Journal of Optoelectronics and Advanced Materials Vol. 7, No. 6, December 2005, p. 2941 - 2944

KAUZMANN TEMPERATURE AND THE GLASS TRANSITION

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Kauzmann temperature was investigated on the As_2Se_3 and As_2S_3 bulk glasses. Novel StepScan DSC technique was used to separate processes during the glass transition on both reversible and irreversible parts. This method is necessary to obtain correct information especially when undercooled melt undergo glass transition and the exothermic change is masked by the increase of total heat flow. It was found that Kauzmann temperature of As_2Se_3 bulk glass coincides with the low temperature onset in the glass transition range. Kauzmann temperature of As_2S_3 was found markedly bellow the glass transformation range. From that follows that the glass transition of As_2Se_3 can be considered as thermodynamic one, contrary to the glass transition of As_2S_3. From this point of view As_2Se_3 is an ideal glass contrary to As_2S_3 glass that preserves to a certain extent the undercooled melt nature.

(Received September 12, 2005; accepted November 24, 2005)

Keywords: Kauzmann temperature, Glass transition, Arsenic triselenide, Arsenic trisulfide, StepScan DSC

1. Introduction

In 1948 Kauzmann pointed out that the entropy of supercooled liquid decreases rapidly on cooling towards the kinetic glass transition temperature, T_g, and extrapolates to the entropy of the crystal not far below T_g, [1]. Temperature dependence of the entropy of glass intersects that of crystal at so called Kauzmann temperature, T_K, If the entropy of the supercooled liquid becomes lower than that of the stable crystal, it would eventually become negative at sufficiently low temperature, thereby violating the Third Law of Thermodynamics. This situation is named Kauzmann's paradox or entropy crisis, see e.g. [2-4] and references cited therein. The entropy crisis arises because the heat capacity of undercooled liquid is greater than that of crystal. Therefore, the entropy of fusion is consumed upon cooling and vanishes at Kauzmann temperature. One way of avoiding the entropy crisis is, for the liquid, to form an "ideal glass" at T_K. This is the thermodynamic view of the glass transition according to which the observable glass transition (for instance by viscosity or DSC measurements) is the manifestation of a second-order phase transition at Kauzmann temperature, masked by kinetics. According to Kauzmann, spontaneous freezing at kinetic glass transition prevents equilibration of supercooled liquid near T_K. Because kinetic glass transition is higher than Kauzmann temperature, it intervenes before the entropy crisis occurs. From it follows that the estimation of T_K can be obtained by extrapolation of supercooled liquid entropy below T_g, [2-4].

Novel experimental techniques of differential scanning calorimetry, temperature modulated DSC (TA Instruments) and, recently, StepScan DSC (Perkin-Elmer), have allowed to separate reversible thermodynamic processes from irreversible kinetic ones. It was found that the glass transition is represented by the reversible part, which is insensitive to the thermal history of glass. Hence the glass transition temperature depends only on the chemical composition [5-7]. Irreversible enthalpy change reflects the thermal history of a glass. Hence, the effect of both isothermal and non-

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isothermal aging proves at the moment of the glass transition measurement that the kinetic part superposed over the reversible (thermodynamic) one, [6,7]. It was also discovered that the irreversible enthalpy change in the course of the glass transition is associated with reversible change not only during the glass to supercooled liquid transformation (endothermic process) but also in the reverse direction (exothermic one), [6,7]. Stemming from these results the glass transition seems not to be only a kinetic phenomenon, as many authors believe, but it could be supposed that the glass transition is a reversible process in the thermodynamic sense [8,9].

From this perspective on the glass transition it is interesting to test whether Kauzmann temperature can be achieved and "ideal glass" in Kauzmann sense can exists in reality. The As_2Se_3 and As_2S_3 bulk glasses were chosen because of their easy preparation in high purity as well as possibility of slow cooling of its undercooled melt without crystallization. Nucleation temperature of As_2Se_3 is lower than the crystallization one. On the other hand, crystalline As_2Se_3 can be prepared relatively easily [10], contrary to crystalline As_2S_3 [11].

