

Compositional dependence of the open volume of GeS_x glasses studied by positron annihilation spectroscopy

BING WANG, HAIZHENG TAO^{a*}, CHANGGUI LIN^a, ZHU WANG^{*}, JIANMIN ZENG^b, HUI LI, XIUJIAN ZHAO^a

Hubei Nuclear Solid Physics Key Laboratory, Department of physics, Wuhan university, Wuhan 430072, China

^aKey Laboratory of Silicate Materials Science and Engineering, Wuhan university of Technology, Wuhan 430070, China

^bGuangxi key laboratory for the advance materials and new preparation technology, Guangxi 541004, China

Positron annihilation lifetime and Doppler broadening measurements of $\text{GeS}_{1.8}$, GeS_2 and GeS_4 glasses have been carried out. A pronounced decrease of the long-lived lifetime (τ_2) and mean lifetime (τ_m) was observed with the gradually increased S content. Combined with the medium-range structural order constructed previously, the correlation among microstructure, open-volume size and positron lifetime was well elucidated according to the well established two-state positron trapping model. The longer bond-length of Ge-Ge bonds, compared with the one of Ge-S bonds, is responsible for the formation of larger open volume in the $\text{GeS}_{1.8}$ glass which has a longer τ_2 and τ_m than the GeS_2 glass; the shortest τ_2 and τ_m of GeS_4 is ascribed to the existence of a second species S_8 rings which uniformly disperse among the glassy network composed of $[\text{GeS}_4]$ tetrahedra and reduce effectively the size of open volume.

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1. Introduction

Defects in topologically disordered chalcogenide glasses greatly influence their electrical and optical properties [1,2], e.g. photo-induced phenomenon, thermal-electric poled second harmonic generation. An adequate understanding of the open volume in these glasses is very important to explore the correlation between their structure and electric-optical properties. Despite a variety of techniques, such as Neutron (or X-ray) diffraction [3], Raman scattering [4] and nuclear magnetic resonance (NMR) [5], have allowed to elucidate the residual medium-range structural order of non-crystalline material, there is still a lack of techniques that are especially sensitive to the nano-sized open volume of materials. An exception is the positron annihilation technique (PAT) [6].

Due to Coulomb repulsion from the atomic cores, positron is known to be trapped easily in the open-volume like vacancies and voids where a longer positron lifetime is characteristics. An open volume with the average diameter size between 0.1 and 10 nm could be revealed by this method, so it is often used to study the single vacancy, double-vacancy, vacancy clusters and micro-voids. To the best of our knowledge, PAT is an occasionally used method for the micro-structural characterization in topologically disordered chalcogenide glasses. However, PAT belongs to a method equally suitable for different solid-state substances despite their structural hierarchy.

Utilizing the PAT, we have analyzed the nano-sized open volume of GeS_x glasses. Starting from the

medium-range order framework of GeS_x glass constructed on the basis of the conventional measurements [7,8], compositional evolution of the open volume is interpreted by the well established two-state positron trapping model.

2. Experiment

All the investigated GeS_x ($x=1.8, 2, 4$) samples were prepared using a traditional melt-quenching method. Details of the preparations were similar to the procedure used in our previous paper [9]. The identical glass discs with ~ 1.2 mm thick were prepared from the bulk glasses and polished to get a mirror surface on both sides.

A conventional fast-fast coincidence spectrometer was used for positron annihilation lifetime (PAL) measurement in this experiment [6]. The time resolution of the system was found to be a sum of two Gaussian with $(\text{fwhm})_1=300$ ps(90%), and $(\text{fwhm})_2=275$ ps(10%). A 20 μCi ^{22}Na positron source was sandwiched between two pieces of identical sample. After being wrapped, the sandwiched samples were placed between two BaF_2 scintillation detectors. 1.5×10^6 total counts for each spectrum were collected at room temperature.

