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Free-volume defects investigation of GeS_2-Ga_2S_3-CsI chalcogenide glasses by positron annihilation spectroscopy

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HIGHLIGHTS

- The free-volume defect of novel GeS_2-Ga_2S_3-CsI glasses is investigated.
- The defects of the glasses were obviously reduced with increment of CsI.
- The atomic density ρ is inversely proportional to the number of these defects.

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ABSTRACT

The transformation behavior of free-volume defect in $(80GeS_2\text{-}20Ga_2S_3)_{100-x}$ $(CsI)_x$ (x = 0, 5, 10, 15 mol%) chalcogenide glasses was studied by employing positron annihilation spectroscopic technique, which could reveal valuable information for in-depth understanding of nano-structural defects in glassy matrix. The results indicate that the structural changes caused by CsI additives can be adequately described by positron trapping modes determined with two-state model. The initial addition of CsI (x = 5 mol%) led to a void contraction, whereas, the void agglomeration occurred with the increase of CsI and the free-volume defects of the glasses were obviously reduced. The atomic density ρ is inversely proportional to the number of these defects. Meanwhile, the UV cut-off edge shifts toward short-wavelength with increasing of CsI. This study provides the valuable information of defects evolution in GeS_2-Ga_2S_3-CsI glasses.

1. Introduction

The sulfide-based chalcogenide glasses (ChGs) such as GeS_2-Ga_2S_3 glasses possess exceptional transparency and high nonlinearity, which have been widely used in multispectral imaging lenses, chemical and biological sensors, optical circuits, and planar waveguides [1–3]. However, disordered covalent-bonded networks proper to ChGs possess notable amount of free-volume defects formed due to the conventional melt-quenching technique [4]. The formation of free-volume defects influences the nonlinearity and optical stability of ChGs, which limiting the application in photonics further [5]. Therefore, the investigation on a free-volume defects transformation in ChGs will be necessary to improve the performance of these materials. Numerous experimental techniques are employed to the investigation of the structure of these glasses, such as scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), etc. Nevertheless, these experimental methods are limited to study the structure of atomic-deficient, especially in nanometer and sub-nanometer scale. Positron annihilation lifetime (PAL) spectroscopy is known as an informative tool for the investigation of free-volume defects in solids, which is grounded on physical phenomenon of electron interaction with its antiparticle (positron) in a matter [6,7]. In chalcogenide glasses, this method is used to identify intrinsic free volumes in the frame of the model that considers competitive channels-positron trapping in extended free-volume defects and positron electron (positronium) decaying in holes [6,8].

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Addition of alkali halides such as CsCl to GeS_2-Ga_2S_3 ternary system not only extends the transparency in the visible region but also influences the voids in the inner structure of the modified glassy matrix at the nanoscale [9]. In recent years, the free-volume defects of the GeS_2-Ga_2S_3-CsCl glasses have been studied intensively [10], and it has been proved that the addition of CsCl could reduce the void defects. In view of the I and Cl located at the same group in chemical element periodic table, it maybe exhibits a similar physical and chemical properties. The transformation behavior of defects in CsI doped GeS_2-Ga_2S_3 glasses was investigated. In this paper, the GeS_2-Ga_2S_3-CsI glasses were performed and the effect of CsI on structural defects in GeS_2-Ga_2S_3 glasses tested by positron annihilation technique has been investigated. The optical properties of the samples were also analyzed with X-ray diffraction, Raman scattering spectra and transmission spectral measurements. The study aims to provide the valuable information of the defects evolution with the CsI concentration in these glass samples.

2. Experimental

$(80GeS_2\text{-}20Ga_2S_3)_{100\text{-}x}$ $(CsI)_x$ (x = 0, 5, 10, 15 mol%) glasses were prepared from Ge, Ga, S and CsI materials in silica ampoule kept under the vacuum of 10^{-3} Pa. Materials were melted at 980 °C in a rocking furnace for 12 h. After that, the bulk samples were obtained by quenching in cold water. Finally, the GeS_2-Ga_2S_3-CsI glasses were annealed at 10 °C below glass transition temperature T_g to minimize inner strains. The obtain rods were cut into disks of ~1 mm and 2 mm in thickness and polished to a high optical quality.

