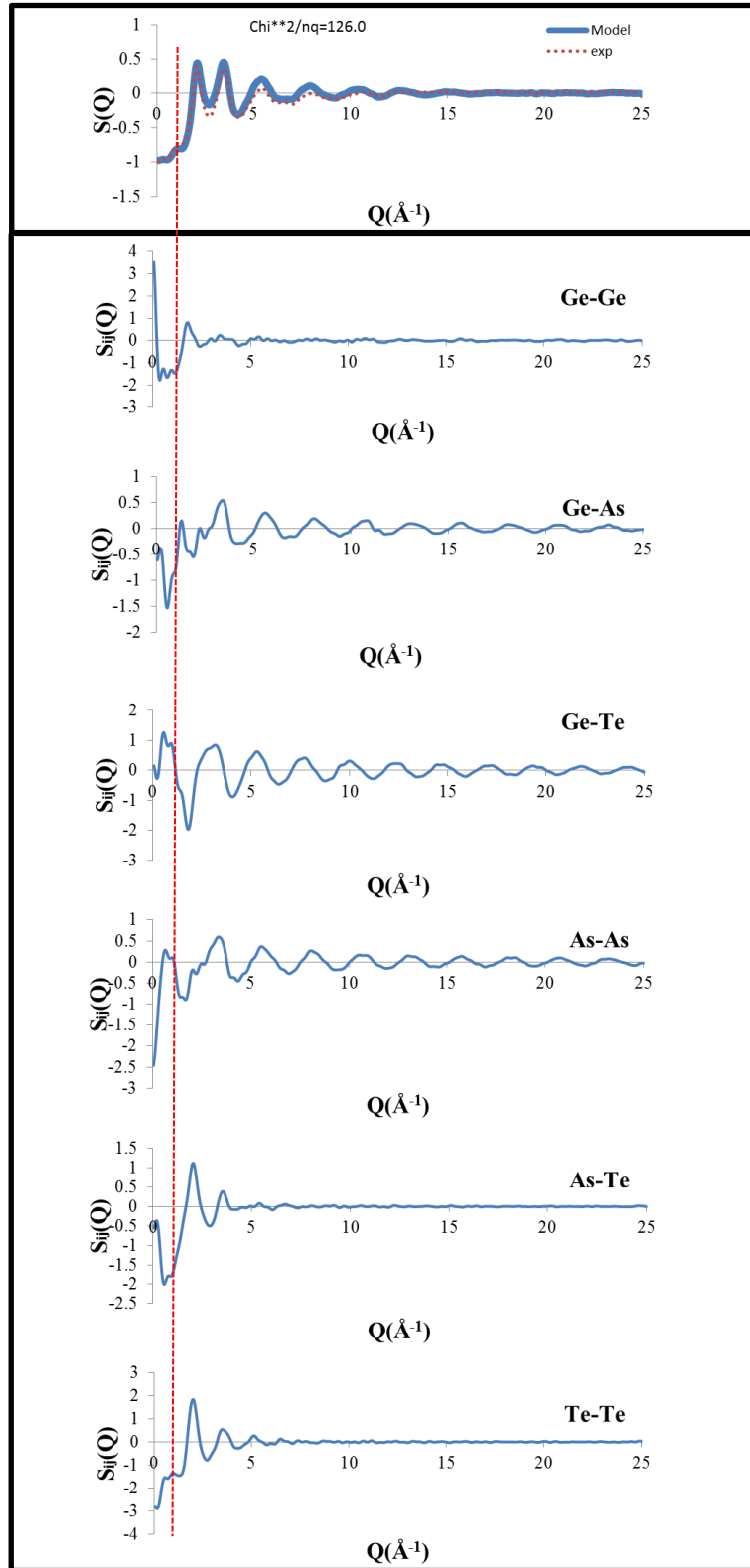


Figure 3.10. Upper panel: Experimental and RMC model structure factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=70$) Lower panel: Partial structure factors $S_{ij}(Q)$ obtained from RMC simulations for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te pairs in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=70$) chalcogenide glass, respectively.

3.2. Partial Pair Distribution Functions

The total radial distribution functions $G_T(r)$ of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses were obtained in a previous study [18] and are shown in Figure 3.11. In order to further investigate the nearest neighbor coordination environment for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses, the partial pair correlation functions $g_{ij}(r)$ are obtained from the RMC simulations and are summarized in Figure 13-36.

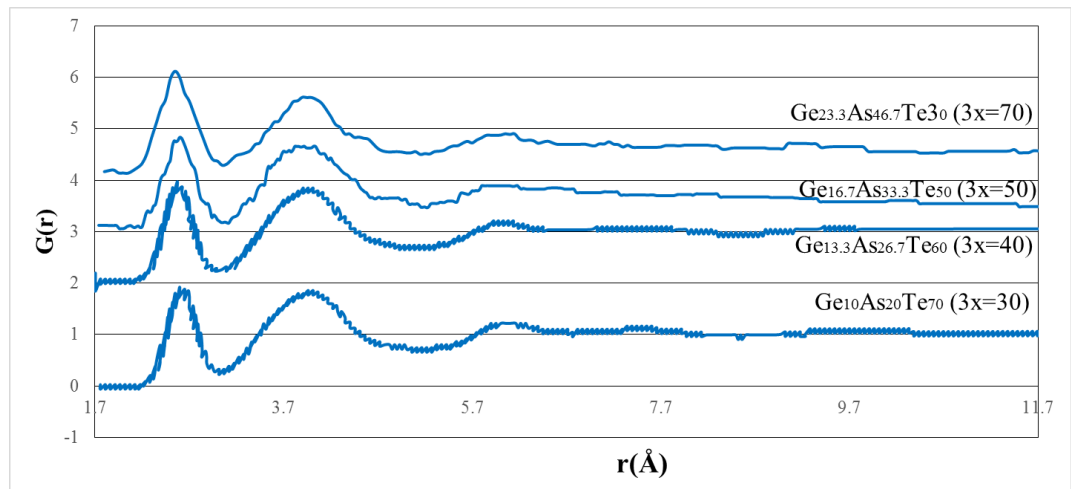


Figure 3.11. Radial distribution functions of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses ($3x=30, 40, 50$ and 70) [18].

An investigation of the partial pair distribution functions in Figure 3.12 reveals that the Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te distances for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30$) chalcogenide glasses are 2.5 Å, 2.5 Å, 2.65 Å, 2.5 Å, 2.65 Å and 2.75 Å, respectively. As it is seen in Figure 3.12, 3.13 and 3.15, the Ge-Ge, Ge-As and As-As partial pair distribution functions display strong peaks at 2.5 Å corresponding to nearest neighbor correlations. The Ge-Te and As-Te partial pair distribution functions show a strong peak at 2.65 Å corresponding to nearest neighbor correlations. The peak centered at 2.75 Å corresponds to Te-Te partial pair distribution functions.

An investigation of the partial pair distribution functions in Figure 3.13 reveals that the Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te distances for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=40$) chalcogenide glass are 2.5 Å, 2.5 Å, 2.65 Å, 2.5 Å, 2.65 Å and 2.75 Å, respectively. The Ge-Ge, Ge-As and As-As partial pair distribution functions display strong peak at 2.5 Å

corresponding to nearest neighbor correlations. The Ge-Te and As-Te partial pair distribution functions are dominated by a peak at 2.65 Å, while the Te-Te partial pair distribution function corresponding to nearest neighbor correlations is centered at 2.75 Å.

Figure 3.14 shows that Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te bond distances for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=50$) chalcogenide glass are 2.5 Å, 2.5 Å, 2.65 Å, 2.5 Å, 2.65 Å and 2.75 Å, respectively. From the analysis of $g_{ij}(r)$, Ge-Ge, Ge-As and As-As partial pair distribution functions exhibit a nearest neighbor peak centered at 2.5 Å. The Ge-Te and As-Te partial pair distribution functions display a strong peak at 2.65 Å, while the peak at 2.75 Å in the Te-Te partial pair distribution function corresponds to Te-Te nearest neighbor correlations.

An investigation of the partial pair distribution functions in Figure 3.15 reveals that the Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te bond distances for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=70$) chalcogenide glass are 2.5 Å, 2.5 Å, 2.65 Å, 2.5 Å, 2.9 Å and 2.9 Å, respectively. As it is seen in Figures 3.12, 3.13 and 3.15, the Ge-Ge, Ge-As and As-As partial pair distribution functions show peaks at 2.5 Å corresponding to nearest neighbor correlations. The Ge-Te partial pair distribution function displays a peak centered at 2.65 Å corresponding to nearest neighbor correlations. The peaks centered at 2.9 Å correspond to and As-Te and Te-Te partial pair distribution functions.

To sum up, the partial pair distribution functions for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ with $3x=30, 40, 50$ and 70 were shown in Figures 3.12-3.15. As it was explained above, the nearest neighbor coordination distances of Ge, As and Te atoms in the structure of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ with $3x=30, 40, 50$ and 70 chalcogenide glasses were indicated by the peaks between 2.5 Å and 3 Å in the partial pair correlation functions $g_{ij}(r)$, which agreed well with the literature values [18]. When the Figures 13-16 were examined in detail, it was seen that partial pair distribution functions $g_{ij}(r)$ of metal-metal correlations such as Ge/As-Ge/As had more stronger peaks, whereas the peaks of Te containing correlations such as Ge-Te, As-Te or Te-Te displayed very low intensities, as it was expected for Te-deficient chalcogenide glasses, $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ with $3x=$ and 70 . This observation stated that most of the partial pair distribution functions of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ with $3x=30, 40, 50$ and 70 chalcogenide glasses were predominated by some metal-metal bond pairs such as Ge/As-Ge/As.

