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RELAXATION BEHAVIOR OF As_2S_3 GLASS CAUSED BY MECHANOCHEMICAL PROCESSING

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Two types of As_2S_3 chalcogenide glasses, the bulks made by melt-quenching and the powders made by mechanochemical processing were prepared, the relaxation behavior was studied by means of differential scanning calorimeter (DSC). It is found that there exist structural relaxation in the bulk glass by melt-quenching and the stress relaxation in the powders glass by mechanochemical processing, respectively. Meanwhile, the fragility *m* is determined by modified AM equation indicating that As_2S_3 glass is rather strong glass. By Raman spectra, the microstructure changes of both the bulk and powders were analyzed. It is found that the strong relaxation behavior occurs in As_2S_3 glass powder due to the structural changes and the increasing of the defects and dislocations during mechanochemical processing.

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1. Introduction

The formation and relaxation mechanism of glass is one of the greatest challenging unsolved problems in the fields of condensed matter physics and materials science [1-5]. The study of relaxation is one of the key scientific researches, some physical and thermodynamic properties may change in a specified range with temperature. Meanwhile, one can obtain plenty of useful information from the changes, which is beneficial to modify the structure or optimize the composition.

Although considerable studies on the relaxation phenomenon have been made in the past decades years, many theories and models were built, the true nature is still under debate. The relaxation behavior is not only found in the high-Tg oxide glasses and some other glasses [6], but also recorded in low-Tg glass such as chalcogenide glasses [7-9]. Nevertheless, most studies of the relaxation, such as structural relaxation, were conducted by ultra-quenching or annealing processing. The relaxation caused by mechanochemical processing is seldom reported. It is well known that mechanochemical processing is a powder processing technique, which involving the deformation, fracturing and cold welding of the particles during repeated collisions with a ball during high-energy milling [10]. Under cyclic high energy ball milling, the bonds are broken and rebuilt and the mechanochemical processing makes the powder particles into a non-equilibrium

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state which should have a relaxation behavior [11].

The main focus of this paper was to illustrate the stress relaxation behavior caused by mechanochemical processing. Differential scanning calorimeter (DSC) was used to measure the heat capacity and the thermal block of the samples made by melt-quenching and mechanochemical processing, respectively. Through the investigation of Raman spectra, the microstructural changes were also analyzed.

2. Experimental

High purity As (Aladdin, 99.99%) and S (Aladdin, 99.99%) powders were used as starting materials for sample preparation. For details, see the previous work in our lab [12-18]. The raw materials in appropriate atomic percentage were weighed and put into quartz tubes which were sealed under a vacuum of 10^{-3} Torr. The sealed tube was melted at 973K to 1073K for 12h in a rocking furnace and then annealed at 473K for 2h after being quenched into ice cooled water. The mechanical milling treatment was carried out for the bulk glass by means of a high energy planetary ball milling apparatus (Fritsch Pulverisette 7). The glass was milled at 600rpm for 6h.

The heat capacity of both the bulks and powders was measured by using differential scanning calorimeter (DSC) (PerkinElmer Pyris1 and Netzsch STA 449F1). The temperature precision of this equipment is ±0.1K in the measured values. Glasses subjected to the first downscan cooled at 10 K/min are called the "standard glasses". The second upscan *C*p curve of the standard glass is termed as the "standard curve". In order to determine the *C*p curve of the samples, both baseline and sapphire (as reference material) were measured.

Raman spectra experiments were performed using a continuous YAG:Nd laser with a wavelength of 1064nm, a typical power of 0.1W, and spectral resolution of 4 cm^{-1} were used for recording spectra in the range 100–800cm^{-1}. The spectra were collected with an Intelligent Fourier infrared spectrometer (Therno Nicolet, Nexus).