The samples are examined by X-ray diffraction (XRD) apparatus with a power diffractometer (German Bruker D2) using Cu k_α radiation (30 kV 20 mA) to confirm the amorphous states. Densities were measured according to Archimedes' principle with Density Determination Kit (ME-DNY-4, METTLER TOLEDO, Zürich, Switzerland) and the accuracy was ±0.001 g/cm^3. The absorption spectra of samples were recorded in the range of 400–700 nm using Perkin–Elmer Lambda 950 UV–vis–NIR spectrophotometer. Raman spectroscopy was conducted at room temperature using the back (180°) scattering configuration by the Renishaw inVia Raman spectra with a LD laser with a wavelength of 785 nm. The resolution of the frequencies was ±1 cm^{-1}. The PALS measurements were performed using a conventional fast–fast coincidence system with an ORTEC spectrometer of 230 ps resolution (FWHM of single Gaussian, determined by measuring ^{60}Co isotope) at the temperature T = 24 °C and relative humidity RH = 37%. In each measurement, the ^{22}Na radioactive source was placed between two identical polished samples like a typical sandwich geometry, used as a source of positrons. The contribution from a source was taken at a level of 8.9%. Each PAL spectrum was recorded in a high-measurement statistics of ~2×10^6 coincidences to ensure a precise lifetime measurement. The channel width of 6.37 ps allows the total number of channels up to 8000. The raw PAL spectra of the investigated glasses were processed with LT 9.0 program.

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of the $(80GeS_2\text{-}20Ga_2S_3)_{100\text{-}x}(CsI)_x$ glass samples, where x = 0 (G0), 5 (G5), 10 (G10), 15 (G15), respectively. These glasses are yellow and nearly transparent in the visible region. In order to confirm the amorphous state of each sample, XRD analysis was conducted. According to Fig. 1, the amorphous state of the glasses was confirmed. The diffraction intensity has only some fluctuations with the instrumental background line when 2θ of the scanning range increases. It manifests that there are no sharp peaks and crystalline phases appeared, implying the typical amorphous nature [11], which is necessary for avoiding the crystalline state to bring errors to the positron annihilation test later.

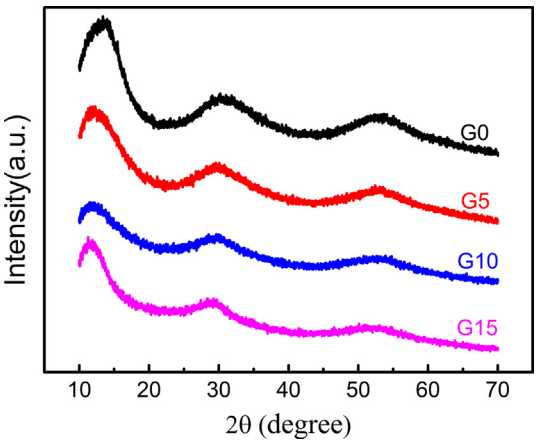

Fig. 1. XRD patterns of the $(80GeS_2\text{-}20Ga_2S_3)_{100\text{-}x}$ $(CsI)_x$ (x = 0, 5, 10, 15 mol%) glass samples.

Fig. 2 presents the vis-NIR absorption spectra of $(80GeS_2\text{-}20Ga_2S_3)_{100\text{-}x}$ CsI_x (x = 0, 5, 10, 15 mol%) glasses. The short-wavelength cut-off edge of the glasses with light yellow color locates at ~450 nm. It is obvious that the short-wavelength cut-off edge shifts toward a shorter wavelength with the increase of CsI content, which is determined by the electrical transition between valence bands and conduction bands [12]. The reason is that Cs^+ and I^- atoms are of less polarizability compared with Ge^{2+}, Ga^{3+} and S^{2+} [13] and the average electron affinity energy of I^- is bigger than that of S^{2-} [14]. Therefore, the required excitation energy of electronic transition is greater, resulting in the short-wavelength cut-off edge shorter [15].