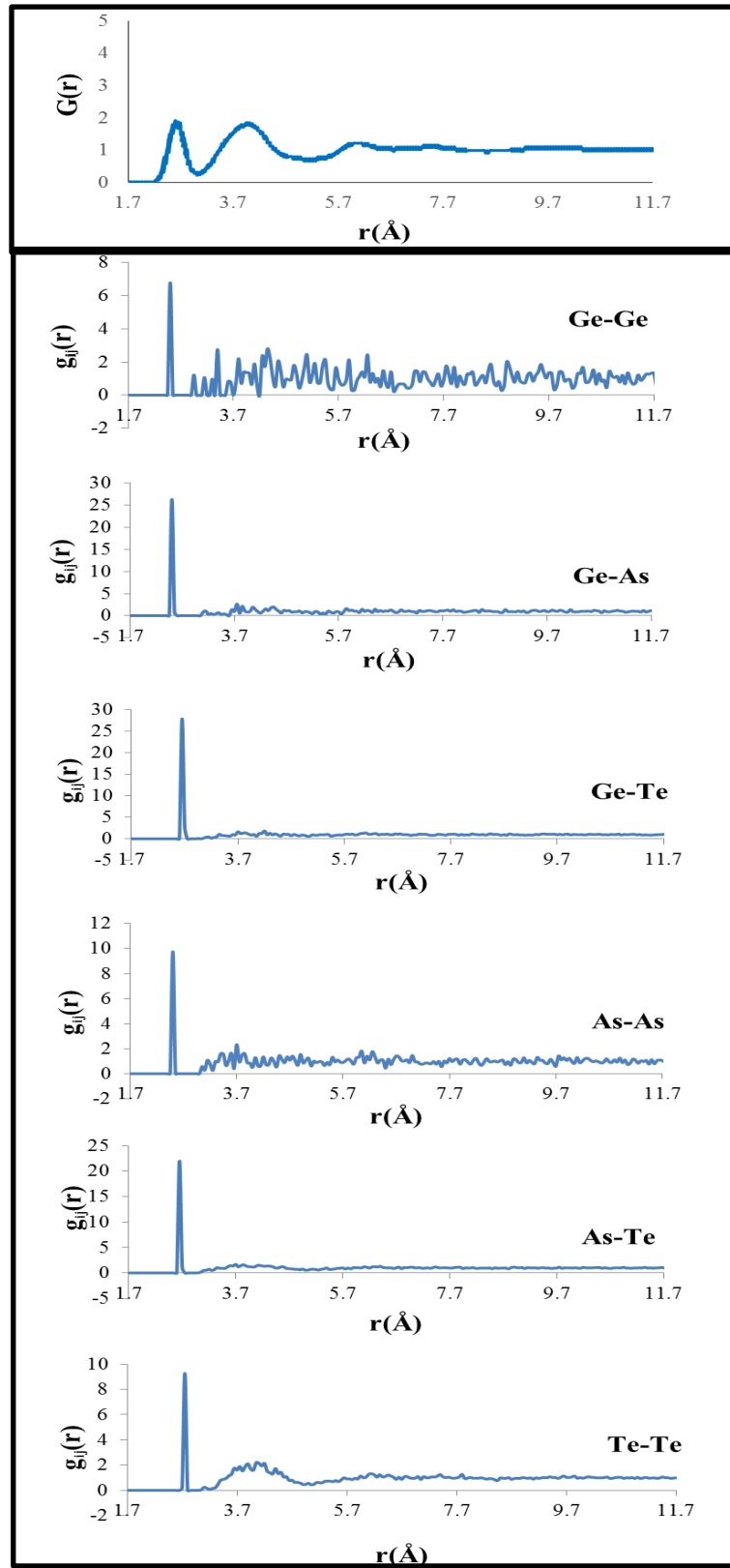


Figure 3.12. Upper panel: Experimental pair distribution factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30$) Lower panel: Partial pair distribution functions $g_{ij}(r)$ obtained from RMC simulations for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te pairs in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30$) chalcogenide glass, respectively.

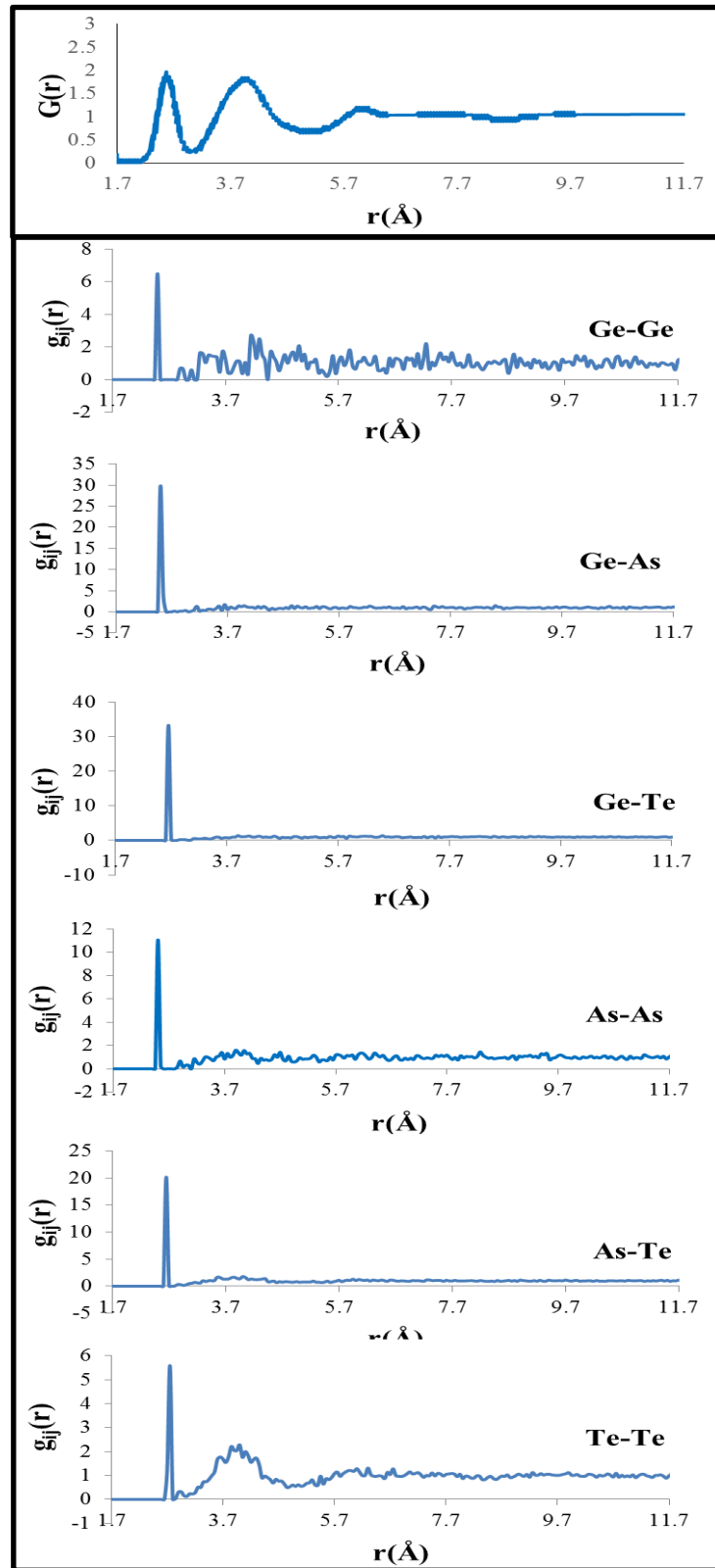


Figure 3.13. Upper panel: Experimental pair distribution factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=40$) Lower panel: Partial pair distribution functions $g_{ij}(r)$ obtained from RMC simulations for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te pairs in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=40$) chalcogenide glass, respectively.

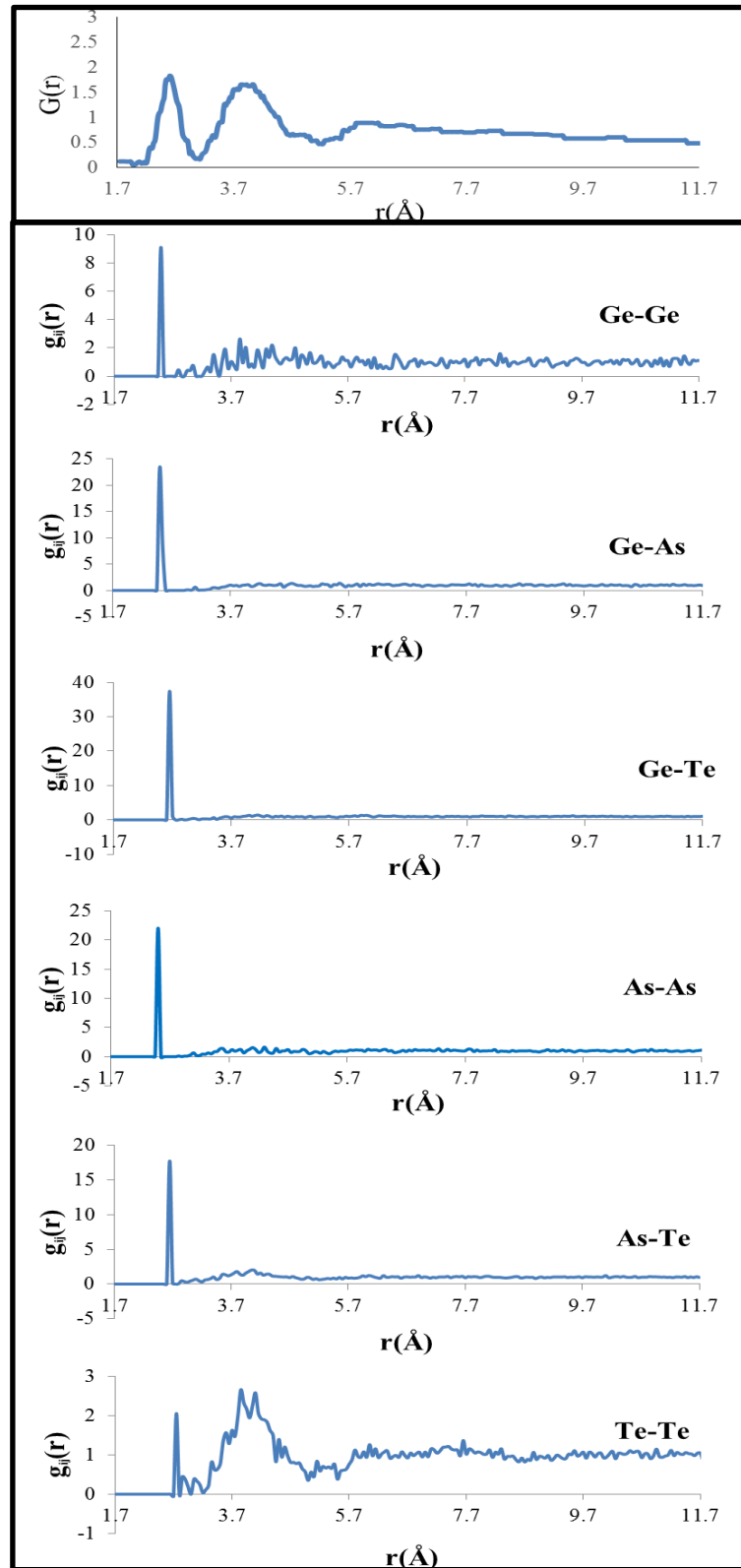


Figure 3.14. Upper panel: Experimental pair distribution factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=50$) Lower panel: Partial pair distribution functions $g_{ij}(r)$ obtained from RMC simulations for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te pairs in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=50$) chalcogenide glass, respectively.

