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Sub-T_g enthalpy relaxation in milled and quenched As_2S_3 glasses

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ABSTRACT

We investigate the sub-T_g relaxation in both the mechanically milled and the quenched As_2S_3 glasses by a differential scanning calorimeter (DSC). The results show that the sub-T_g enthalpy relaxation pattern of the milled As_2S_3 glass is similar to that of the quenched glass, but the fictive temperature (T_f) of the former is higher than that of the latter. By performing sub-T_g annealing, we find that the quenched As_2S_3 glass exhibits the Johari-Goldstein (JG) relaxation, whereas the milled glass shows the relaxation behavior with the activation energy of $\sim 32RT_g$ that deviates from the average value of $24RT_g$ for the JG relaxation. An endotherm occurs prior to the sub-T_g relaxation peak when the milled glass undergoes sufficient sub-T_g annealing (temperature and time). The occurrence of the endothermic pre-peak and the higher activation energy of the milled glass imply its higher structural heterogeneity compared to the quenched glass. The Raman and X-ray photoelectron spectra indicate the existence of the As_4S_4 clusters and -S-S- chains in both the milled and the quenched glasses, confirming their structural heterogeneity.

1. Introduction

Glass is a kind of metastable material with higher potential energy than their crystalline counterpart. Thus it will gradually approach their more stable state upon changing some external parameters such as temperature and pressure [1–3]. This process is the so-called relaxation, which is one of the most important features of glasses. Different types of relaxation can occur in the glass, e.g., surface relaxation [4], structural anisotropy relaxation [5], volume relaxation [6], enthalpy relaxation [7]. Among these relaxation behaviors, the sub-T_g enthalpy relaxation is a key to understand the nature, dynamics, thermodynamics of glass, since it is sensitive to the change of the potential energy in glass [8]. The sub-T_g enthalpy relaxation in hyperquenched glasses has been intensively studied in the past decade [7–10]. The sub-T_g enthalpy relaxation in glass refers to the release of the excess energy trapped by hyperquenching, when the glass is subjected to dynamic heating (DSC upscanning) or to isothermal annealing below T_g [11]. The excess energy is the difference in potential energy between the hyperquenched glass and the glass cooled at the standard rate of 10 K/min. By measuring the sub-T_g relaxed enthalpy using differential scanning calorimetry (DSC), we can access the energetic and structural heterogeneities in glass [7].

Although the common technique to produce glass is by the melt-quenching, other routes have also been used, e.g., pressurizing, sol-gel technique, high energy radiation, mechanical milling, solvent evaporation [2]. Among them, high-energy ball milling is an effective approach to fabricate glassy materials from crystalline ones [12–14]. In contrary to the melt-quenching approach, the ball-milling is a mechanical process directly using a series of mechanical effects including impact, friction, shearing, grinding etc. The physical features and microstructure of the milling-derived glasses have been studied using different characterization tools in recent years [15–17]. Now a critical question is: what happens or how do they relax when these glasses are annealed below T_g? In other words, how does the sub-T_g enthalpy relaxation proceed upon annealing? This question has been only partially answered so far.

As_2S_3 glass has found extensive applications as important components of the infrared optical devices [18–21]. The structural relaxation, stress relaxation and photo-induced fluidity in this glass are important scientific and technological issues, which have been investigated by several research groups [18, 22, 23]. However, to the best of our knowledge, the sub-T_g enthalpy relaxation in As_2S_3 glass has not been reported. It is known that the sub-T_g enthalpy relaxation in glass is a complicated thermodynamic and dynamic process, since it involves not only the primary (α) relaxation, but also other relaxation modes such as secondary (β) relaxation and γ relaxation. β relaxation in many glass

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systems manifests itself as both fast and slow β relaxations. The slow β relaxation is also called the Johari-Goldstein (JG) relaxation [24, 25], which is a precursor of α relaxation. The JG relaxation has intrinsic correlation with glass transition and involves the inter-molecular motion in glass [26]. The JG relaxation pattern is often hidden in the α relaxation pattern, and therefore it is hard to be detected. To identify the JG relaxation in glasses, an effective method was established, namely, the hyperquenching-annealing-calorimetry (HAC) approach [27, 28]. Hyperquenching (cooling at the rate of $> 10^5$ K/s) is applied to trap the higher potential energy or the excess enthalpy over that of the glass cooled at the standard rate of 10 K/min, whereas annealing at different temperatures below T_g for various durations is conducted to let the trapped enthalpy gradually release. Then, the released enthalpy can be quantified through DSC upscanning to find the temperature dependence of relaxation time, and thereby to determine the activation energy of the sub-T_g relaxation. Finally, the derived activation energy is compared to the empirical value for JG relaxation, i.e., $E_\beta \approx 24RT_g$, where R is the gas constant [29]. If the former is close to $24RT_g$, the JG relaxation occurs. In this work, we are interested in finding whether or not the quenched and milled As_2S_3 glasses exhibit the JG relaxation, by using the DSC data of sub-T_g enthalpy relaxation. We compare the sub-T_g enthalpy relaxation features (i.e., both the endothermic pre-peak and the energy release peak below T_g) in the milled As_2S_3 glass with those in the quenched As_2S_3 glass. Moreover, we perform the Raman and the XPS measurements to detect the structural changes in the As_2S_3 glass induced by both milling and quenching.

