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Structural characterization and topological threshold in chalcogenide $Ge_xSb_{40-x}Se_{60}$ glasses

Z. G. IVANOVA[a*], E. CERNOSKOVA[b], K. MELANOVA[b]
[a]*Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chausse Blvd., 1784 Sofia, Bulgaria*
[b]*Joint Laboratory of Solid State Chemistry of Institute of Macromolecular Chemistry, Academy of Sciences, Czech Republic, v.v.i and University of Pardubice, Studentská 84,*
53210 Pardubice, Czech Republic

The compositional dependences of some basic thermal properties of bulk $Ge_xSb_{40-x}Se_{60}$ glasses have been evaluated, taking into consideration the average coordination number (Z). In particular, the glass transition temperature (T_g), softening temperature (T_s), coefficient of thermal expansion in glass (α_g), specific heat capacity (ΔC_p) and fragility (m) have been investigated by a complex application of differential thermal and thermomechanical analyses, X-ray diffraction and differential scanning calorimetry as well. The obtained peculiarities in their change at Z ~ 2.67 have been discussed in terms of topological structural transitions in chalcogenide glasses.

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Keywords: Chalcogenide glasses, X-ray diffraction, Thermal properties

1. Introduction

Chalcogenide glasses are well known as perspective materials in view of their potential applications such as memory switching, photolithography, infrared detection, xerography, etc. Studies on the property-composition relationship in them are still of interest, especially related to improvement of some parameters by changing the chemical composition [1]. Rare-earth doped glasses are important for their luminescence properties [2,3]. The observed features in the variation of physicochemical, thermal and optical properties of some glasses have been explained by the chemical ordered covalent network (COCN) model, which is based on the constraint theory [4,5] and on the network dimensionality considerations [6]. According to this model, the properties can be evaluated in terms of the average coordination number (Z), which is defined as the atom-averaged covalent coordination of the constituents and is useful for describing the cross-linking in a glass. Consequently, the interpretation of the compositional dependence of the properties at Z~2.67 is attributed to a topological transition from a layered structure to a three-dimensional network due to cross-linking and to a chemical threshold as well [7,8].

In this connection, some physical and optical properties of Ge-Sb-Se glasses, in particular the $Ge_xSb_{40-x}Se_{60}$ family, have been intensively studied [1,5-9]. The obtained results have been discussed on the basis of both the bond energy and the structural arrangement in them. In this paper, the main results from the complex study of these glasses by the methods of X-ray diffraction, differential scanning calorimetry (DSC), differential thermal and thermomechanical analyses (DTA and TMA), around the topological threshold at Z ~ 2.67 have been summarized.

2. Experimental

Bulk $Ge_xSb_{40-x}Se_{60}$ glasses (x = 15, 20, 25, 27, 32 and 35) were prepared by the well-known procedure of heating up to 900°C and cooling in air [9,10]. The identification of the corresponding arisen crystalline phases was made by X-ray diffractometer (Krystalloflex, Siemens, Germany) with Fe-filtered Co Kα radiation. The differential thermal analysis was carried out by an instrument R.M.I.-DTA 003 (Electronic Measuring Instruments, Czech Republic) at heating rates of 5, 10, 15 and 20 K min^{-1}. The thermomechanical analysis was made using a TMA CX04R instrument (R.M.I., Czech Republic) on polished to optical quality samples. The calorimetric measurements were performed by a Mettler DSC 13E calorimeter controlled by a computer.

3. Results

Summarizing the X-ray diffraction patterns (Fig. 1), the samples at x = 20, 25 and 27 do not exhibit any crystalline phases (only, the weak traces at x = 25 could be attributed to GeSe phase). At x = 15, the Sb_2Se_3 phase crystallizes, while reflexes both of c-$GeSe_2$ and c-GeSe phases at x = 32 are observed, and predominantly the $GeSe_2$ phase at x =35 crystallizes. Therefore, the compositions at x = 20, 25 and 27 give very good glasses, and this is confirmed by their DTA thermograms, where after the glass transition region any crystallization effects are not observed. In particular, more pronounced increase of the glass transition temperature (T_g) at a heating rate 20 K min^{-1} in the very narrow range of Z = 2.65-2.67 is observed (Fig. 2).