To elucidate the structural evolution, Raman spectra were recorded and collected as shown in Fig. 3. Two main regions in these spectra are distinguishable: (a) there is a decreasing trend of dominate band at 340 cm^{-1} along with shoulder around 370 and 430 cm^{-1}, respectively, (b) with increasing of CsI content, the broad bands between 200 and 300 cm^{-1} have an inverse change in intensity. According to the previous studies of Raman spectra in GeS_2-Ga_2S_3 based glasses, the most intense band at 340 cm^{-1} is attributed to the overlap of (ν_1) symmetric stretching modes of [Ge(Ga)S_4] tetrahedral [16], while the shoulder at 370 cm^{-1} corresponds to the edge-sharing [Ge(Ga)S_4] units [17].

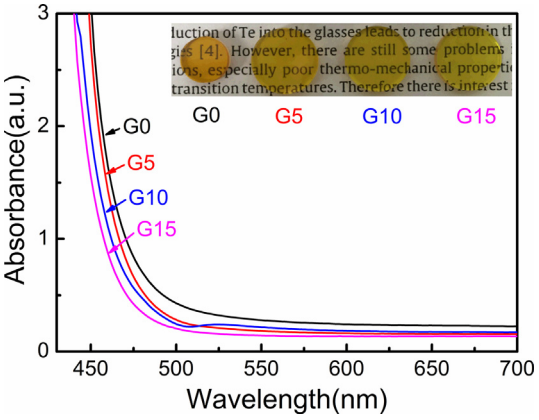

Fig. 2. The vis-NIR absorption spectra of $(80GeS_2\text{-}20Ga_2S_3)_{100\text{-}x}$ CsI_x (x = 0, 5, 10, 15 mol%) glass samples. The inset shows the picture of these glasses.

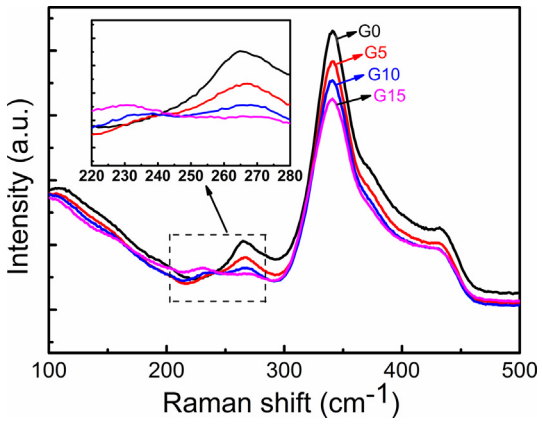

Fig. 3. Raman spectra of $(80GeS_2\text{-}20Ga_2S_3)_{100\text{-}x}$ $(CsI)_x$ (x = 0, 5, 10, 15 mol%) glass samples. The inset is an amplification ranging from 220 to 280 cm^{-1}.

There is still a controversial problem now about the ascription of the band at 430 cm^{-1}. The intensity decreases from 340 to 370 cm^{-1} with the increasing CsI. It is due to the formation of [Ge(Ga)S_3I] units. In the inset of Fig. 3, the variation of these Raman bands attracts more attention. This change can be split into two bands that are located near 240 and 270 cm^{-1}, respectively. It is well known that the band at 240 cm^{-1} is associated with the asymmetrical stretching vibration (ν_2) of Ge-I in the [S_2GeI_2] structural units [18]. And the band at 270 cm^{-1} is chiefly assigned to the [S_3Ge(Ga)-(Ga)GeS_3] ethane-like units [19]. With the addition of CsI, I atoms can substitute some S atoms in [GeS_4] tetrahedral, which leads to an increase in 240 cm^{-1} Raman band due to the formation of [S_2GeI_2]. Meanwhile, the linkage of [S_3Ge(Ga)-(Ga)GeS_3] ethane-like unit have been broken with lack of sulfur, leading to the formation of the mixed-anion [$I_xS_{3\text{-}x}$Ge(Ga)-(Ga)$GeS_{3\text{-}x}I_x$] unit. This will result in the decreasing feature of Raman band at 270 cm^{-1}. Consequently, it is obvious that the connectivity of the glassy network is decreased with the break of Ge-S or Ga-S bonds in the GeS_2-Ga_2S_3-CsI glasses. And the reduction of T_g also indicates that the glass network is loose with the addition of CsI [20]. The most possible explanation is that the free volume defects agglomeration with the increase of CsI results in the loosing network of glasses.