2. Experimental

Bulk glasses of As_2Se_3 and As_2S_3 were prepared by direct synthesis from elements of 5N purity in evacuated silica ampoules in a rocking furnace (750 °C, 24 hrs.) and melts were quenched in air. Crystalline As_2Se_3 was obtained by slow heating from the glass transition temperature up to 300 °C, followed by isothermal crystallization (24 hrs.) of undercooled melt at this temperature. Crystalline As_2S_3 was obtained by our method described in [11] and checked by X-ray diffraction.

To obtain both temperature dependencies of C_p and irreversible enthalpy changes at the glass transition, Fig. 1a, as well as at the crystal melting (Fig. 1b), novel stepwise technique StepScan DSC and power compensated DSC Pyris 1 (both by Perkin-Elmer) were used. Crystalline samples were measured in the heating mode; cooling mode was used for measuring of non-crystalline material (undercooled melt and glass). Temperature step +1 or -1 °C and step heating rate +100 or -100 °C/min., followed by approx. 1 min. isothermal lag was used in all cases.

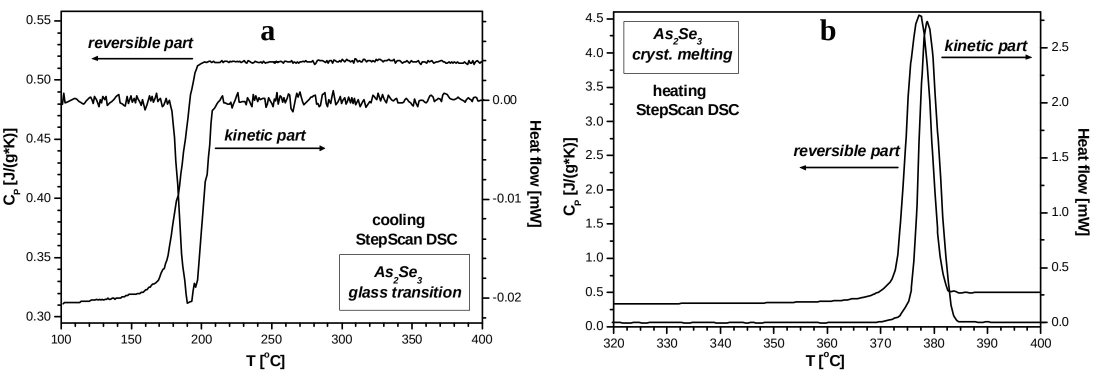

Fig. 1. StepScan DSC results, As_2Se_3 system: a) glass transition during supercooled melt cooling, b) melting of crystals.

3. Results and discussion

Results obtained by StepScan DSC on the crystalline and glassy arsenic trichalcogenides have been used to calculate the temperature dependence of entropy changes (within experimental accuracy). The temperature dependence of the entropy change for both crystalline and non-crystalline samples is given by the sum of the thermodynamic contribution and of the enthalpy change of kinetic process divided by its temperature:

$$\Delta S(T) = \int_{T_1}^{T_2} \frac{C_P}{T} dT + \frac{\Delta H_{kin}}{T_x} . \quad (1)$$

In this equation C_p is isobaric heat capacity, ΔH_{kin} is enthalpy changes obtained from irreversible kinetic part, T_x is either the glass transition temperature, T_g, or the crystal melting one, T_m, and $T_1 << T_g$ and $T_2 >> T_m$.

In fact, because the irreversible kinetic processes are spread over indispensable temperature interval (see Fig. 1), the contribution of the kinetic part to the entropy change in course of the glass transformation and/or of the crystal melting was replaced by $\Delta S_{kin}(T)$ and calculated according to equation:

$$\frac{\Delta H_{kin}}{T_x} \approx \Delta S_{kin}(T) = \frac{1}{m \cdot \beta} \int_{T_1}^{T_2} \frac{Q_{kin}(T)}{T} dT \,, \qquad (2)$$

where m is the sample mass, β is the underlying heating/cooling rate, $Q_{kin}(T)$ is the heat flow related to kinetic processes.

Using entropy-temperature dependence obtained, the Kauzmann temperature of As_2Se_3 was found to be T_K = 164 °C (see Fig. 3). This temperature is 23 °C below the glass transition temperature, T_g = 187 °C, [2].

