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Heat capacity of vitreous GeS_2

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ABSTRACT

The heat capacity for GeS_2 glass was measured by relaxation method, adiabatic calorimetry and DSC from $T/\mathrm{K} = (2 \text{ to } 600)$. Values of the standard molar enthalpy and the standard molar entropy are $12.713\ \mathrm{kJ \cdot mol^{-1}}$ and $88.46\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively. The molar heat capacity data for GeS_2 glass were compared with those reported previously for crystalline α-GeS_2. The molar heat capacity of the glass is higher than of the crystal above $T = 75$ K. However, the molar heat capacity of the glass is lower than that of crystal in the temperature range between (23 and 70) K. This anomaly can probably be attributed to structural differences between vitreous and crystalline state considering that the medium range order of the germanium sulfide glass is similar to that of the crystalline polymorph α-GeS_2 although the dimensionality of network is probably higher than 2D. The heat capacity of GeS_2 glass obtained by quenching from equilibrium liquid at $T = 1270$ K is higher than that of the glass resulting from quenching from metastable supercooled liquid within the glass transition range (about 0.2% for $100 < T/\mathrm{K} < 200$ and 0.4% at $T = 50$ K). This proves that parameters defining thermal history of the glass (*i.e.* cooling rate and initial temperature) may affect the value of heat capacity.

1. Introduction

Chalcogenide materials have attracted much interest both from technological and scientific point of view. It stems from their unique physical properties, such as sensitive variability of band gap with composition as well as large distinction of vitreous and crystalline states that can be detected by means of their reflectivity, electrical conductivity, photoconductive effects or high transmittance in near, middle and far infrared region. Most important applications of chalcogenide glasses then involve large capacity data-storage media (*i.e.* non-volatile PCRAMs where data are written via electric pulses or optically recorded CDs, DVDs and BlueRay Discs), sophisticated devices and elements for infrared optics and optoelectronics (fibers, planar guides, lenses) or various electronic thresholds and memory switches [1]. Such high-tech application, however, are in some contrast with apparent scarcity of thermodynamic data for these materials, especially in a broad temperature range, as O'Hare pointed out more than 25 year ago [2]. The thermodynamic data are important, *e.g.* for formulation of crystal growth models at higher temperatures where the equilibrium can be attained. Therefore, it is of interest to study heat capacity behavior of some selected chalcogenide compounds in crystalline and vitreous state.

Germanium disulphide is a congruently melting compound with a complex crystal structure that can also be prepared in vitreous form (g-GeS_2) by fast cooling of the melt of the same composition [3,4]. There are two crystalline polymorphic forms at atmospheric pressure. According to the phase diagram described by Viaene and Moh [5,6] α-GeS_2 is stable in equilibrium with GeS above approx. $T = 793$ K and with excess sulfur above (770 ± 5) K and β-GeS_2 is stable below α–β inversion range. The high temperature α-GeS_2 polymorph is a two-dimensional (2D) network layer structure. A single layer is formed by chains of corner linked GeS_4 tetrahedral, cross-linked by edge-sharing tetrahedral. This means that there are pairs of Ge atoms which are connected by two sulfur bridges, producing six and four member rings in a 2:1 ratio. The structure crystallizes in the monoclinic space group $P2_1/c$ with $a = 672.0(5)$, $b = 1610.1(5)$, $c = 1143.6(5)$ pm, $\beta = 90.88(5)°$, $Z = 16$ [7]. The low temperature β-GeS_2 polymorph is a complicated three-dimensional (3D) structure containing large elliptical hollows surrounded by 24 corner-sharing GeS_4 tetrahedral. It crystallizes in the monoclinic space group Pc with cell constants $a = 687.5(5)$, $b = 2255(1)$, $c = 608.9(5)$ pm, $\beta = 120.45(5)°$, $Z = 12$ [8]. Phillips [9] argued that the structural difference between α-GeS_2 and β-GeS_2 is actually subtle as there are only chalcogen atoms at the internal surfaces (layers or hollows). The topological difference then stems from the radius of curvature of these internal surfaces which is infinite (layers) for α-GeS_2 but finite (hollows) for β-GeS_2. Weinstein *et al.* [10] carried out a series of nice experiments

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to determine the effect of pressure on the optical absorption edge and near infrared refractive index of both crystalline forms and GeS_2 glass. Their analysis has clearly shown that GeS_2 glass is not a 3D network similar to SiO_2 but instead has a lower network dimensionality typical for molecular glasses. In this particular case the observed behavior was not so different from α-GeS_2 [10]. One of the first works on the heat capacity of crystalline GeS_2 and $GeSe_2$ is the article by Tarasov *et al.* [11]. These authors present data on the heat capacity from $T = (52 \text{ to } 307)$ K.

Therefore, the medium range order of the germanium sulfide glass is probably similar to that of the crystalline polymorph α-GeS_2 although the dimensionality of network is higher than 2D and of course there is no long range order. Such structural similarities of limited extension should be reflected in low temperature heat capacity. In this paper, the results of heat capacity measurements on vitreous g-GeS_2 are given, and compared with previously reported data on crystalline α-GeS_2 [12].

2. Experimental

The vitreous GeS_2 for low-temperature heat capacity measurement was prepared from high purity germanium and sulfur (5 N). They were mixed in the stoichiometric ratio and put into a silica glass ampule, which was evacuated by a rotary pump with a liquid nitrogen trap at room temperature for 1 day and then sealed. The ampoule was heated in an electric furnace at $T = 1270$ K for 10 h. There were two samples. The first was kept at $T = 1270$ K for several hours, and then dropped into a liquid nitrogen bath. The second glass was cooled down from $T = (1270 \text{ to } 770)$ K, kept at this lower temperature for 20 h and then dropped into a liquid nitrogen bath. The amorphous nature of glassy sample was verified by powder X-ray diffraction at room temperature using a MacScience M18XHF-SRA diffractometer and Bruker AXS-D8 diffractometer.