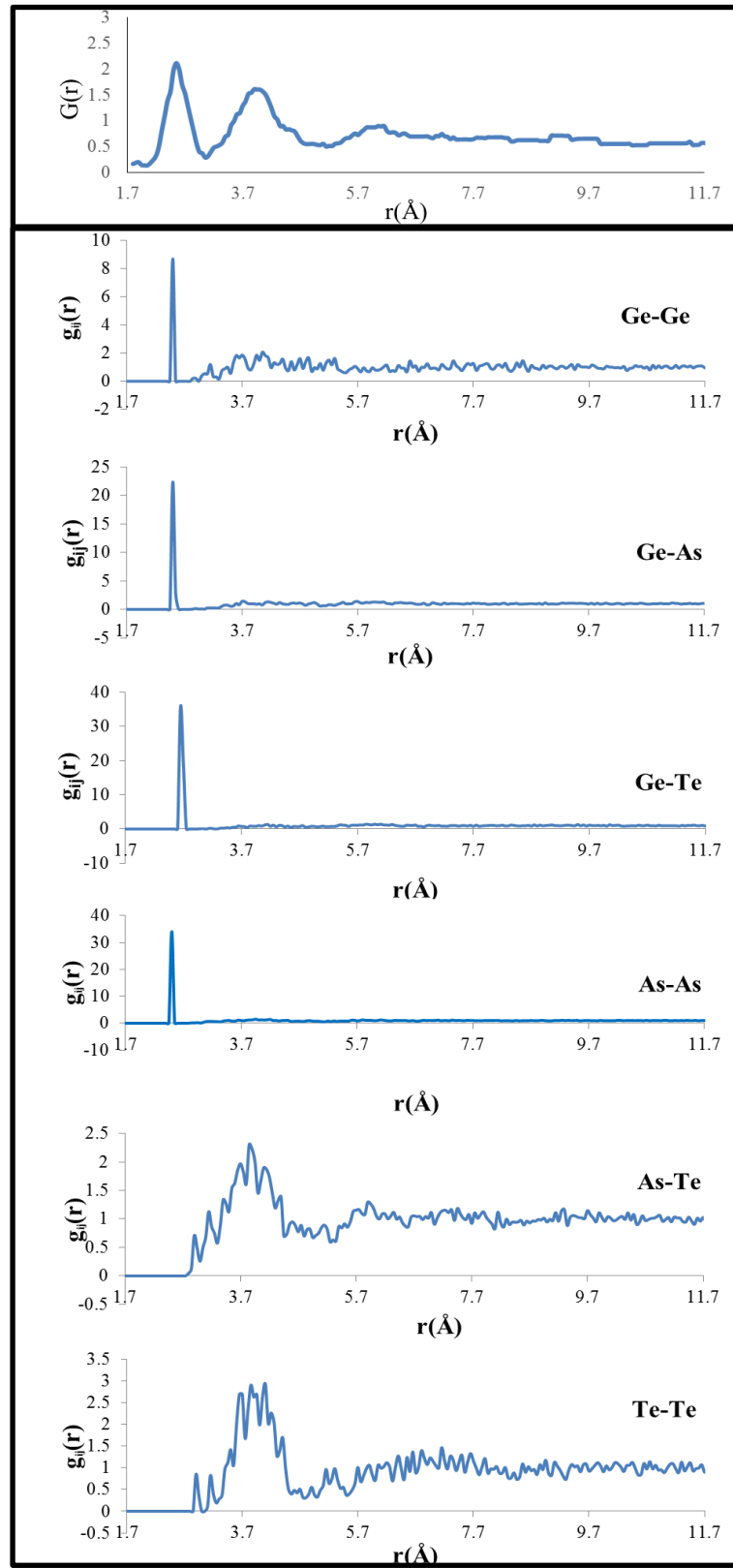


Figure 3.15. Upper panel: Experimental pair distribution factors for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=70$) Lower panel: Partial pair distribution functions $g_{ij}(r)$ obtained from RMC simulations for Ge-Ge, Ge-As, Ge-Te, As-As, As-Te and Te-Te pairs in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=70$) chalcogenide glass, respectively.

3.3. Coordination Numbers

The local structure in the RMC models of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses with $3x=30, 40, 50, 70$ was investigated employing Neigh.exe. Coordination numbers corresponding to Ge-Ge, Ge-As, Ge-Te, As-As, As-Te, and Te-Te pairs in this system are plotted as a function of total metal content ($3x$) in Figures 37-42.

An investigation of the Ge-Ge coordination numbers in Figure 3.16 shows that it increases continuously with increasing metal contents ($3x$) in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses system. Ge-Ge coordination numbers were 0.08, 0.11, 0.19 and 0.27 for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50, 70$, respectively.

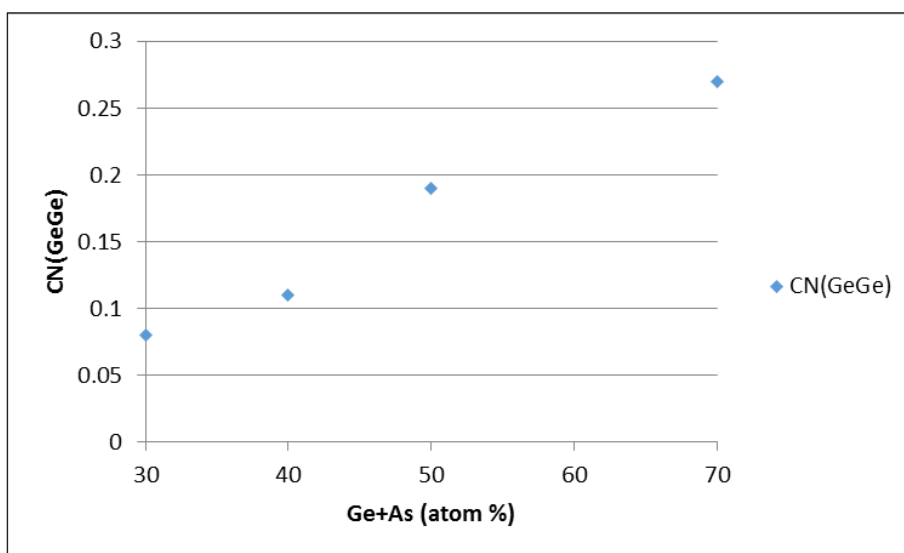


Figure 3.16. Ge-Ge coordination numbers for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30, 40, 50, 70$) glasses.

An investigation of the Ge-As coordination numbers in Figure 3.17 reveals that it shows an increasing trend with increasing metal contents in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses. Ge-As coordination number increases gradually from 0.08 to 0.27 for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50$, and 70.

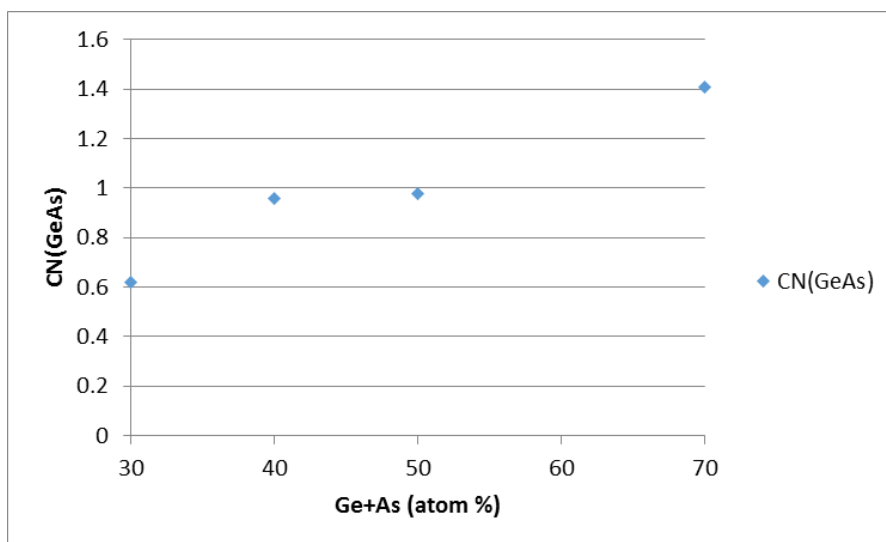


Figure 3.17. Ge-As coordination numbers for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30, 40, 50, 70$) glasses.

From the analysis of Figure 3.18, Ge-Te coordination numbers shows a decreasing trend with increasing metal contents (Ge+As %) in the structure of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses with $3x=30, 40, 50, 70$. Ge-Te coordination numbers obtained from the RMC models for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50, 70$ were 2.85, 2.74, 2.72 and 2.52, respectively.

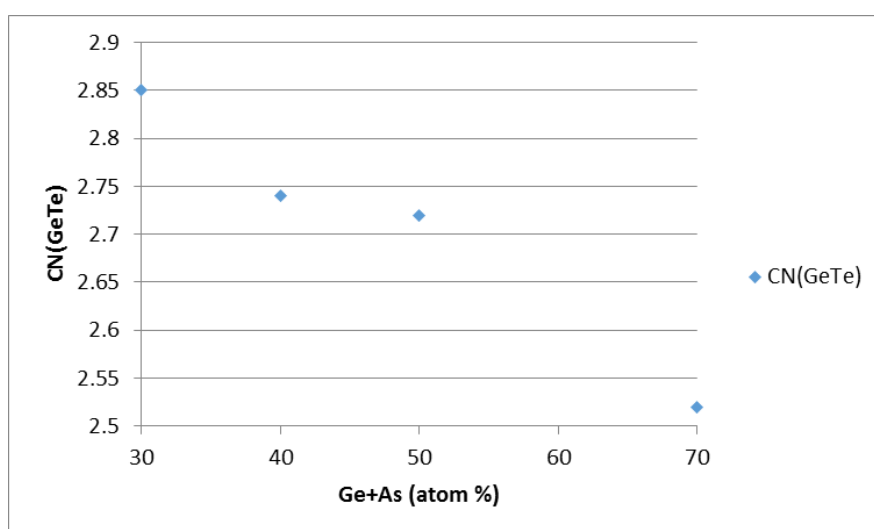


Figure 3.18. Ge-Te coordination numbers for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30, 40, 50, 70$) glasses.

An investigation of the As-As coordination numbers in Figure 3.19 reveals that it shows an increasing trend with increasing metal contents (Ge+As %) in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$

chalcogenide glass system. As-As coordination number was found to increase from 0.23 to 2.16 as the total metal content increases in the system.

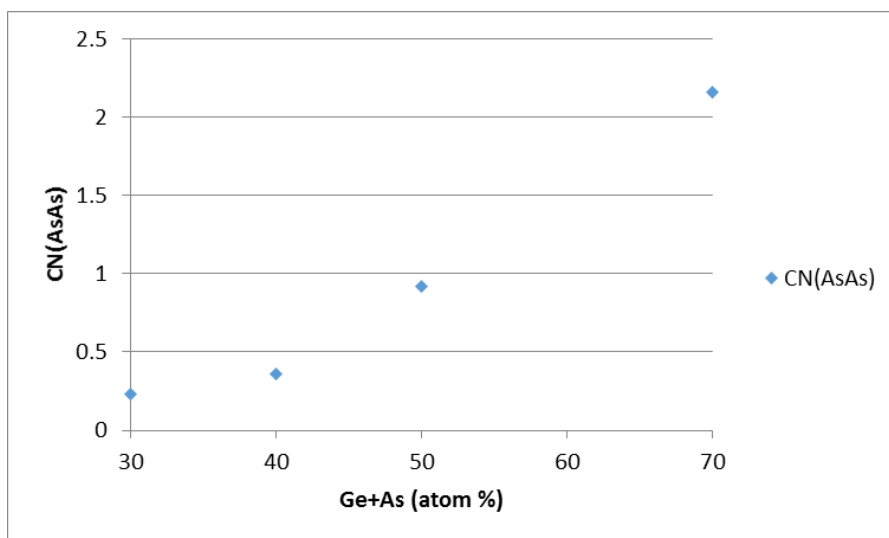


Figure 3.19. As-As coordination numbers for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30, 40, 50, 70$) glasses.