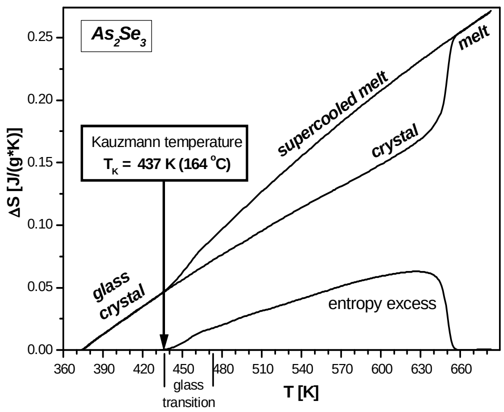

Fig. 2. Temperature dependence of both entropy of As_2Se_3 system and entropy excess of supercooled melt and the Kauzmann temperature.

Confronting the obtained Kauzmann temperature and thermodynamic part of the glass transition of As_2Se_3, we have found that T_K is identifiable with the low-T onset of the glass transition region (Fig. 4), and very close to the viscosity near the onset of T_g = 166 °C ($\eta = 10^{12}$ Pa.s). The temperature of this low-T onset is exactly that one at which supercooled liquid is completely transformed to glass. This result has physical meaning and according to the Kauzmann idea, the glass transition of As_2Se_3 bulk glass is the thermodynamic one and this glass can be named an ideal glass.

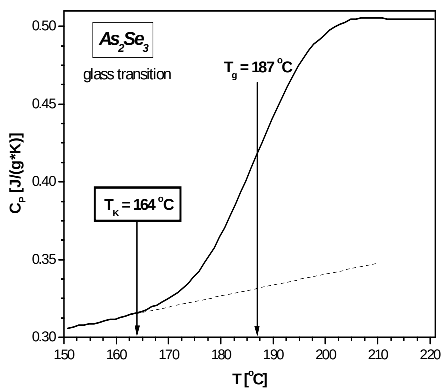

Fig. 3. Kauzmann temperature and the glass transition region (reversible part) of As_2Se_3 bulk glass.

On the other hand, a surprising result was obtained on As_2S_3 bulk glass. As one can find anywhere, this glass has been widely used as an "ideal glass" because of its easy preparation and extremely low crystallization tendency of its undercooled melt [12]. Kauzmann temperature of As_2S_3 was found at around 97 ^oC (Fig. 4). This temperature is ~ 78 ^oC below low-T onset (175 ^oC) of the glass transition region and it is clear, that ideal glass transition (thermodynamic one) is masked by the kinetic effects at significantly higher temperature. Based on the idea of Kauzmann temperature, the As_2S_3 glass contains some excess of the entropy of fusion and, therefore, glass preserves to a certain extent the undercooled melt nature.

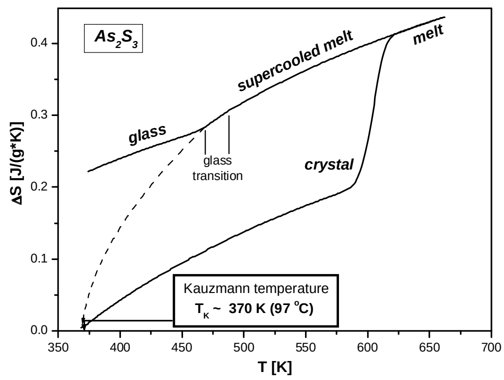

Fig. 4. Temperature dependence of entropy of As_2S_3 system and approximation of the Kauzmann temperature.

Finally, we must point out that it is not possible to obtain the same results using conventional DSC because cooling scans over the glass transition region are distorted due to the simultaneous endothermic and exothermic events (for details see [6]).

4. Conclusions

Using the StepScan DSC, we have shown, contrary to the commonly accepted opinion, that the undercooled liquid can really achieve the Kauzmann temperature and thus avoids the entropy crisis thermodynamically and not only by the kinetic effects. This ideal behavior was found for As_2Se_3 undercooled melt, but, surprisingly, not for As_2S_3 one.

Acknowledgements

This work was supported by the projects MSM 0021627501.

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