3. Result and discussion

The fragility *m* is an index to evaluate the ability of glass-forming which is defined as the slope of the log η versus T_g/T curve at T_g [19]:

$$m = \left.\frac{\mathrm{d}\lg\eta}{\mathrm{d}\left(T_g/T\right)}\right|_{T=T_g} \tag{1}$$

Recent studies have shown the correlation between the cooling rate and the viscosity of glasses [20, 21], so the calculation of fragility *m* can be simplified as the modified AM equation:

$$m = \left.\frac{\mathrm{d}\lg(1/q_c)}{\mathrm{d}\left(T_g/T\right)}\right|_{T=T_g} \tag{2}$$

Where η is the shear viscosity of the glass. q_c is the cooling rate during differential scanning calorimeter (DSC) measurement and T_g is the glass transition temperature which is equal to the shear viscosity of the glass at 10^{12} Pa s [22].

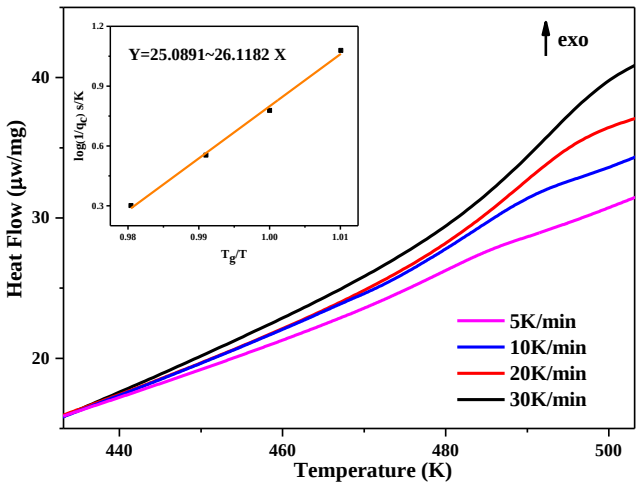

Fig.1. DSC curves of the bulk As_2S_3 glasses at different selected heating rates. The inset: the plot by fitting Eq. (2) where the slope represent the "fragility m".

Fig.1 is the DSC curves of the bulk glass. As shown in Fig.1, in order to determine the fragility *m*, the bulk As_2S_3 glass was heating and cooling at 5k/min, 10k/min, 20k/min and 30k/min respectively. The glass transition temperatures (T_g) of the four curves above are determined at 465K, 470K, 474K, 479K, respectively with different heat rates. By fitting Eq. (2) to the experimental lg ($1/q_c$) ~T_g/T data as shown in Fig.1 inset, *m* is found to be 25~26. Although there is no standards to determine the strong or fragile characters of glasses based on *m* value, a value of m<20 typically implies a strong glasses and m>20 implies a fragile glass [23]. Therefore, the As_2S_3 glass can be considered as a rather strong glass.