Figure 3.20 displays the changes in As-Te coordination numbers with increasing metal content ($3x = \text{Ge+As at.}\%$) in the structure of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses. As-Te coordination number was found to decrease from about 2.15 to 0.0 as a function of increasing metal content in the system.

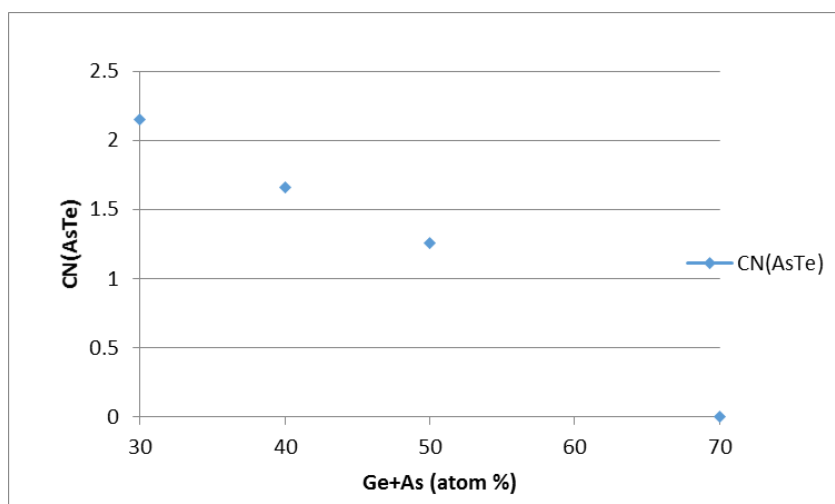


Figure 3.20. As-Te coordination numbers for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30, 40, 50, 70$) glasses.

Te-Te coordination numbers were plotted as a function of total metal content in Figure 3.21. It was observed that Te-Te coordination numbers were 0.95, 0.60, 0.15 and 0.0 for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50, 70$, respectively.

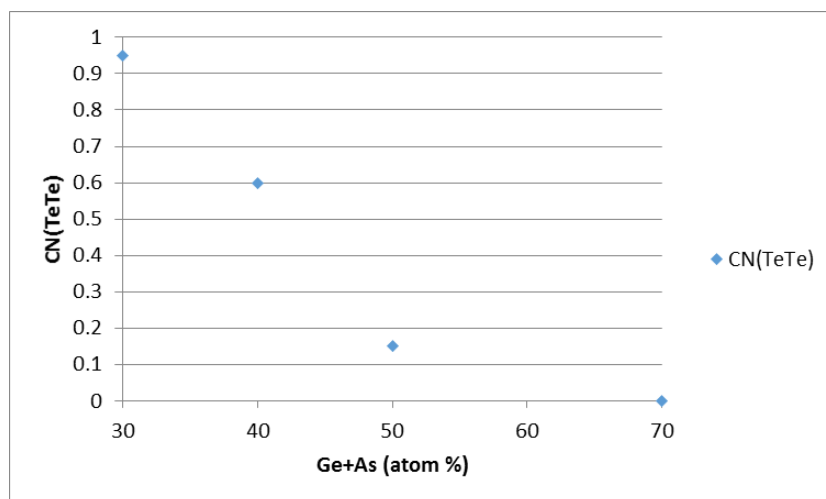


Figure 3.21. Te-Te coordination numbers for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=30, 40, 50, 70$) glasses.

The partial and total coordination numbers obtained from the RMC models in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ system are shown in Table 3.4.

Table 3.4. Coordination Numbers of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses obtained from Neigh.exe.

Composition	CN GeGe	CN GeAs	CN GeTe	CN AsAs	CN AsTe	CN TeTe	CN _T Ge	CN _T As	CN _T Te
$\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ ($3x=30$)	0.08	0.62	2.85	0.23	2.15	0.95	3.55	2.69	1.97
$\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ ($3x=40$)	0.11	0.96	2.74	0.36	1.66	0.60	3.81	2.50	1.95
$\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ ($3x=50$)	0.19	0.98	2.72	0.92	1.26	0.15	3.89	2.67	1.90
$\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ ($3x=70$)	0.27	1.41	2.52	2.16	0.0	0.0	4.20	2.86	1.96

A comparison of the results given in Table 3.4 and the literature results indicate that the total coordination numbers of Ge, As, and Te atoms were about 4, 3, and 2, respectively, indicating that the system obeyed the 8-N coordination rule [5,18, 27]. In this study, total coordination number of Ge atoms were 3.55, 3.81, 3.89 and 4.20 for glass compositions with $3x=30, 40, 50$ and 70 , respectively. The corresponding As coordination numbers were obtained to be 2.69, 2.50, 2.67 and 2.86, in consistence with the values given for chalcogenide glasses in literature [5, 18, 27]. In addition to Ge and As coordination numbers, total coordination number of Te atoms were found to be around 1.97, 1.95, 1.90 and 1.96 for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses with $3x=30, 40, 50, 70$, which are in agreement with the results in the work of Lippens *et al.* and Sen *et al.* [5, 18, 27]. In their study, Lippens *et al.* reported that the coordination number of Ge, As and Te atoms were around 4, 3 and 2, respectively [27]. Lippens *et al.* stated that in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass with $3x=30$, Ge atoms bonded to 3 Te atoms and 1 Ge/As atoms, As atoms bonded to 2.2 Te atoms and 0.8 Ge/As atoms and Te-Te coordination number was found to be 0.94 ± 0.1 to obey chemical order [27]. This observation is in good agreement with the results of Ge, As and Te coordination numbers for the $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass with $3x=30$ in this study.

3.4 Bond Angle Distributions

In this study, the bond angle distributions in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass system are obtained based on the RMC models generated. Ge-Ge-Ge, Ge-Te-Ge, Te-Ge-Te, Te-As-Te, As-Te-As, As-As-As, Te-Te-Te and Te-Te-As angle distributions are given in Figures 3.23-3.29. Table 3.5 represents a comparison of the bond angle values obtained from the RMC models. The high intensity peak positions along with the mean angle values for each of the atom triplets given in Figures 3.23-3.29 are presented in Table 3.5.

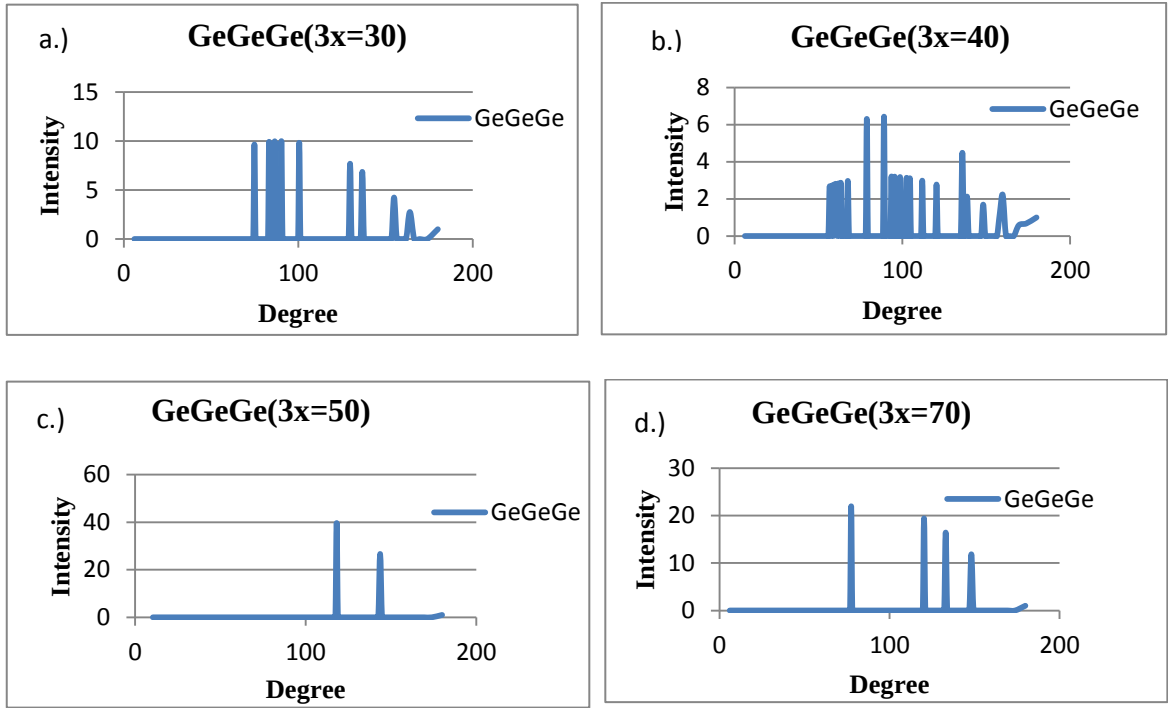


Figure 3.22. Ge-Ge-Ge bond angle distribution for (a) $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ glass ($3x=30$), (b) $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ glass ($3x=40$), (c) $\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ glass ($3x=50$), (d) $\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ glass ($3x=70$).

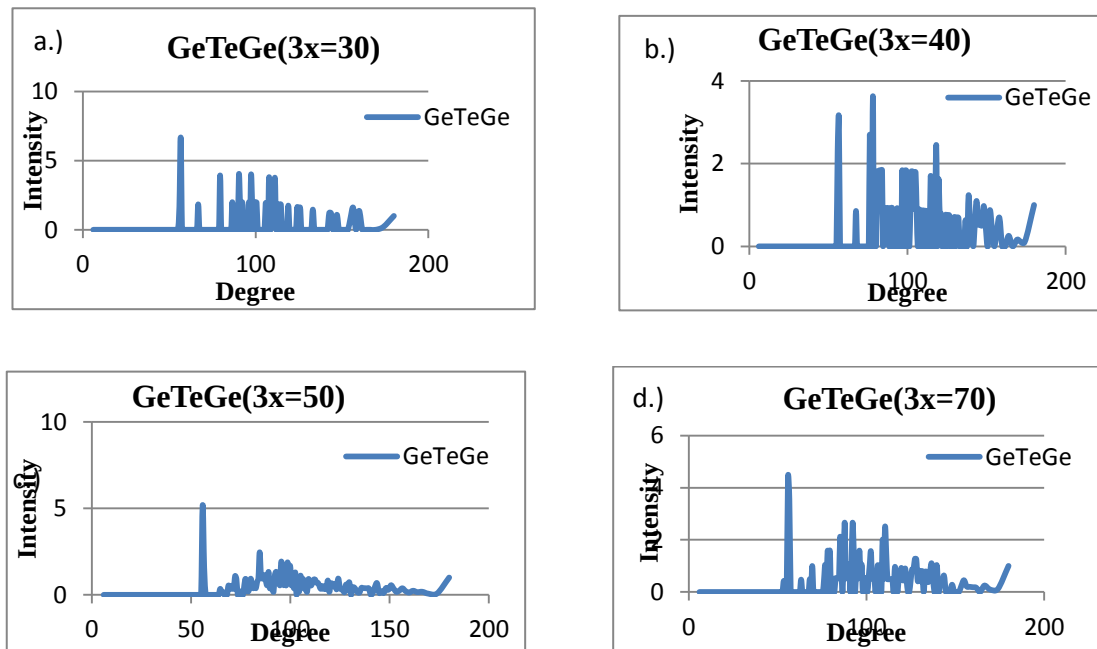


Figure 3.23. Ge-Te-Ge bond angle distribution for (a) $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ glass ($3x=30$), (b) $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ glass ($3x=40$), (c) $\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ glass ($3x=50$), (d) $\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ glass ($3x=70$).