The obtained spectra were decomposed by PATFIT program. Details of the decomposition process are described as follows: single crystal silicon was chosen as the criterion sample to find the standard source correction [10]. Through decomposing the PAL spectra of silicon by PATFIT program, we obtain one component lifetime of ~ 226 ps, 100% which is close to that of the reported

literature [11]. The source correction of 388 ps, 6.48%, 190ps, 5.16% and 1690 ps, 0.36% were set as criterion parameters for PATFIT program when decomposing the PAL spectra of GeS_x. While applying one-component, two-component, and three-component positron lifetime models, only two-component positron lifetime decomposition worth further consideration via the judgment of the variance of fit which ranges from 1.0~1.2 [12]. Therefore, the average positron lifetime (τ_m) was calculated using these decomposed τ_1 , τ_2 , I_1 and I_2 values:

$$\tau_m = I_1\tau_1 + I_2\tau_2 \quad (1)$$

In order to further check the validity of above PAL results, Doppler broadening spectra were collected by high purity Ge detector. The S and W parameter was used to analyze Doppler line shape, which is defined as the ratio of the central and wing regions of 511 keV peak to the total area, respectively. It could detect the vacancy-type defect of material. The total count was 5×10^6 in Doppler broadening spectrum measurement.

3. Results

According to the two-state model, two-component fitting parameters of GeS_x glasses based on the PATFIT program together with the S parameter are listed in Table 1. With increasingly enhanced sulfur content, the positron trapping lifetime τ_2 and average positron lifetime τ_m shorten gradually. Also, the S-parameter obtained from Doppler broadening measurements showed the same tendency of compositional variation, further verifying the validity of PALS results.

Table 1. The numerical parameters of as-prepared GeS_x glasses obtained from positron lifetime and Doppler broadening measurements. τ_1 : normally associated with the so-called reduced positron bulk lifetime, τ_2 : the positron lifetime localized at defects; τ_m : the average positron lifetime; I_2 : the concentration of vacancies.

Sample	τ_1 (ps)	τ_2 (ps)	I_2	τ_m (ps)	S
GeS _{1.8}	226±9	455±3	0.78±0.02	404.6±0.2	0.5254±0.0004
GeS ₂	221±9	431±3	0.76±0.02	380.6±0.2	0.5211±0.0004
GeS ₄	245±10	426±3	0.71±0.03	373.5±0.2	0.5199±0.0004

4. Discussion

It is well known that a positron is trapped easily in open volume like vacancies and voids due to the Coulomb repulsion from the atomic cores. Although no discrete microvoids (such as vacancies in crystals) in chalcogenide

glasses, the open volume of size from 0.5-1 to 10 nm³ can be effective traps by positrons with a characteristic lifetime of 0.20-0.40 ns. According to the two-state model, the shorter one τ_1 is normally associated with the so-called reduced positron bulk lifetime, and the longer lifetimes τ_2 is identical to τ_d , i.e. positron lifetime trapping by the open-volume structures. Open volume with larger size will have longer lifetime of trapped positrons because of the lower electron density. Consequently, with the addition of sulfur in GeS_x glasses, the reduction of size of these open-volume defects can be deduced.

In addition, according to the correlation between the number of vacancies and lifetime [13], the lifetime τ_2 increases with the number of vacancies per cluster. In large voids ($R > 1$ nm, 100-1000 atoms), the positron lifetime has a value around 500 ps independent of the void size [14,15]. Based on the facts shown in Table 1 that the τ_2 value of all samples is around 450 ps, we can deduce that there exists three-dimensional open volume with a size on the order of nanometer scale. So the results can be explained according to the open volume with a size similar to vacancy cluster. In other words, the studied glasses have a compact three-dimensional disordered micro-structure.

Despite their lack of long-range translational and orientational order, covalent amorphous solids, e.g. chalcogenide glasses, can exhibit structural order over both short and medium length scales, the latter reaching 2 nm or so [16]. The medium-range structural order in chalcogenide glasses has been well demonstrated through neutron diffraction, Raman scattering and IR spectroscopy, etc. In the following, based on the framework constructed by the refs [3,7,8], the evolution of the open volume formed because of the bond angle deformation and mis-coordination of the covalent bonds can be interpreted properly in terms of the compositional variation of the microstructure of GeS_x glasses.