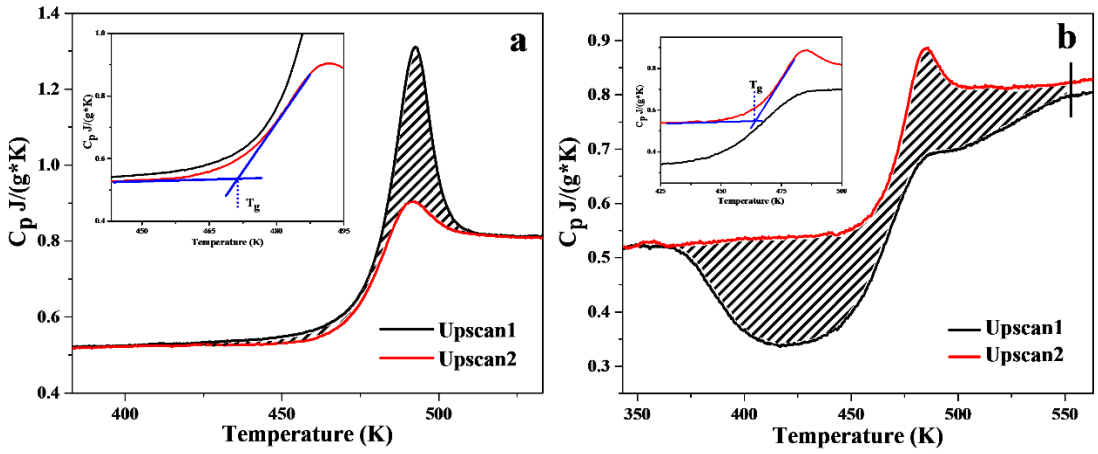

Fig.2. The heat capacity (C_p) curves of As_2S_3 glass samples, (a): the bulks and (b): the powders. In both the two figures, upscan1 and upscan2 represent the heat capacity (C_p) curves obtained from the first and second upscan of the DSC measurement, respectively. And the second upscan C_p curve is termed as standard curve. The heating and cooling rates used in the DSC measurements are 10K/min. The inset of both a and b: T_g determined by the second upscan C_p curve (standard curve).

Fig.2 (a) shows the heat capacity obtained from the first and second upscans and the second upscan is termed as the standard curve. The upscan1 curve in Fig.2 (a) reflects thermal history of the bulk As_2S_3 glass where a strong endothermic peak is shown in upscan1 curve, indicating the structural relaxation which is due to the annealing process. The bulk glass is suppressed in an elastic low-energy state in the annealing process. Thus, the glass will rebound to the high-energy state soon with a strong endothermic process (the endothermic area of the shadow is 6.1177 J/g) during heating.

The curves shown in Fig.2 (b) are quite different because the sample formed by mechanochemical processing. In Fig.2 (b), a broad exothermic peak is observed from the first upscan curve, reflecting the release of the excess enthalpy of the powder prepared by mechanochemical processing. This phenomenon can be supposed that plenty of defects and dislocations are formed during milling. Meanwhile, with the decrease of the particles size and the change of the structure by grinding, great energy is stored. The area (22.597 J/g) between upscan1 and upscan2 curves corresponds to the trapped excess enthalpy relative to that being stored in powders during milling.

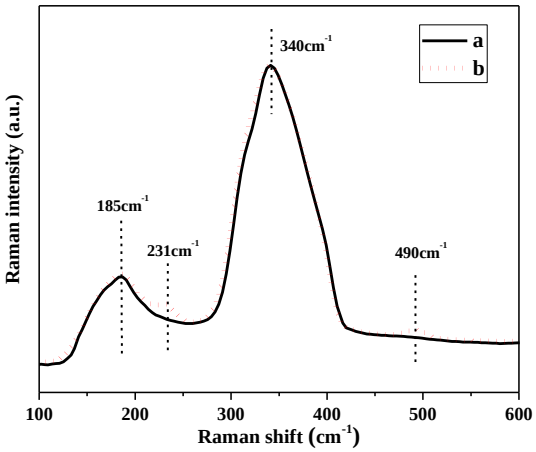

Fig.3. Raman spectra of As_2S_3 glass, curve a is for the bulk glass and curve b is for the powders obtained by normalization the range from 100cm^{-1} to 600cm^{-1}, respectively.

To explain the relaxation behavior of the powders in Fig. (2) b, Raman spectra experiments are performed. From the Raman spectra in Fig.3, the stretching vibrational mode related to As_2S_3 glass can be observed at four main positions near 185cm^{-1}, 231cm^{-1}, 340cm^{-1} and 490cm^{-1}. According to the previous research on Raman spectra of As_2S_3 glass [24, 25], the strong peak at 340cm^{-1} and the weak peak at 312cm^{-1} are attributed to the stretching vibration and interaction of AsS_3 pyramid, and the peak at 185cm^{-1} is considered as the cage structure of As_4S_4 unit [26]. The difference is the appearance of the weak peaks near 231cm^{-1} and 490cm^{-1} which is attributed to the presence of As_4S_4 fragments [27] and S-S bonds [28] due to the collision by mechanochemical processing. This phenomenon can be explained that dozens of surface dangling bonds are formed with the breaking of particle chemical bonds caused by mechanical collision during milling. Then, the dangling bonds combine with each other to form new bonds or structure. Meanwhile, energy is stored in this processing which is in accord with the thermal analysis results in Fig.2 (b). Thus, the mechanochemical processing do cause a strong relaxation due to the structural changes and the increasing of defects and dislocations during milling.