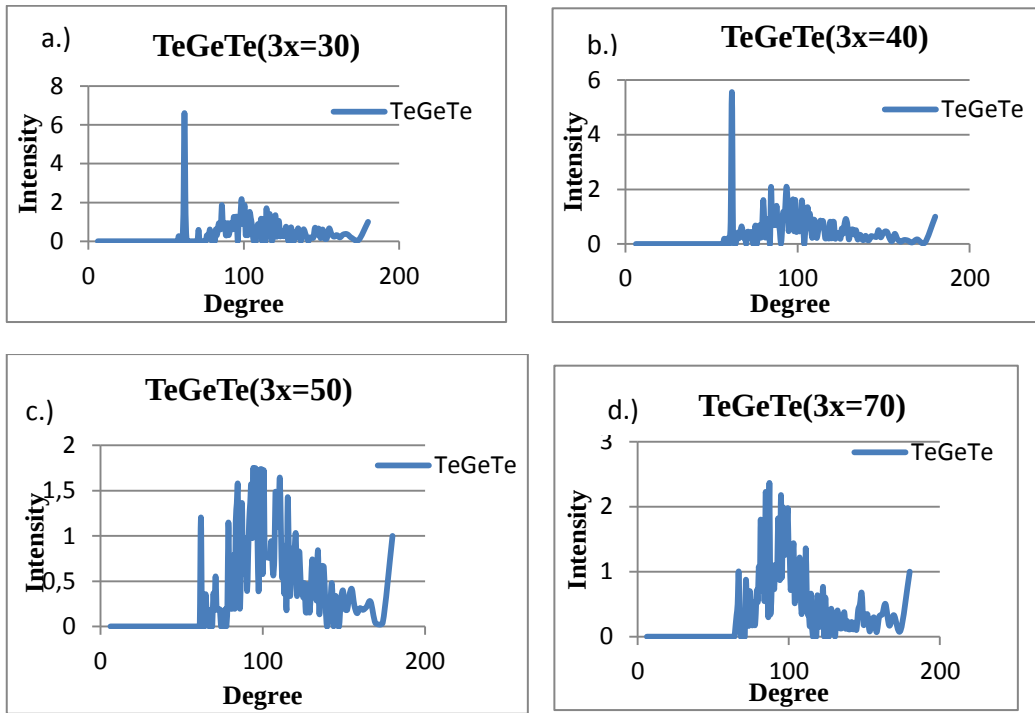


Figure 3.24. Te-Ge-Te bond angle distribution for (a) $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ glass ($3x=30$), (b) $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ glass ($3x=40$), (c) $\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ glass ($3x=50$), (d) $\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ glass ($3x=70$).

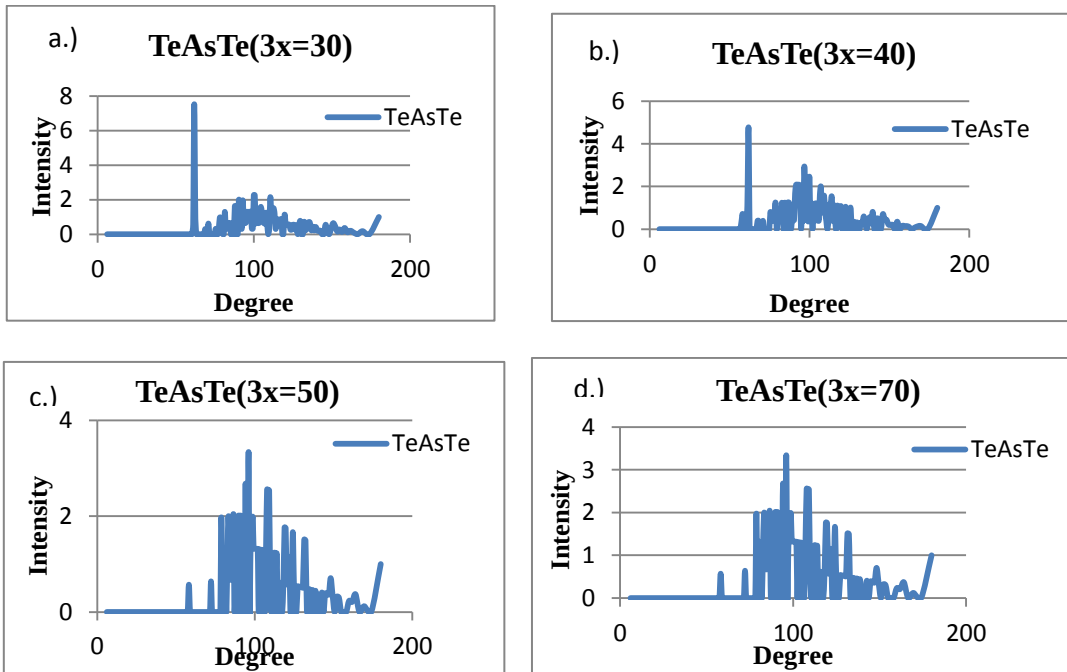


Figure 3.25. Te-As-Te bond angle distribution for (a) $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ glass ($3x=30$), (b) $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ glass ($3x=40$), (c) $\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ glass ($3x=50$), (d) $\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ glass ($3x=70$).

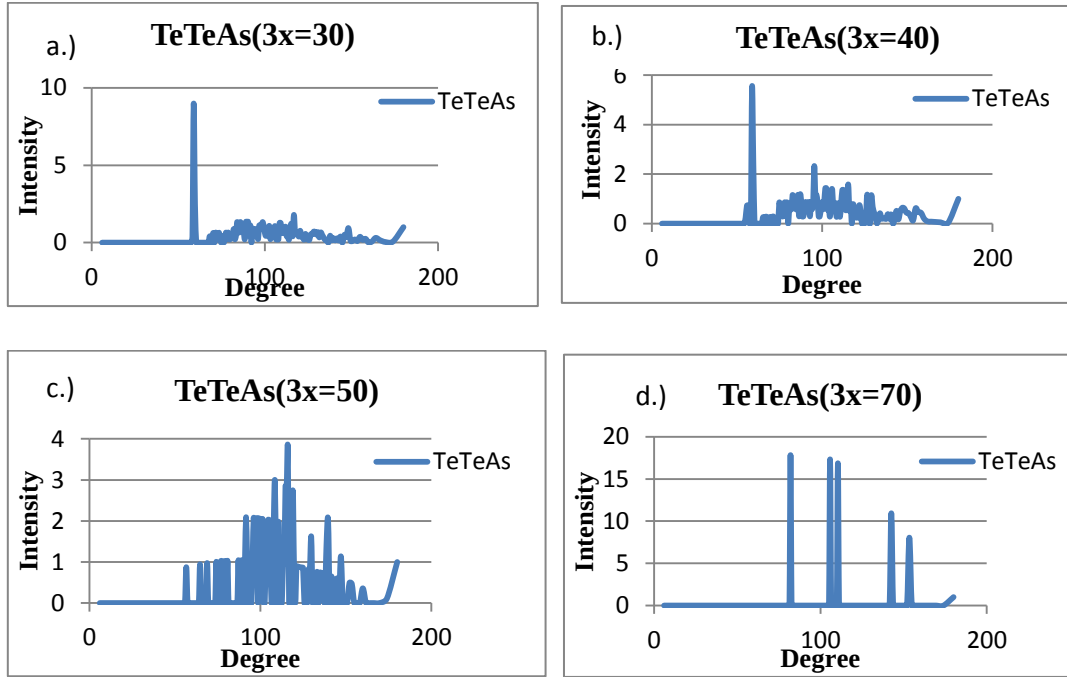


Figure 3.26. Te-Te-As bond angle distribution for (a) $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ glass ($3x=30$), (b) $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ glass ($3x=40$), (c) $\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ glass ($3x=50$), (d) $\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ glass ($3x=70$).

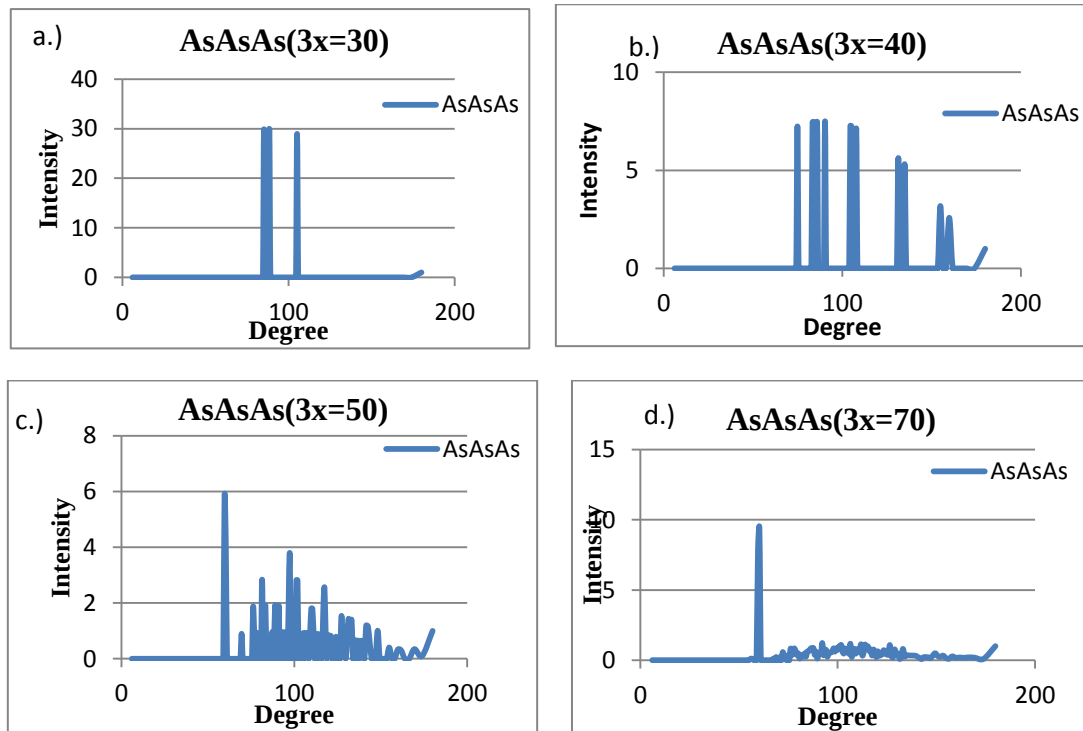


Figure 3.27. As-As-As bond angle distribution for (a) $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ glass ($3x=30$), (b) $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ glass ($3x=40$), (c) $\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ glass ($3x=50$), (d) $\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ glass ($3x=70$).

