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Preparation and properties of Ge_4Se_{96} glass

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HIGHLIGHTS

- The Ge_4Se_{96} glass was prepared by melt quenched method.
- The specific heat of Ge_4Se_{96} glass was measured by stepwise method.
- The Kauzmann temperature increases with rise of Ge content.

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ABSTRACT

The chalcogenide glass Ge_4Se_{96} was prepared by melt-quenched method. The characteristic temperatures (the strain point, annealing point, glass transition point, yielding point and soften point) were determined by thermal analysis. The result shows that the glass transition point is 52 °C; the average thermal expansion coefficient is $\Delta L/L_0 = (0.0557*T-1.7576)/1000$. The specific heat of Ge_4Se_{96} glass was measured by stepwise method. The difference in specific heat between amorphous structure and undercooled liquid was determined as $\Delta C_p = 0.1812–5.20 \times 10^{-4}\ T–4.92 \times 10^{-7}\ T^2\ JK^{-1}\ g^{-1}$. Based on the result of ΔC_p, the Gibbs energy and the entropy curves were calculated, and the Kauzmann temperature was determined as $T_k = 233.5$ K, which is between that for pure Se glass (216 K) and that for $Ge_{7.4}Se_{92.6}$ glass (250 K). It indicates that for Ge-Se glass with low Ge content, the Kauzmann temperature increases with increasing the content of Ge.

1. Introduction

Se-based glass is an important system on account of its excellence glass formation ability [1–5]. For example, the pure Se can form glass with a normal cooling rate [6]. The study of binary Se-based glass can help in directing preparation of the multi-system chalcogenide glass owing to the similar infrared transmittance [7]. In addition, Se-based glass crystallization will result in eutectic structure, so it is also important for studying the nucleation and growth theory of eutectic. With Se-based glass, the formation of primary phase and eutectic phase can be observed by proper heat treatment, and the result can be compared with that from solidification. Ge_4Se_{96} glass is a hypoeutectic alloy according to the phase diagram. Its crystallization can help understand the solidification of hypoeutectic alloy. Thus, the Ge_4Se_{96} glass was studied here.

The specific heat is an important parameter for understanding the thermodynamic properties of materials [8–21]. The earliest paper concerning thermodynamic functions of chalcogenide glasses established a maximum-like dependence of the specific heat [8]. It could be used to determine the Kauzmann temperature (the lowest theoretical boundary for the glass transformation) for the glass system [8]. Malek et al. studied the heat capacity and thermodynamic properties of GeS_2, and the standard molar entropy and enthalpy were calculated [9]. They also found that thermal history of glass could affect the value of heat capacity [10]. Moynihan et al. studied the heat capacities of glassy and liquid Se and compared that with the theory calculated result [11]. Sharma et al. studied the specific heat of the Se–Te–Sn–Pb system using modulated differential scanning calorimetry, and observed the specific heat values increase rapidly at the glass transition temperature, and they explained the compositionla dependence of specific heat values [12–14]. Goel et al. found that the specific heat provides information about the solubility and the consequence of doping ions on thermal transport properties of glass-forming materials [15]. Stølen et al. studied the heat capacity and entropy of liquids in the Se-rich chalcogenide systems and the thermodynamics of the system are evaluated and discussed in light of earlier reported viscosities and recent structural studies of liquid $GeSe_2$

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[16]. Atake et al. studied the heat capacities of glassy and crystalline $GeSe_2$, and found that heat capacity of the former was smaller than that of the latter below about 60 K [17]. Medina et al. studied the thermal relaxation method for determine specific heat and found that specific heat of As_2S_3 glasses is 0.653 Jg^{-1} K^{-1} [18]. Thomas et al. studied the specific heat of Ge-As-Te glasses; found that the values are between 0.25 and 0.44 Jg^{-1} K^{-1} [19]. Wachter et al. studied the specific heat of $TmSe_{0.45}Te_{0.55}$ glass under pressure and at low temperatures [20]. Generally, the specific heats are measured by using the stepwise method. However, the heat measuring process of the stepwise method and calculated method, which have an obvious effect on the result of specific heat, are not elucidated in detail. Instead of giving the calculated details of specific heat from the stepwise method, it should be given the calculation details for different methods.

In this study we report the preparation of Ge_4Se_{96} glass and the specific heat measurement by stepwise methods with differential scanning calorimeter (DSC) equipment. In final, effect of Ge content on the specific heat was discussed.

2. Experimental methods

Ge_4Se_{96} glass (batch composition) was prepared by melting the elemental Ge and Se with purities ranging from 99.99% to 99.999% in quartz tube. The quartz tube was evacuated to 2×10^{-3} Pa and placed into a rocking furnace. The furnace was slowly heated to 873 K and kept for 48 h, and then the tube was taken out and quenched in hot water, thus, the glass sample was obtained. The sample powder was analyzed by Shimadzu Corporation XRD-6000 X-ray diffraction (XRD) with Cu target and scanning rate of 2°/min. The calorimetric measurements were performed in Perkin-elmer DSC 8500 equipment with high-purity standard aluminum pans under a constant flow of high-purity argon. About 20 mg powder samples were sealed in standard aluminum pans and scanned from room temperature to melting temperature at heating rate of 10 K min^{-1}. Thermal expansion properties of the sample were measured by using the thermal mechanical analyzer (TMA/SDTA840) of METTLER Company, and the thickness of the sample at 25 °C is 2.5 mm. The absolute values of the specific heat capacity of the amorphous sample, crystalline sample and undercooled liquid (weighs 20 mg) were determined in reference to that of a sapphire standard. The method consisted of heating the specimen in the DSC at a constant rate of 10 K min^{-1} to a certain temperature and holding isothermally for 180 s (Fig. 1).