2. Experimental procedure

2.1. As_2S_3 glass preparation

The As_2S_3 glass was prepared by melt-quenching method. High purity As (Aladdin, 99.99%) and S (Aladdin, 99.99%) were used as raw materials. The raw materials were weighed according to their atomic percentages and sealed in silica tube under a vacuum of 10^{-3} Pa. The mixtures were melted at 1073 K for 12 h and frequently rocked to ensure the homogeneity. The sample was additionally annealed at 453 K for 2 h after being quenched in water.

2.2. Quenching and ball milling

Some as-prepared samples were sealed in the small aluminum container and held at 723 K for 1 h and then quenched in liquid nitrogen, whereas some were milled by a high energy planetary ball milling apparatus (Fritsch Pulverisette 7). ZrO_2 balls (3 mm in diameter) were used as the milling media and the sample to ball weight ratio was 1:15. The glass was milled at 600 rpm for 6 h.

2.3. Characterizations

Both the milled and the quenched samples were sealed in aluminum containers to avoid oxidation during heat-treatment, and were annealed at different temperatures (363–403 K) for various annealing time (t_a) (0-24 h) in an oven. These samples were subjected to a heating process in a differential scanning calorimetry (DSC) (Netzsch STA449 F1), during which the energy release can be observed. The samples were placed in a platinum crucible at room temperature and kept for 5 min at 313 K, then heated at 10 K/min to 523 K in Argon and immediately cooled at 10 K/min to room temperature. The obtained second upscans were termed the "standard curve" [30]. To obtain the isobaric heat capacity (C_p) curves, both the baseline (blank) and the sapphire as the reference were measured under the same conditions as those for the samples. From the C_p curves obtained from the second DSC upscan, the T_g of As_2S_3 glass was found to be 466 K (Fig. S1). In order to increase the credibility of experimental data, we conducted DSC measurements twice for each annealed sample to get the average value and the error range of the released enthalpy.

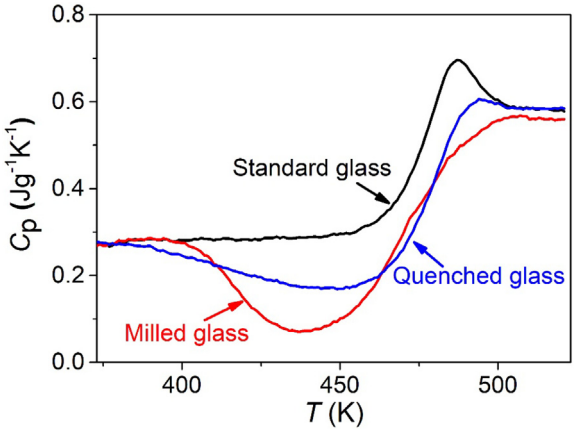

Fig. 1. Isobaric heat capacity (C_p) as a function of temperature for the quenched, the milled and the standard As_2S_3 glasses. The C_p curves of the quenched and the milled glasses were obtained during the first DSC upscans at 10 K/min in argon. The standard C_p curve was obtained during the DSC second upcan of the quenched sample at 10 K/min in argon. The rate of the DSC downscan was 10 K/min.

Raman spectra were recorded using a Raman spectrometer (Thermo Nicolet, Nexus) with a YAG:Nd laser (1064 nm). To avoid laser-induced damage, a typical power lower than 5 mW was used for recording spectra in the range 100–3500 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were performed by an ESCALAB 250Xi X-ray photoelectron spectrometer using Al K_α radiation. The spectra were calibrated by referencing the binding energy of carbon (C 1 s, 284.6 eV).

3. Results

As shown in Fig. 1, broad exothermic peaks appear prior to the glass transition during the first DSC upscans of both the quenched and the milled As_2S_3 glasses. Immediately after cooling at 10 K/min to room temperature, the samples were subjected to the second upscans to detect the standard glass transition (T_g = 466 K). The area between the first and the second upscan curves represents the excess energy trapped in the excited samples, which is released during the first DSC upscan. The energy release is an enthalpy recovery process, i.e., a recovery from the enthalpy of the excited glasses to that of the standard glass. The excess energy of the milled glass starts to be released at higher temperature than that of quenched sample, indicating that the milled glass needs relatively higher energy to start to release its excess energy. In addition, it is seen that the milled glass has a higher energy release peak and a larger area (i.e. more excess energy) than that of the quenched one. In addition, as shown in Fig. S1, the initial As_2S_3 glass did not display the energy release peak during the DSC first upscan.

The fictive temperatures, T_f, of the sample were determined using the energy-matching method (Fig. S2) [31]. The T_f values of both the milled and the quenched glasses are calculated to be $1.13T_g$ and $1.09T_g$, respectively. This means that both melt-quenching and mechanical milling can excite the glasses to higher energy state compared to the standard glass, and the milled As_2S_3 glass locates at higher position than the quenched one in potential energy landscape (PEL). It should be mentioned that the deviation of the first-upscan liquid C_p curve from the second upscan curve is relatively small, and hence, has a slight influence on the T_f determination, i.e., an error range of $0.03T_g$. Moreover, we found the fragility index m of the As_2S_3 liquid to be 27 through the heating rate dependence of T_f [32] (Fig. 2).

To understand the sub-T_g relaxation mechanism of both the milled and the quenched glasses, we performed the annealing-calorimetry experiments. Figs. 3, S3 and S4 show the C_p curves of both the milled