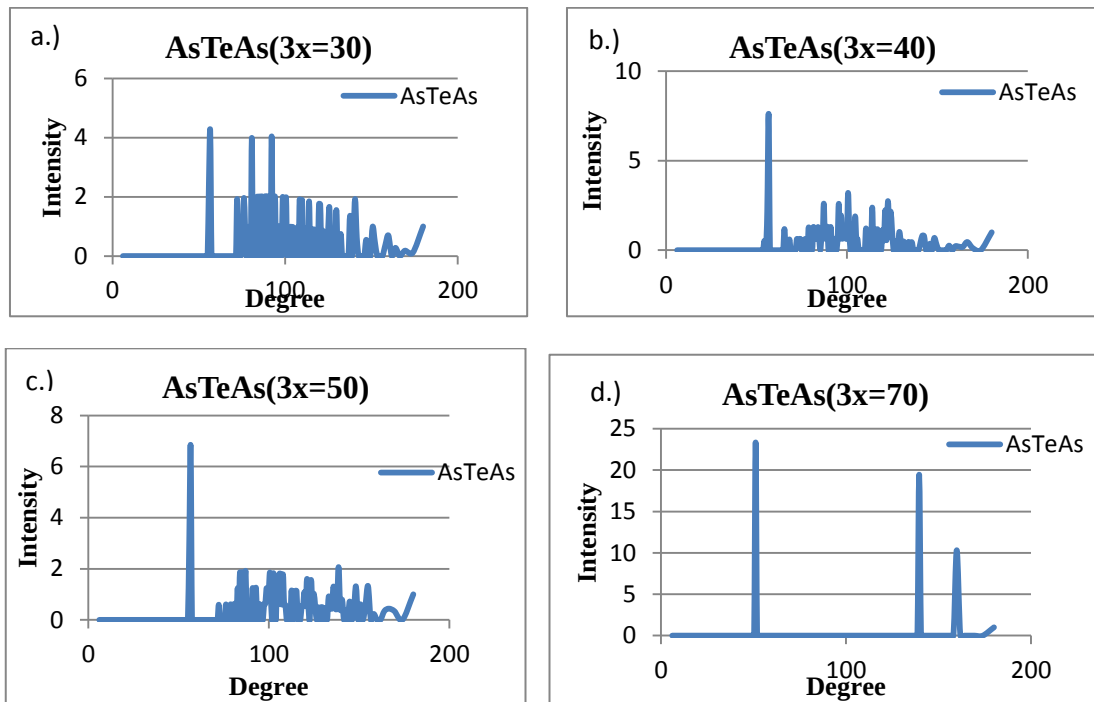


Figure 3.28. As-Te-As bond angle distribution for (a) $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ glass ($3x=30$), (b) $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ glass ($3x=40$), (c) $\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ glass ($3x=50$), (d) $\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ glass ($3x=70$).

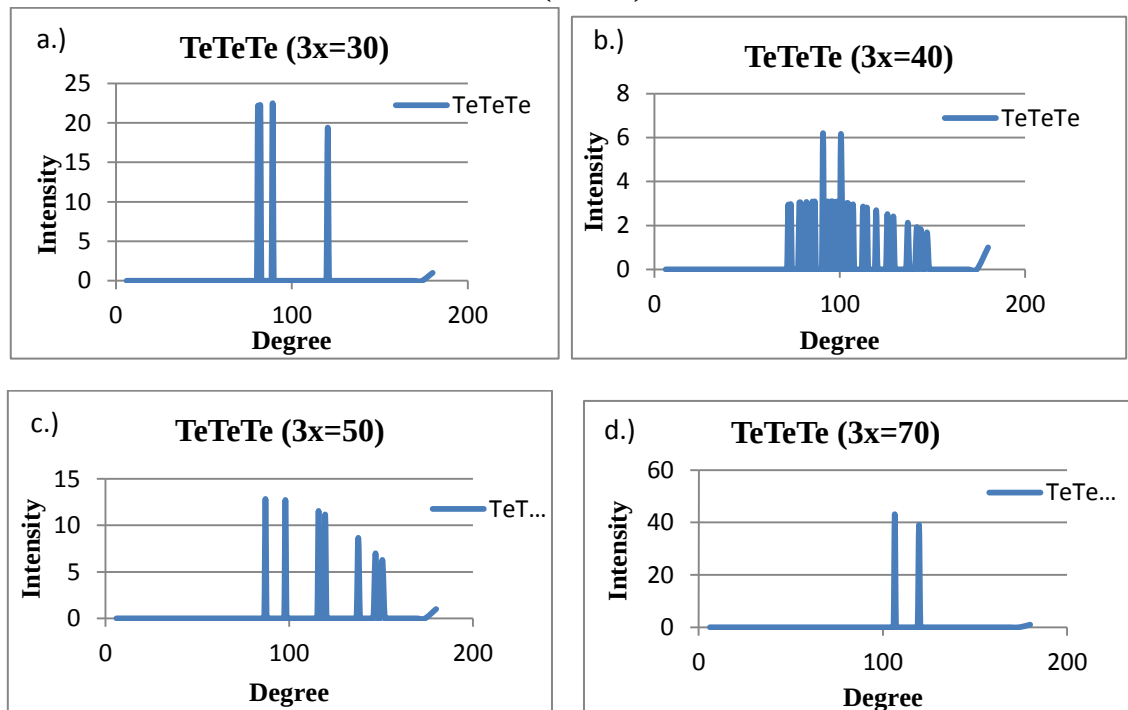


Figure 3.29. Te-Te-Te bond angle distribution for (a) $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ glass ($3x=30$), (b) $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ glass ($3x=40$), (c) $\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ glass ($3x=50$), (d) $\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ glass ($3x=70$).

Table 3.5. Bond angle values obtained from the RMC models of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses. The values marked with * correspond to bond angles with higher intensities in the bond angle distributions.

Bond Angle	DEGREES			
	$\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ (3x=30)	$\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ (3x=40)	$\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ (3x=50)	$\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ (3x=70)
GeGeGe	74.86*	78.78*	118.18*	77.49*
	86.50*	89.05*	143.66*	120.37*
	90.0*	135.78*		133.10*
	100.56*	95.41*		148.21*
	129.7*	98.62*		
	154.89	104.47*		
		120.36		
		111.85		
		159.86		
	Mean of Angles: 120.082	Mean of Angles: 107.74	Mean of Angles: 147.28	Mean of Angles: 119.80
GeTeGe	56.63*	56.6*	55.86*	55.86*
	79.43*	76.45*	84.58*	87.77*
	90.32*	78.1*	92.28	92.23*
	97.34*	83.95*	110.5	109.14 *
	111.17*	118.18*	79.4	96.05
	107.8	105.13	102.5	84.6
	125.68	90.31	98.62	98.6
	118.9	138.59	99.92	99.9
	133.1	67.45	105.13*	92.2
	143.67	99.27	109.14	110.49*
	147.02	102.57	69.5	128.07
	156.45	119.63		139.56
	159.87	148.21		156.44
	66.78	152.05		
	Mean of Angles: 113.11	Mean of Angles: 113.84	Mean of Angles: 111.42	Mean of Angles: 109.89

Table 3.5. Bond angle values obtained from the RMC models of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses. The values marked with * correspond to bond angles with higher intensities in the bond angle distributions (con't).

Bond Angle	DEGREES			
	$\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ (3x=30)	$\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ (3x=40)	$\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ (3x=50)	$\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ (3x=70)
TeGeTe	61.82*	61.82*	61.82*	81.37*
	98.62*	84.58*	78.78*	84.58*
	104.47	93.50*	84.58*	87.13
	110.48	80.08*	99.27*	97.78*
	94.78	107.12	100.56*	99.27*
	85.85	128.89	110.49*	103.17*
	122.6	87.77	115.33*	111.17*
			120.37	122.6
			133.98	148.21
			142.6	71.54
			70.86	66.78
	Mean of Angles:	Mean of Angles:	Mean of Angles:	Mean of Angles:
	113.34	108.87	110.75	110.53
TeAsTe	61.82*	61.82*	96.06*	98.62*
	100.56	96.69*	94.1*	
	110.48	99.91*	109.13*	
	92.86	93.50*	90.95*	
	81.37	107.15*	89.68*	
	107.79	113.92	119.63	
			132.24	
	Mean of Angles:	Mean of Angles:	Mean of Angles:	Mean of Angles:
	112.98	109.29	113.86	139.31

Table 3.5. Bond angle values obtained from the RMC models of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses. The values marked with * correspond to bond angles with higher intensities in the bond angle distributions (con't).

Bond Angle	DEGREES			
	$\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ (3x=30)	$\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ (3x=40)	$\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ (3x=50)	$\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ (3x=70)
AsTeAs	56.63*	56.6*	56.6*	51.11*
	80.73*	100.56*	87.13 *	139.56*
	92.22*	87.13 *	92.86	159.86*
	98.63*	95.4 *	107.8	
	113.3	96.7*	102.5	
	100.56	87.13	138.59	
	109.89	104.48	121.1	
	140.55	122.6	148.2	
	72.21	113.9	154.9	
	76.18			
	89.7			
	88.4			
	Mean of Angles: 111.95	Mean of Angles: 108.17	Mean of Angles: 114.36	Mean of Angles: 132.64
AsAsAs	88.41*	74.86*	59.63*	60.36*
	85.21*	85.86*	97.34*	92.22
	105.1*	83.94*	81.37	105.14
		90.32*	101.86*	128.07
		107.8*	117.5*	130.54
		105.14*	76.18	148.21
		131.38*	90.95	
		134.88*	110.5	
		154.89	69.51	
		159.87	127.26	
			148.21	
	Mean of Angles: 114.69	Mean of Angles: 115.13	Mean of Angles: 114.83	Mean of Angles: 111.14

Table 3.5. Bond angle values obtained from the RMC models of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses. The values marked with * correspond to bond angles with higher intensities in the bond angle distributions (con't).

Bond Angle	DEGREES			
	$\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ (3x=30)	$\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ (3x=40)	$\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ (3x=50)	$\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ (3x=70)
TeTeTe	80.72*	90.95*	87.13*	106.46*
	82.01*	100.56*	97.98*	119.63*
	89.04*	73.54	118.9*	
	120.4*	81.37	119.6*	
		85.21	137.6*	
		86.5	147.02*	
		98.6	150.7*	
		107.13		
		104.5		
		114.62		
		119.6		
		128.9		
		136.7		
		147.02		
	Mean of Angles: 110.43	Mean of Angles: 107.02	Mean of Angles: 129.52	Mean of Angles: 135.36
TeTeAs	58.89*	58.89*	115.32*	82.01*
	99.27	95.41 *	108.46*	105.8*
	89.94	115.32 *	139.56*	110.5*
	111.85	105.13	118.9*	142.6*
	138.6	128.9	91.6*	153.43*
	116.7	82.65	108.46*	
	148.2	74.86	107.8*	
		125.68	129.7*	
		145.87	80.7	
			68.8	
			56.6	
			64.7	
	Mean of Angles: 110.52	Mean of Angles: 108.98	Mean of Angles: 112.76	Mean of Angles: 129.06

Ge-Ge-Ge bond angle distributions of the studied compositions are presented in Figure 3.22. The values of 100.56° , 104.47° and 111.85° are in good agreement with those presented in a study that reported average Ge bond angles as 107.5° and 110.2° [49]. Mean Ge-Ge-Ge angle was obtained as 107.7° for chalcogenide glass system with $3x=40$ indicates tetrahedral coordination of Ge atoms in the system as it is close to the tetrahedral value (109.47°). However, mean Ge-Ge-Ge bond angle values in glass systems with other compositions ($3x=30, 50, 70$) displayed higher values.