The typical PAL spectra of $80GeS_2$-$20Ga_2S_3$ glasses are depicted in Fig. 4, which reconstructed from two-component fitting at general background of standard source contribution. It can be also decomposed into three combined positron-positronium components, but could not improve decomposition goodness significantly, the estimated input from this positronium component in the PAL spectra being less than 1% [21]. As a typical PAL spectrum of positron annihilation event histograms, this figure was characterized by narrow peaks and regions of long fluent decaying of coincidence counts in a time. According to Fig. 4, the contribution of standard sources is about 8.9%, which could be achieved satisfactorily within the permissible range of error. Thus, the decaying behavior of such curve can be represented by sum of two exponents with the power inversely proportional to positron lifetimes τ_1 and τ_2 while the area under each of these exponential curves being proportional to the intensities I_1 and I_2 [22,23].

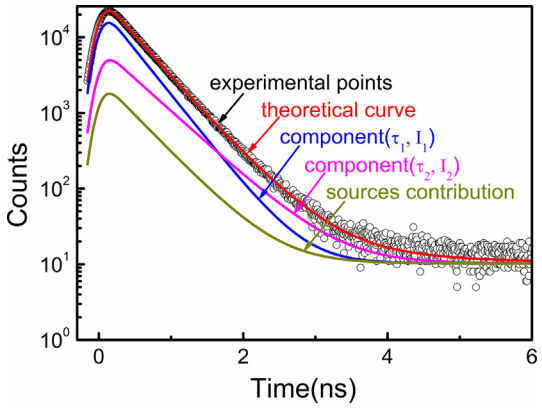

Fig. 4. Typical PAL spectrum for $80GeS_2$-$20Ga_2S_3$ glass decomposed into two components.

Fitting parameters for PAL spectra of $(80GeS_2\text{-}20Ga_2S_3)_{100\text{-}x}(CsI)_x$ (x = 0, 5, 10, 15 mol%) glasses are given in Table 1, which is calculated with two-component fitting procedure. In H. Klym's works [24,25], it has been confirmed that the first component (τ_1, I_1) is of no physical meaning for chalcogenide glasses. The intensity I_2 is proportional to the number of these voids, and the lifetime τ_2 shows the size of free voids where positrons are trapped [24–26]. Now, we will focus on analyzing the parameters of τ_2 and I_2 which are regarded as the main nanostructural free-volume void transformation in GeS_2-Ga_2S_3-CsI chalcogenide glasses with different amounts of CsI in the glass matrix. With the changes of CsI amount, the intensity I_2 decreases and the lifetime τ_2 decreases first and then increases compared to $80GeS_2$-$20Ga_2S_3$ glass. The addition of CsI results in voids contraction and agglomeration in glasses formation process as shown in Fig. 5.

The parameters of τ_2 and I_2 for G5 are less than those of G0, indicating the voids contraction. In other words, the free-volume voids have shrinked accompanying with the reduction of defects in the number. With increasing of CsI content, the lifetime τ_2 of G10 increases slightly and the intensity I_2 decreases, which means that the free-volume voids are expanded a little and some defects are vanished. In the case of G15, an obvious transformation is observed. The lifetime τ_2 increases from 0.500 ns for G10 glass to 0.510 ns for G15 glass and the intensity I_2 decreases from 0.263 (a.u.) to 0.230 (a.u.). Such behavior corresponds to voids agglomeration, when the addition of CsI content is mainly responsible for the number of free-volume defects.

In order to investigate positron trapping rate and defects concentration, a quantitative analysis of positron trapping modes was taken by a so-called two-state positron trapping model [27–29]:

$$\tau_{av} = (\tau_1 I_1 + \tau_2 I_2)/(I_1 + I_2) \quad (1)$$

$$\tau_b = (I_1 + I_2)/(I_1\tau_1^{-1} + I_2\tau_2^{-1}) \quad (2)$$

$$\kappa_d = I_2/I_1(\tau_b^{-1} - \tau_d^{-1}) \quad (3)$$

where τ_{av} is the average positron lifetime while τ_b is the positron annihilation lifetime in bulk (defect-free region). τ_d is equal to τ_2 which is the positron annihilation lifetime in defects, and κ_d is the total positron trapping rate at the defects. In addition, the difference ($\tau_d - \tau_b$) demonstrates the size of expanded free-volume defects where positrons are trapped, and the ratio τ_d/τ_b was taken in a direct correlation to the nature of these defects [30].