According to Ref. [3,7,8], the three-dimension framework of GeS₂ glass is comprised of corner- and edge- shared [GeS₄] tetrahedral units connected through bridging sulfur. Due to the shortage of sulfur, in the GeS_{1.8} glasses, there are some [S₃Ge-GeS₃] ethane-like units besides [GeS₄] tetrahedral units. When it comes to the GeS₄ glass, S₈ rings exist due to the excess sulfur in the glassy network composed of [GeS₄] tetrahedral units.

As mentioned above, besides Ge-S bonds, Ge-Ge bonds exist simultaneously among the GeS_{1.8} glasses. According to the Refs [17,18], the bond length of Ge-Ge (~0.245 nm) is greater than that of Ge-S (~0.22 nm). Despite the bond length of Ge-Ge or Ge-S bonds is quite different in glasses compared with that in crystals, the tendency of $L_{\text{Ge-Ge}} > L_{\text{Ge-S}}$ is still acceptable. Based on this fact that larger Ge-Ge interatomic distance in the [S₃Ge-GeS₃] ethane-like units occur, in the GeS_{1.8} glass compared with that of Ge-S bonds in GeS₂ glass, it can be deduced that the open volume formed by the broken Ge-Ge bonds in GeS_{1.8} glass has a larger size than that formed by the broken Ge-S bonds in GeS₂ glass. Therefore, the lifetime of positron trapped by this larger size open

volume is also longer, which is in good agreement with our experimental results.

With respect to GeS_4 glasses, its shortest τ_2 and τ_m can be well interpreted according to the existence of a second species (S_8) rings among the glassy network. The existence of S_8 rings means that the GeS_4 glass could be viewed as a homogeneously mixed solution of two kinds of molecular glasses which are composed of micro-structural units S_8 rings and $[\text{GeS}_4]$ tetrahedra. Certainly, the existence of a second species should not be confused with a phase separation. Phase separation in a system implies inhomogeneity on an observable scale and is therefore differentiable from a homogeneous system. Furthermore, because the two different molecules can fill in their interstices reciprocally, it is well-known that the volume of a solution of two different molecular species is considerably smaller than the simple sum of two pure solutions. Therefore, GeS_4 glass has a shortest τ_2 and τ_m compared to those of $\text{GeS}_{1.8}$ and GeS_2 glasses.

The distribution of electron momentum can be obtained through the Doppler shift of γ -ray produced by positron annihilation. If positrons are trapped at open-volume sites, the probability of annihilation with core electrons is reduced, therefore the larger S-parameter than the bulk value indicates the existence of open-volume sites [19]. In the GeS_x glasses, the Doppler S-parameters listed in Table 1 also show the same tendency of variance as the values of τ_2 and τ_m . The larger S-parameter implies that there exists more open volume or larger size of open volume. So the validity of the evolution of τ_2 and τ_m has been verified again through the Doppler broadening measurement.

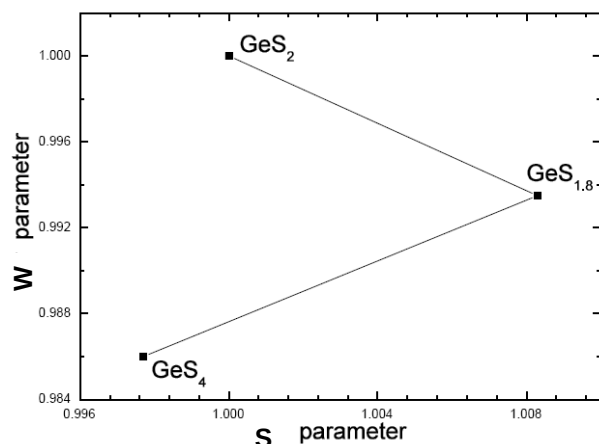


Fig. 1. S-W plot obtained from the Doppler broadening measurements in GeS_x glasses.

A detailed analysis of the correlation of S and W parameters obtained from the Doppler broadening measurements gives us more complementary inform about the defect evolution that occurs with the increased x in GeS_x glasses. The S and W parameters of GeS_2 were

normalized to one unit in Fig. 1. Therefore, $S > 1$ or $W < 1$ means that there exists a larger open volume or higher concentration of open volume. There are two different lines on S-W data, which reflect the different dependence of W parameter on S parameter, indicating that different types of defect exists in the three samples. This further certifies the rationality of the above interpretation about the evolution of τ_2 and τ_m .