In order to measure the specific heat, the area of scanning region is generally calculated by the method shown in Fig. 1. The area stands for the heat release during heating, the calculated process can be found in [22,23]:

Method 1: (1) Area of scanning region of empty pan S_e = (ABCE); (2) Area of scanning region of sapphire S_s = (AB'C'E); (3) Area of scanning region of sample S_g = (AB"C"E), then the specific heat of sample can be calculated by,

$$C_g(T) = \frac{S_g - S_e}{S_s - S_e} \times \frac{m_s}{m_g} \times C_s(T) \quad (1)$$

where $C_s(T)$ is the standard specific heat of the sapphire. m_s and m_g are the weights of sample and sapphire, respectively.

Method 1 does not consider the relaxation of heat flow in isothermal region (ECD), and the curve as seen in Fig. 1 is scarcely seen in practice. Most of the DSC curves obtained from the stepwise method are always found such as that displayed in Fig. 2. The main differences are (1) the baselines for empty pan and loaded pan do not coincide and (2) the initial heating and final heating are not gentle, in isothermal stage the heat flow does not turn to stable immediately. Therefore, the area region for calculating the heat release in each heating step should be the whole instable region in curve (ABCDE), not only the region from start heating to end heating (ABCE). Thus, considering the relaxation heat in isothermal region, we can obtain method 2.

Method 2: (1) Area of scanning region of empty pan S_e = (ABCDE); (2) Area of scanning region of sapphire S_s = (AB'C'D'E); (3) Area of scanning region of sample S_g = (AB"C"D"E). The specific heat of sample can be calculated by Eq. (1).

Two ways can verify that method 2 will provide a more accurate value. The First is that with increasing temperature, because of the heat change of the empty pan, S_e should be nearly equal to zero. From Fig. 2, with method 2, heat release integral (dashed area) of the empty pan indeed approaches to zero compared with that of the loaded pan, while it does not approach zero with method 1. Further, if the measured result is accurate, the change tendency of the heat integral area from method 1 or method 2 should be consistent with that of the standard value of specific heat for the result of the standard sapphire. That is, the calculated area will be very similar to that of several times of standard value. For the present study, the measured heat integral areas from methods 1 and 2 are shown in Fig. 3. The standard specific heat of sapphire, C_s, is from Ref. [24]. We found that $2.6*C_s$ approaches the measured area of sapphire from method 1, and $3.12*C_s$ approaches the measured result from method 2. However, for all the temperature ranges, the area of heat release of sapphire from method 2 has a smaller deviation than that from method 1, indicating that the method 2 will result in a more accurate specific heat for stepwise method.

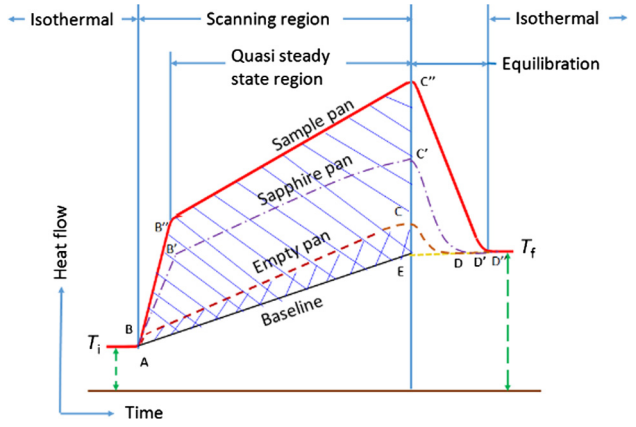

Fig. 1. Schematic curves showing instrumental response as empty and loaded pans are heated from one isothermal temperature (T_i) to another (T_f).

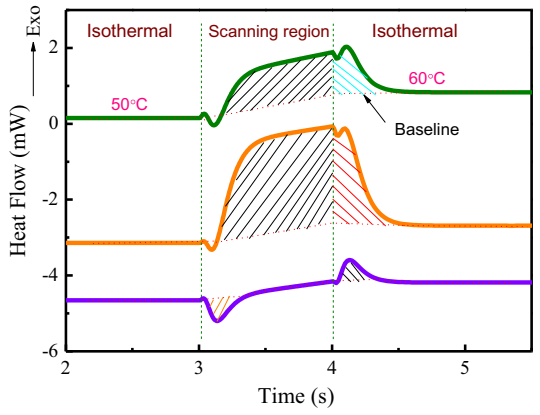

Fig. 2. The practical DSC curve of stepwise method for specific heat measurement.