The Physical Property Measurement System (Quantum Design Inc.) was used for the measurement in the region from $T = (2 \text{ to } 50)$ K. The apparatus and experimental method are described in detail by Lashley *et al.* [13]. A sample which was quenched from $T = 1270$ K mass of 6.790 mg was used in the experiments. The second sample quenched from $T = 770$ K mass of 3.647 mg. A sample platform made of thin alumina square of 3 mm · 3 mm and a puck frame which worked as heat sink were placed in the PPMS apparatus. A thermometer and heater were attached on the lower side of the sample platform. The platform was thermally linked to the heat sink held at a constant temperature by thin wires. A sample of α-GeS_2 was then attached on the sample platform with Apiezon N grease for good thermal contact. The uncertainties of the heat capacity determinations are about ±1%. More experimental details are given by Akaogi *et al.* [14]. The heat capacity of GeS_2 glass over the temperature region from $T = (8.5 \text{ to } 307)$ K was determined by a laboratory – made, stepwise heated, low – temperature adiabatic calorimeter. A sample which was quenched from $T = 1270$ K mass of 8.36375 g was used in the experiments. The second sample quenched from $T = 770$ K mass of 7.69836 g. The temperature was measured with an iron-rhodium resistance thermometer (Tinsley, 5187U) which was calibrated at the National Physical Laboratory (UK) below $T = 27.1$ K and Oxford Instruments Ltd. above $T = 27.1$ K on the basis of the international temperature scale (ITS-90). The adiabatic control system gives the temperature stability of calorimeter vessel within $T = 10^{-5}$ K under a high vacuum of $1.33 \cdot 10^{-5}$ Pa. More experimental details are given by Atake *et al.* [15,16] and Kawaji *et al.* [17]. The accuracy of the heat capacity determinations is approximately 0.1% and the precision is better than ±0.05% for $(100 < T/\text{K} < 307)$, and decreases with decreasing temperature to about ±0.2% at $T/\text{K} = 13$.

The preparation of vitreous g-GeS_2 for high-temperature DSC heat capacity measurements was performed in a similar way as described above, *i.e.* in an evacuated silica ampoule placed in a rocking furnace at $T = 1220$ K for 24 h and then quenched in a mixture of water and ice. Bulk glass was crushed to powders of size, (50 to 125) μm. The amorphous nature of the sample was checked by X-ray diffraction.

High-temperature heat capacity of the prepared glass was measured using a conventional DSC Q2000 (TA Instruments) equipped with cooling accessory, autolid, auto sampler and T-zero Technology. Dry nitrogen was used as the purge gas at a rate of $50 \text{ cm}^3 \cdot \text{min}^{-1}$. The calorimeter was calibrated through the use of melting temperatures of In, Zn and H_2O. The zero-line course was checked daily. A thin layer of the GeS_2 powder was spread at the bottom of T-zero aluminum pans to improve the thermal contact; crimping lids were used to further improve thermal contact and to avoid deformation of the pan at high temperatures. The sample mass was approximately 20 mg, precision of mass determination was ±0.005 mg.

Heat capacity was determined by means of the so-called ratio method [18], where C_p is calculated from the comparison of heat flow signals (normalized with respect to sample mass and corrected for the cell asymmetry, thermal gradients and heat capacity of aluminum pans) of the sample and sapphire standard material. The DSC temperature program was following: after a 3 min equilibration at $T = 293$ K, the sample was heated at $10 \text{ K} \cdot \text{min}^{-1}$ to $T = 823$ K, where a 3 min isotherm was applied. Error in heat capacity determination did not exceed 2% of the standard C_p value in the whole temperature range $(305 < T/\text{K} < 600)$.

3. Results

The experimental molar heat capacity values $C_{p,\text{m}}$ of germanium disulphide glass (g-GeS_2) are given in tables 1–5. The data from tables 1 and 2 correspond to glassy sample obtained by quenching from $T = 1270$ K, while the data in table 3 were measured by DSC for sample quenched from $T = 1220$ K. Tables 4 and 5 involve the sample which was quenched from $T = 770$ K. It is the sample with different thermal history.

TABLE 1

Molar heat capacity, $C_{p,\text{m}}$, of g-GeS_2 (which was cooling from $T = 1270$ K) measured by thermal relaxation method.

T/K	$C_{p,\text{m}}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T/K	$C_{p,\text{m}}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T/K	$C_{p,\text{m}}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T/K	$C_{p,\text{m}}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
2.50	0.029	5.68	0.367	12.02	2.048	27.26	8.269
2.68	0.036	6.07	0.445	12.87	2.325	29.18	9.165
2.86	0.045	6.51	0.521	14.77	2.983	31.27	10.173
3.06	0.056	6.96	0.630	15.79	3.356	33.45	11.300
3.29	0.070	7.46	0.738	16.91	3.784	35.87	12.406
3.77	0.108	7.98	0.869	18.10	4.259	38.42	13.563
4.04	0.135	8.55	1.012	19.38	4.775	41.12	14.846
4.32	0.173	9.15	1.168	20.73	5.347	44.03	16.200
4.63	0.208	9.79	1.354	22.21	5.979	47.14	17.596
4.95	0.253	10.48	1.567	23.79	6.675	50.48	19.065
5.30	0.302	11.22	1.787	25.47	7.453		