4. Conclusions

In summary, the fragility *m* of As_2S_3 glass is determined by modified AM equation. The *m* value of As_2S_3 glass is found to be 25~26 which indicates that As_2S_3 glass can be considered as a rather strong glass. The structural relaxation of the bulk glass due to annealing is demonstrated. The glass powders made by mechanochemical method behave a typical strong relaxation, too excess energy stored in the glass powders due to milling is determined from two rounds of DSC upscan. The appearance of As_4S_4 fragments and S-S bonds show the structural changes during milling, which causes the relaxation behavior of the powders.

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References

[1] P G Debenedetti, F H. Stillinger, Nature **41**, 259 (2001).
[2] H Z Tao, X J Zhao, Q M Liu, J. Non-Cryst. Solids **377**, 146 (2013).
[3] X Han, H Tao, L Gong, XY Wang, X J Zhao, YZ. Yue J. Non-Cryst. Solids **391**, 117 (2014).
[4] H Z Tao, C G Lin, S X Gu, C B Jing, XJ Zhao, Appl. Phys. Lett **91**, 904 (2007).
[5] H P Chen, H Z Tao, Q D Wu, X J Zhao, J. Am. Ceram. Soc **96**, 801 (2013).
[6] Y Z Yue, S L Jensen, Chemical Physics Letters **357**, 20 (2002).
[7] H Z Tao, Z Y Yang, P. Lucas Opt. Exp **17**, 18165 (2009).
[8] P Lucas, A Doraiswamy, E A. King, J. Non-Cryst. Solids **332**, 35 (2003).
[9] A. Kozdras, Journal of Non-Crystalline Solids **409**, 83 (2015).
[10] M L Trudeau, R Schulz, D Dussault, et al. Physical review letters **64**, 99 (1990).
[11] K Meyer, W. Meier, Crystal Research and Technology **3**, 399 (1968).
[12] SX Gu, D X Pi, H Z Tao, Q Zeng, X J Zhao, H T Guo, H Y Chen, J. Non-Cryst. Solids **383**, 205 (2014).
[19] H Z Tao, X J Zhao, W Tong, S Mao, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **64**, 1039 (2006).
[14] H Z Tao, S Mao, G P Dong, H Y Xiao, X J Zhao, Solid State Comm **137**, 408 (2006).
[15] H Z Tao, X J Zhao, C B Jing, H Yang, S Mao, Solid State Comm **133**, 327 (2005).
[16] G P Dong, H Z Tao, X D Xiao, CG Lin, Y Q Gong, X J Zhao, S S Chu, S F Wang, Q H Gong, Opt. Exp **15**, 2399 (2007).
[17] R K Pan, H Z Tao, J Z Wang, H F Chu, T J Zhang, D F Wang, X J Zhao, OPTIK **124**, 4943 **(**2013).
[18] H Z Tao, X J Zhao, C B Jing, J. Molecular Structure **697**, 23 (2004).

[19] C A. Angell, Science **267**, 1924 (1995).
[20] Y Z Yue, R von der Ohe, S L. Jensen, The Journal of Chemical Physics **120**, 8053 (2004).
[21] M M Smedskjaer, J C Mauro, S Sen, et al. Chemistry of Materials **22**, 5358,(2010).
[22] Y Z. Yue, J. Non-Cryst. Solids **355**, 737(2009).
[23] I. Avramov, J. Non-Cryst. Solids **357**, 391 (2011).
[24] X Han, H Tao, L Gong, J Han, S Gu, Chalcogenide Letters, **11**, 181 (2014).
[25] T. Wagner, S. O. Kasap, Journal of Materials Science **33**, 5581 (1998).
[26] S Mamedov, A Kisliuk, D. Quitmann, Journal of Materials Science **33**, 41 (1998).
[27] N V Surovtsev, A M Pugachev, B G. Nenashev, Journal of Physics: Condensed Matter **15**, 7651 (2003).
[28] C G Lin, H Z Tao, Z Wang, B Wang, X L Zheng, H C Zang, X J. Zhao, J. Non-Cryst. Solids **355**, 438(2009).