Figure 3.23 presents Ge-Te-Ge bond angle distributions of the studied compositions. In a previous RMC study $\theta_{\text{Ge-Te-Ge}}$ for amorphous GeTe was reported to be around 50 and 90 degrees. As it is seen in Figure 3.23 and Table 3.5, all $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-x}$ chalcogenide glasses exhibit intense peaks around at 56.63° and 90.32° , which are in good accordance with the results from Chen et.al, where they reported that Ge-Te-Ge bond angle distribution in amorphous binary GeTe chalcogenide glass was found to be 90° and 50° [57]. Additionally, Ge-Te-Ge bond angles present at 97.34° , 99.00° and 98.6° were in a good agreement with the work of Fabian et.al. where $94 \pm 5^\circ$ was reported for $\text{Ge}_{20}\text{Sb}_{20}\text{S}_{50}\text{Te}_{10}$ and $\text{Ge}_{20}\text{Sb}_{20}\text{Se}_{50}\text{Te}_{10}$ chalcogenide glasses [42]. In addition, Ge-Te-Ge bond angle distributions display features at 107.8° , 109.14° , 110.49° and 111.17° , which are close the ideal value of 109.4° for tetrahedral structure. Similarly, Wang et al reported that Ge-Se-Ge bond angle was approximated to the ideal value of 109.4° in selenide chalcogenide glass system [35].

Te-Ge-Te bond angle distributions are shown in Figure 3.24. Bond angle distributions of Te-Ge-Te in our chalcogenide glasses present main peaks around at 61.82° , 81.37° , 84.58° , 93.50° and 110.49° . These values are in agreement with previous studies [42,43,47,57,58]. In their research, Fabian *et al.* found that Te-Ge-Te bond angle was $90(82) \pm 3^\circ$ for $\text{Ge}_{20}\text{Sb}_{20}\text{S}_{50}\text{Te}_{10}$ and $\text{Ge}_{20}\text{Sb}_{20}\text{Se}_{50}\text{Te}_{10}$ chalcogenide glasses [42]. In their study, Moharram reported that Te-Ge-Te bond angle distribution in $\text{Ge}_{20}\text{Se}_{80}$ glasses presented a main peak around 104.2° and small peak at 60° [43]. Moritomo *et al.* reported that Te-Ge-Te bond angle distributions of in amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ displayed a peak around 90° [57,58].

Figure 3.25 illustrates Te-As-Te bond angle distributions of the studied compositions. Te-As-Te in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-x}$ chalcogenide glass exhibits peaks around at 96.06° and 98.62° ,

which are in good accordance with previously reported values in Se-containing systems [45, 50]. In their study, Fabian *et al.* reported that Se-As-Se bond angle was $95\pm5^\circ$ in $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{40}\text{Se}_{50}\text{Te}_{10}$ chalcogenide glasses [45]. In another study, Fabian *et al.* reported Te-As-Se bond angles of $96\pm2^\circ$ and $60\pm2^\circ$ in $\text{As}_{40}\text{Se}_{45}\text{Te}_{15}$ and $\text{As}_{40}\text{Se}_{50}\text{Te}_{10}$ chalcogenide glasses [50].

As-Te-As bond angle distributions are presented in Figure 3.28. The values of 92.22° , 95.4° and 96.7° and 98.63° are in good agreement with those reported in the literature [45, 50]. In their study, Fabian *et al.* reported that As-Se-As bond angle was found to be $95\pm5^\circ$ in $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{40}\text{Se}_{50}\text{Te}_{10}$ chalcogenide glasses [45]. In another study, Fabian *et al.* reported As-Se-As bond angle as $97\pm2^\circ$ in $\text{As}_{40}\text{Se}_{45}\text{Te}_{15}$ and $\text{As}_{40}\text{Se}_{50}\text{Te}_{10}$ chalcogenide glasses [50].

As-As-As bond angle distributions are given in Figure 3.27. As-As-As bond angles are mainly at 101.86° , 105.1° and 107.8° , which are in good accordance with what is reported previously [49]. In this study, the average As bond angle value was found to be 107.3° and 113.3° in $\text{Ge}_{0.05}\text{As}_{0.20}\text{Te}_{0.75}$ and $\text{Ge}_{0.10}\text{As}_{0.20}\text{Te}_{0.70}$ chalcogenide systems, respectively [49].

Te-Te-Te bond angle distribution revealed peaks at 106.46° and 100.56° , indicating possible tetrahedral arrangements (109.5°), which is in good agreement with previous studies [43, 52]. In their study, Moharram reported that Se-Se-Se bond angle distribution displayed a main peak at 60° and small peak at 104.2° in $\text{Ge}_{20}\text{Te}_{80}$ [43]. Furthermore, Moharram also reported in another his study that Se-Se-Se bond angle was found to be 60° as a main peak and sub peak at 109° in $\text{Ge}_{20}\text{Se}_{80-x}\text{Te}_x$ chalcogenide glass system [52].

In a previous study, Fabian *et al.* reported Te-Se-As bond angles of $88\pm2^\circ$ and $92\pm2^\circ$ in $\text{As}_{40}\text{Se}_{50}\text{Te}_{10}$ and $\text{As}_{40}\text{Se}_{45}\text{Te}_{15}$ chalcogenide glasses, respectively. Te-Se-As bond angle of $60\pm2^\circ$ was present in both $\text{As}_{40}\text{Se}_{45}\text{Te}_{15}$ and $\text{As}_{40}\text{Se}_{50}\text{Te}_{10}$ glasses [50]. In the glass system studied in this thesis Te-Te-As bond angles were seen at 58.89° , 82.01° and 95.41° , which are comparable to the results of Fabian *et al.* [50].

3.5. Ring Size Distributions

Ring size distributions are important structural factors that play an important role in determining functionalities of chalcogenide glasses. Therefore, the ring size distributions for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass system with $3x=30, 40, 50$ and 70 have been obtained and analyzed by ISAACS (Interactive Structure Analysis of Amorphous and Crystalline Systems) program [63].

King's algorithm, in which the definition of a ring was considered as the shortest path to a given node from one of the neighbor atoms, is used in the ring analysis [64]. Radius of the first coordination sphere for each chemical species and first minimum of the total RDF were given as inputs to the software. $2.60, 2.80$ and $2.85 \text{ \AA}$ were taken as the radius of the first coordination sphere for Ge-Ge (Ge: Ge or As), Ge-Ge and Te-Te pairs, respectively, and the first minimum of the total RDF was given as 3.0 to the software for $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ glass ($3x=30$). For $\text{Ge}_{13.3}\text{As}_{26.7}\text{Te}_{60}$ glass ($3x=40$), $2.65, 2.75$ and $2.85 \text{ \AA}$ were taken as the radius of the first coordination sphere for Ge-Ge (Ge: Ge or As), Ge-Ge and Te-Te pairs, respectively, and the first minimum of the total RDF was given as 2.96 to the software. For $\text{Ge}_{16.7}\text{As}_{33.3}\text{Te}_{50}$ glass ($3x=50$); $2.65, 2.70$ and $2.80 \text{ \AA}$ were taken as the radius of the first coordination sphere for Ge-Ge (Ge: Ge or As), Ge-Ge and Te-Te pairs, respectively, and the first minimum of the total RDF was taken as 2.95 . The radius of the first coordination sphere for Ge-Ge (Ge: Ge or As), Ge-Ge and Te-Te pairs were taken as $2.65, 2.93$ and $2.93 \text{ \AA}$, respectively, and the first minimum of the total RDF was given as 2.95 to the software for $\text{Ge}_{23.3}\text{As}_{46.7}\text{Te}_{30}$ glass ($3x=70$).

Figures 3.30-3.33 present ring size distributions for glasses with $3x=30, 40, 50$ and 70 , respectively. Determination of ring sizes were obtained using 40 nodes as maximum search depth and partial $g(r)$ values. The results have been averaged over 10000 configurations. Moreover, the shortest path search was introduced using all nodes and homopolar bonds such as GeGe, AsAs or TeTe bonds.

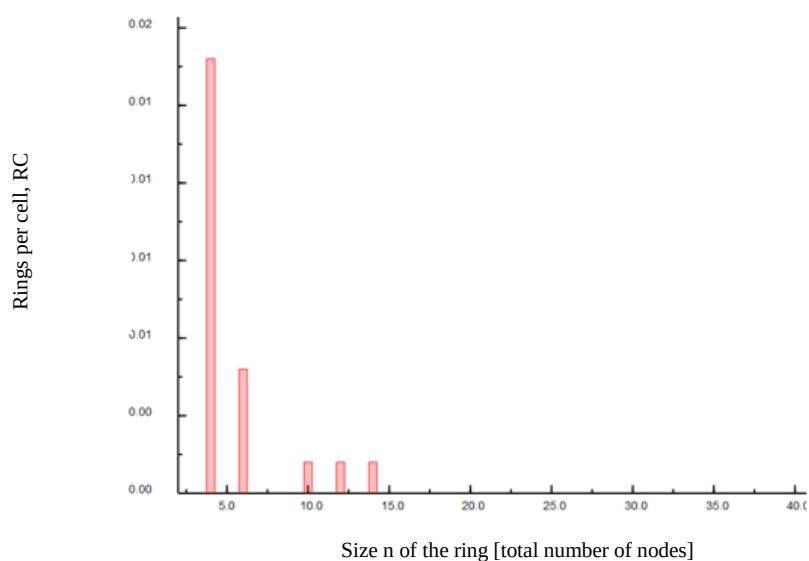


Figure 3.30. Ring size distribution for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass ($3x=30$). n represents the total number of nodes. For instance, $n=4$ corresponds a ring consisting of 2 Ge or As and 2 Te atoms.

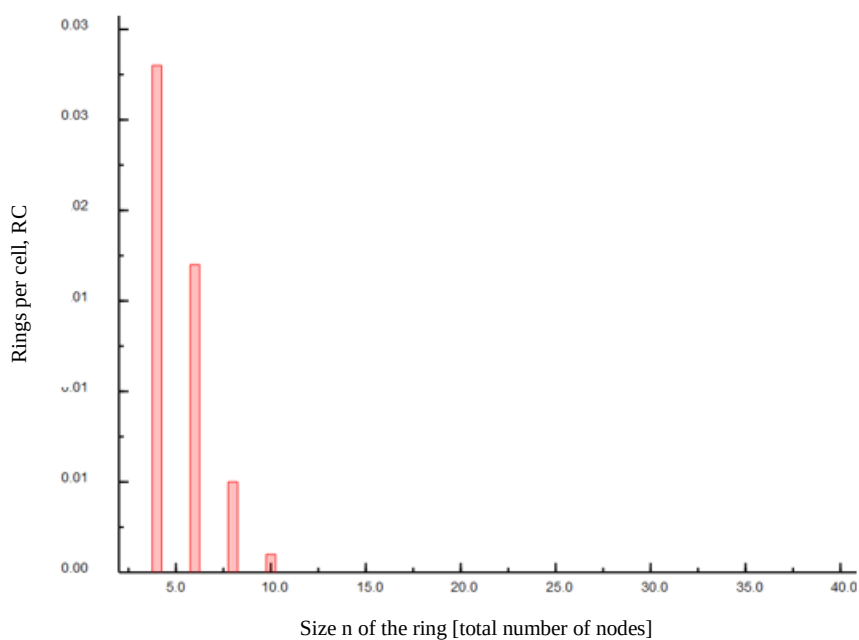


Figure 3.31. Ring size distribution for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass ($3x=40$). n represents the total number of nodes. For instance, $n=4$ corresponds a ring consisting of 2 Ge or As and 2 Te atoms.