The other positron trapping parameters are listed in Table 2, in order to comprehend the free-volume transformation more deeply. The average positron lifetime τ_{av} and defect-free lifetime τ_b almost have any changes with addition of CsI. The positron trapping rate κ_d in voids reduces mainly due to the drop of the intensity I_2. It is confirmed that the number of free-volume defects have reduced when the positron trapping rate in defects κ_d decreases with further CsI. From the previous Raman spectra, a plausible hypothesis is that the break of Ge-S or Ga-S bonds are associated with void

Table 1
Fitting parameters for PAL spectra of $(80GeS_2\text{-}20Ga_2S_3)_{100-x}(CsI)_x$ (x = 0, 5, 10, 15 mol %) glasses.

Sample	τ_1 (ns)	I_1 (a.u.)	τ_2 (ns)	I_2 (a.u.)
G0	0.364	0.715	0.505	0.284
G5	0.365	0.728	0.499	0.272
G10	0.363	0.737	0.500	0.263
G15	0.365	0.770	0.510	0.230

transformations in glassy matrix [31]. Although the degree of glass network connectivity decreases, the samples possess a better optical property. Also, the contraction and agglomeration of free-volume voids in the inner structure of materials are described by other PAL parameters. The difference $(\tau_2 - \tau_b)$ decreases from 0.109 ns to 0.104 ns, indicating that the free-volume voids have contracted due to unfavorable environment. However, with the further CsI, the $\tau_2 - \tau_b$ increase from 0.104 ns to 0.119 ns, it is shown that the free volume void will expand by voids agglomeration.

Furthermore, the relationship between the positron trapping rate κ_d and density ρ have been studied as shown in Fig. 6. The positron trapping rate κ_d in defects decreases from 0.217 ns^{-1} to 0.178 ns^{-1}, while the density ρ increases with increasing of CsI content. There is an abnormal tendency in κ_d-ρ correlation, and the free volume of positron trapping voids is mainly responsible for atomic density of the glasses [32]. In other words, it is possible

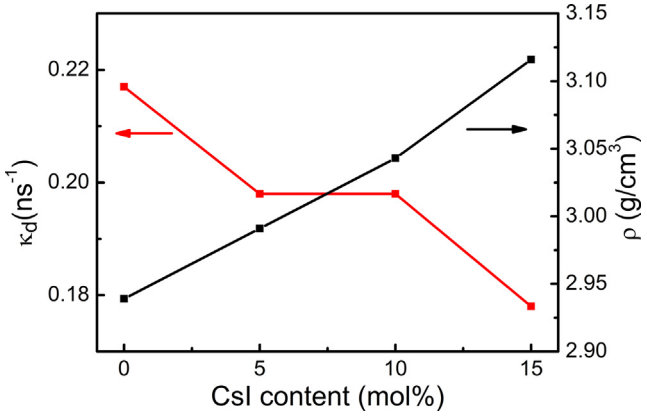

Fig. 6. The relationship between positron trapping rate κ_d and density ρ within different CsI content.

that the Cs^+ occupied the position of defects, which can reduce the number of defects, meanwhile the atomic density of unit volume increased. This process is accompanied with void contraction and agglomeration.

The study also provides a chance to compare the void transformation between GeS_2-Ga_2S_3-CsI and GeS_2-Ga_2S_3-CsCl glassy matrices. According to the data from Table 1, Table 2 and Ref. [33], two major points can be concluded: (a) The changes of intensity I_2 and