5. Conclusion

A detailed micro-structural understanding of the GeS_x chalcogenide glasses greatly contributes to elucidate the correlation between the structure and electric-optical properties. In this paper, the positron annihilation lifetime and Doppler-broadening measurements of the $\text{GeS}_{1.8}$, GeS_2 and GeS_4 glasses were performed to explore the nano-sized open volume within these glassy networks. It reveals that open volume of larger size is formed in the topological framework of $\text{GeS}_{1.8}$ glass due to the longer bond-length of Ge-Ge metal bond compared to that of GeS_2 glass; and for the GeS_4 glass, the open-volume size is correspondingly less compared to that of GeS_2 glasses, due to the “frozen” mixture of S_8 rings and $[\text{GeS}_4]$ tetrahedral structural units, which compose the glassy network.

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References

- [1] N. A. Davydovaa, V. V. Tishchenko, J. Baran, M. Vlček, J. Mol. Struct. **450**, 117(1998).
- [2] S. X. Gu, Z. J. Ma, H.Z. Tao, C. G. Lin, H. P. Hu, X. J. Zhao, Y. Q. Gong, J. Phys. Chem. Solids **69**, 97(2008).
- [3] S. Jayakumar, P. Predeep, C. H. Unnithan, Phys. Stat. Sol. B **241**, 2457(2004).
- [4] H. Z. Tao, C. G. Lin, Y. Q. Gong, S. Mao, X. J. Zhao, Optoelectronics and Advanced Materials – Rapid Communications **2**, 29(2008).
- [5] B. Bureau, X. H. Zhang, F. Smektala, J. L. Adam, J. Troles, H. L. Ma, C. Boussard-Ple' del, J. Lucas, P. Lucas, D.L. Coq, M. R. Riley, J. H. Simmons, J. Non-Cryst. Solids **345&346**, 276(2004).
- [6] W. Gong, Y. Y. Mai, Y. F. Zhou, N. Qi, B. Wang, D.Y. Yan, Macromolecules **38**, 9644(2005).
- [7] G. Lucovsky, F. L. Galeener, R. C. Keezer, R. H. Geils, H. A. Six, Phys. Rev. **B 10**, 5134(1974).

- [8] H. Takebe, H. Maeda, K. Morinaga, *J. Non-Cryst. Solids* **291**, 14(2001).
- [9] H. Z. Tao, C. G. Lin, S. X. Gu, C. B. Jing, X. J. Zhao, *Appl. Phys. Lett.* **91**, 011904-1(2007).
- [10] B. Somieski, T. T. M. Staab, *Nucl. Instrum. Meth. A* **381**, 128 (1996).
- [11] M. J. Puska, *J. Phys.-Condens. Mat.* **3**, 3455 (1991).
- [12] R. Krause-Rehberg, H. S. Leipner, *Positron Annihilation in Semiconductors*, Springer-Verlag, Berlin-Heidelberg-New York, 1999
- [13] P. Hautojarvi, C. Corbel, in: A. Dupasquier, A. P. Mills, *Positron Spectroscopy of Solid State*, IOS Press, Amsterdam, 1995, p. 491.
- [14] M. J. Puska, C. Corbel, *Phys. Rev. B* **38**, 9874 (1998).
- [15] M. Saito, A. Oshiyama, *Phys. Rev. B* **53**, 7810 (1996).
- [16] S. R. Elliott, *Nature*, **354**, 445(1991).
- [17] I. Yonenaga, M. Sakurai, *Phys. Rev. B* **64**, 113206 (2001).
- [18] J. H. Lee, A. P. Owens, A. Pradel, A. C. Hannon, M. Ribes, S. R. Elliott, *Phys. Rev. B* **54**, 3895(1996).
- [19] Z. Q. Chen, Z. Wang, S. J. Wang, *Nucl. Instrum. Meth. B* **160**, 139 (2000).

*Corresponding author: wangz@whu.edu.cn
taohaizheng@hotmail.com