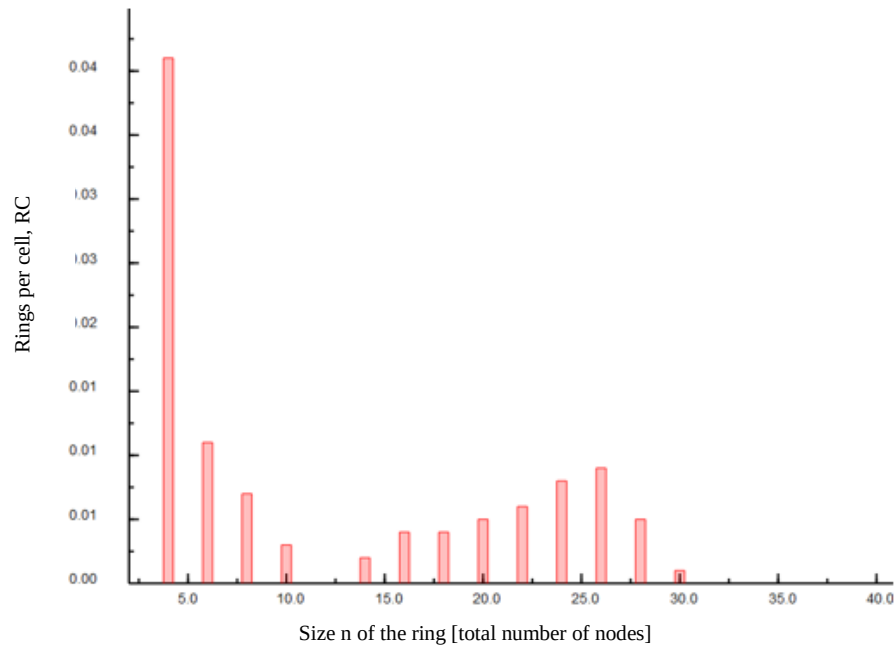


Figure 3.32. Ring size distribution for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass ($3x=50$). n represents the total number of nodes. For instance, $n=4$ corresponds a ring consisting of 2 Ge or As and 2 Te atoms.

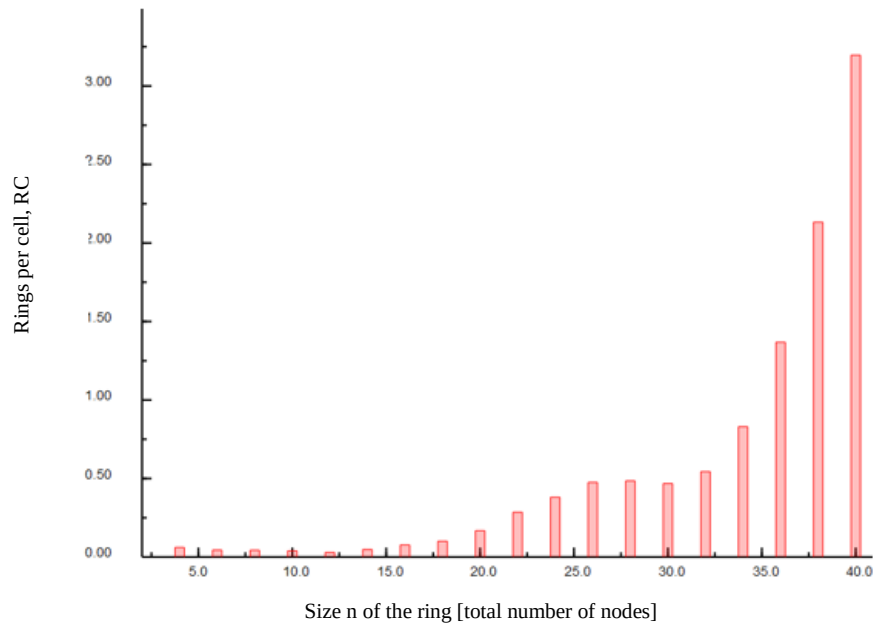


Figure 3.33. Ring size distribution for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass ($3x=70$). n represents the total number of nodes. For instance, $n=4$ corresponds a ring consisting of 2 Ge or As and 2 Te atoms.

It is clearly seen that ring size distributions are tighter in chalcogenide glasses with $3x=30, 40$, however, the distributions of ring sizes span a much wider range in chalcogenide glasses with $3x=50$ and 70 . $\text{Ge}_{10}\text{As}_{20}\text{Te}_{70}$ ($3x=30$) chalcogenide glass displayed mainly 4 and 6 membered rings with minor proportion of 10, 12 and 14 membered rings. Similarly, $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass ($3x=40$) involved 4-6 membered rings together with some part of 8-10 membered rings. On the other hand, although $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ ($3x=50$) glass had significant amount of 4-membered rings, the number of nodes in the distribution started to display a very broad scattering that ranges in intervals 4-10 and 14-30. It was observed that the ring size distribution in $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass with $3x=70$ dramatically changed such that the 4-membered rings became minority. For this composition, the ring sizes ranged between 4 and 40 where the majority of the distribution was in 32-40 range.

There are various studies in the literature that deal with the ring sizes present in the structure of chalcogenide glasses. In a study performed on $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$, $\text{GeTe-Sb}_2\text{Te}_3$ amorphous systems using density functional/molecular dynamics simulations, ring statistics analysis resulted in many four-membered rings with few triangular configurations in all cases [36]. The results presented here (Figure 3.30-3.32) are consistent with this finding such that the most prominent ring size for glasses with $3x=30, 40, 50$ is the 4 membered rings.

Kohara *et al.* investigated the three dimensional atomic configuration of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe system using by RMC simulations and it was reported that only even numbered rings occurred in amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and 4 and 6 membered rings occurred dominantly during phase transition from amorphous to crystalline. In amorphous GeTe system, both odd and even numbered rings arose due to the formation of GeGe bonds [57]. In the glass systems studied in this thesis, only even numbered rings are observed. As it can be seen in Figures 31 and 34, the coordination number regarding homopolar Ge-Ge bonds are in 0-0.8 range whereas heteropolar Ge-As bonds are in 1.30-3.50 range showing predominantly the presence of heteropolar bonds. This could be the reason of the absence of odd numbered rings in the chalcogenide glass system investigated here.

In another research performed by Yasuda *et. al* it was aimed to investigate three dimensional atomic structure of amorphous GeTe and amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ systems by Reverse Monte Carlo Modeling based on synchrotron-radiation high energy x-ray diffraction

data. It was found that ring structure of α -Ge₂Sb₂Te₅ was even numbered and α -GeTe was odd- and even-numbered both due to the existing Ge-Ge homopolar bonds. [57, 58]. Analysis of ring size distributions in this study reveals that all of the glasses studied in this thesis display even numbered rings. As pointed above, it is thought that the presence of only even numbered rings could have resulted from the presence of mainly heteropolar Ge-As bonds in the system.

Jund *et al.* studied the topological network of amorphous GeS₂ glass systems using ring statistics to determine the structural connectivity properties. In this study, it was aimed to obtain the network connectivity profiles using the ring statistics at a farther scale than the first or the second coordination shell. It was highlighted that the ring size of GeS₂ was mainly distributed between 4, 6 and 24-29 nodes [60]. As it is seen in Figures 3.30 and 3.31, the majority of the rings in GeAsTe glasses with 3x=30 and 40 includes 4 and 6 membered rings. Larger ring sizes were observed as the metal content (3x) increased and as Te content decreased in the system. For example, for GeAsTe (3x=50) the ring size distributions were mainly in 4-10 and 14-30 ranges. For the glass system with the highest metal content (3x=70), the ring sizes up to 40-membered nodes were observed. Therefore, it was found that ring size distributions spanned a wider range as the tellurium content decreased in the system.

In this section, it was shown that there are dramatic changes in ring size distributions in Ge_xAs_{2x}Te_{100-3x} systems as a function of composition. Ring size distributions change into more complex forms as the metal content increases in the system. Therefore, one might speculate that the transition between amorphous and crystalline phases in Ge₁₀As₂₀Te₇₀ can occur in a faster and simpler way compared to other three chalcogenide glasses. As it is seen in Table 3.1, the structures of chalcogenide glasses becomes more complex with increasing of T_g as metal content increases [18].

4. CONCLUSIONS AND RECOMMENDATIONS

In this study, RMC modeling technique was used to generate three dimensional representations of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses with $3x=30, 40, 50$ and 70 based on experimental high energy x-ray diffraction data. Based on these models, partial structure factors and partial pair distribution functions were obtained. The origin of the first sharp diffraction peak (FSDP) in this system was investigated analyzing partial structure factors. Characteristic structural parameters involving coordination numbers, bond angle and ring size distributions were obtained and evaluated for these glasses.

Coordination number analysis on the RMC models of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50$ and 70 indicated that the Ge, As and Te atoms obeyed the 8-N coordination rule in this system. It was seen that total coordination numbers of Ge, As, and Te atoms were approximately 4, 3 and 2 for all glasses.

The experimental and RMC-generated total structure factors were in good agreement with χ^2 values of 107.6, 61.86, 109.9, and 126.0 for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30, 40, 50$ and 70 , respectively. The FSDP was not observed in $S(Q)$ of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ with $3x=30$, while it was present in the $S(Q)$ patterns of $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ chalcogenide glasses with $3x=40, 50$ and 70 . It was seen that the FSDP intensity showed an increasing trend with increasing metal content in Ge-As-Te glasses. Based on partial structure factors it was found that metal-metal correlations such as Ge-Ge, As-As and Ge-As were the main contributors to the FSDP feature therefore to the intermediate-range order in this system.

Ring size statistics were also studied for the glasses in this system to further investigate the intermediate-range order. It was found that $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glasses with $3x=30$ and 40 consisted predominantly of 4- to 6-membered rings. Larger ring sizes were observed as the metal content ($3x$) increased and Te content decreased in the system. For example, for $\text{Ge}_x\text{As}_{2x}\text{Te}_{100-3x}$ glass with $3x=50$ the ring size distributions were mainly in the ranges of 4-10 and 14-30. For the glass system with the highest metal content ($3x=70$), the ring sizes up to 40-membered nodes were observed. Therefore, it was found that ring size distributions spanned a wider range as the tellurium content decreased in the system.

For future studies it could be interesting to perform small angle x-ray scattering (SAXS) experiments for these glasses to complement the findings of the current study. SAXS will be a valuable technique since it will give information regarding intermediate-range order extending to nanometer length-scales which could then be connected to the existence of larger rings suggested by this study. Additionally, the structures of technologically more competent chalcogenide glass systems such as Ge-Sb-Te glasses could be studied by RMC modeling.

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