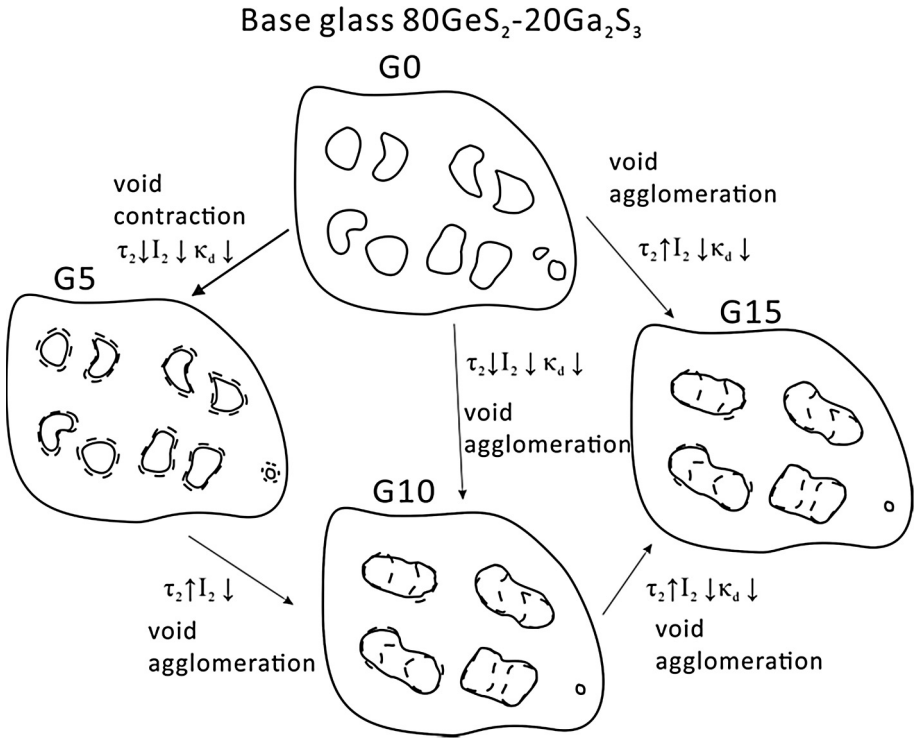

Fig. 5. Schematic assumption of nanoscale free-volume void evolution in GeS_2-Ga_2S_3-CsI chalcogenide glasses caused by CsI additions.

Table 2
Positron trapping modes for PAL spectra of $(80GeS_2\text{-}20Ga_2S_3)_{100-x}(CsI)_x$ (x = 0, 5, 10, 15 mol%) glasses.

Sample	τ_{av} (ns)	τ_b (ns)	κ_d (ns^{-1})	τ_2-τ_b (ns)	τ_2/τ_b
G0	0.404	0.396	0.217	0.109	1.27
G5	0.402	0.394	0.198	0.104	1.26
G10	0.399	0.399	0.198	0.108	1.27
G15	0.398	0.398	0.178	0.119	1.30

positron trapping rate κ_d in GeS_2-Ga_2S_3-CsI glasses have the same tendency with those in GeS_2-Ga_2S_3-CsCl glasses, indicating that the addition of halide can reduce the number of free-volume defects in GeS_2-Ga_2S_3 glassy matrix. (b) The changes of lifetime τ_2 in both glass samples are different. In H. Klym's works [33], the lifetime τ_2 increases from 0.426 to 0.499 ns with the increase of CsCl concentration. This means that the size of the free-volume defects become larger by voids agglomeration in GeS_2-Ga_2S_3-CsCl glasses. In the case of $(80GeS_2\text{-}20Ga_2S_3)_{85}$ $(CsCl)_{15}$ glass, the defects contract because of higher concentration of CsCl. In comparison, as for GeS_2-Ga_2S_3-CsI glasses, the lifetime τ_2 decreases from 0.505 ns to 0.499 ns with the increase of CsI content. The possible reason is that the initial CsI will bring the compactness of glass structure which results in a void contraction. With increasing of CsI content, the free-volume defects are expanded by voids agglomeration.

4. Conclusion

In this study, a series of GeS_2-Ga_2S_3-CsI chalcogenide glasses were prepared by the conventional melt-quenching technique. The defects transformation behavior was systemically studied by positron annihilation measurement. For the glasses of $(80GeS_2\text{-}20Ga_2S_3)_{100\text{-}x}$ $(CsI)_x$ (x = 0, 5, 10, 15 mol%), the number of free-volume defects will be reduced with increasing of CsI content. The defects contraction was observed when CsI concentration is 5 mol%. With the further addition of CsI, the size of the defects become larger due to voids agglomeration. The atomic density ρ is inversely proportional to the number of these defects. The possible reason is that the Cs^+ occupy the position of defects, resulting in the less number of defects and higher density of samples. The defects evolution with the CsI amount in these glass samples provides the valuable information of inner structure, which is useful for improving the quality of GeS_2-Ga_2S_3 glasses or doping the rare earth ions.

Acknowledgments

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