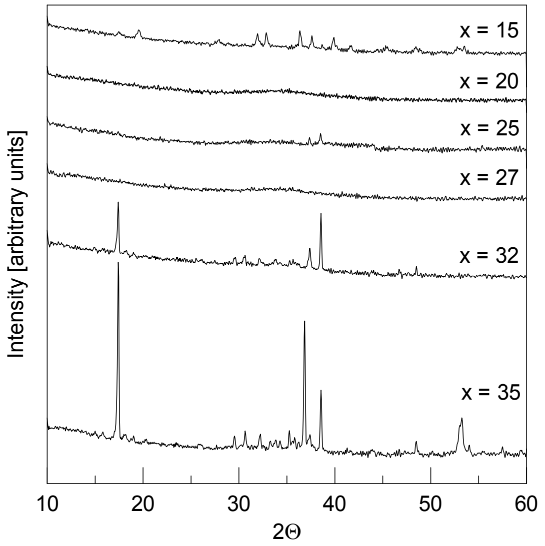

Fig. 1. X-ray diffraction patterns of the glasses studied.

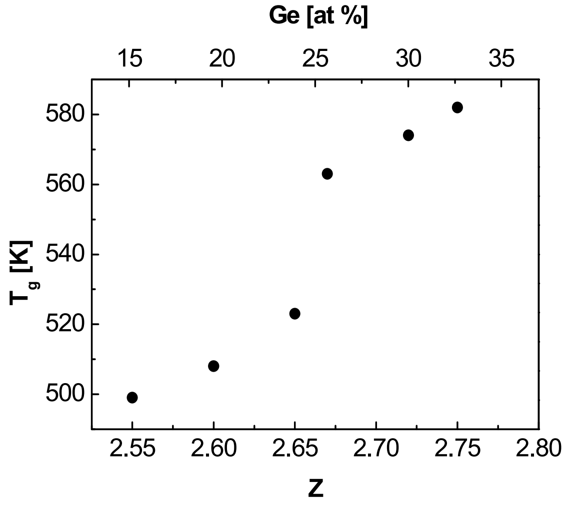

Fig. 2. Dependence of T_g on Z for the glasses studied (DTA measurement).

The dilatometric properties such as softening temperature (T_s) and coefficient of thermal expansion in glass (α_g) are presented in Fig. 3 a, b. The T_s values exceed by ~60 K those of T_g and show a threshold at Z ≈ 2.67 (case a), while α_g ones rapidly increase with Z variation from 2.65 to 2.67 (case b). A similar behavior in the calorimetric parameters of these glasses is observed by the change of the specific heat capacity (ΔC_p) and fragility (m) with Z (Figs. 4 a, b). Consequently, heat capacity rapidly increases at Z ~ 2.65-2.67 and remains almost constant at Z ≥ 2.67 (case a), while the variation of m with Z follows that of α_g (case b).

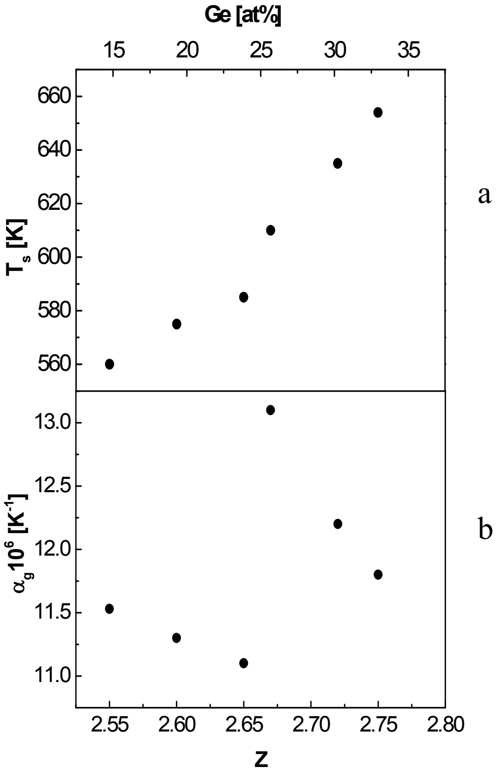

Fig. 3. Dependence of T_s (a) and α_g (b) on Z for the glasses studied (TMA measurement).

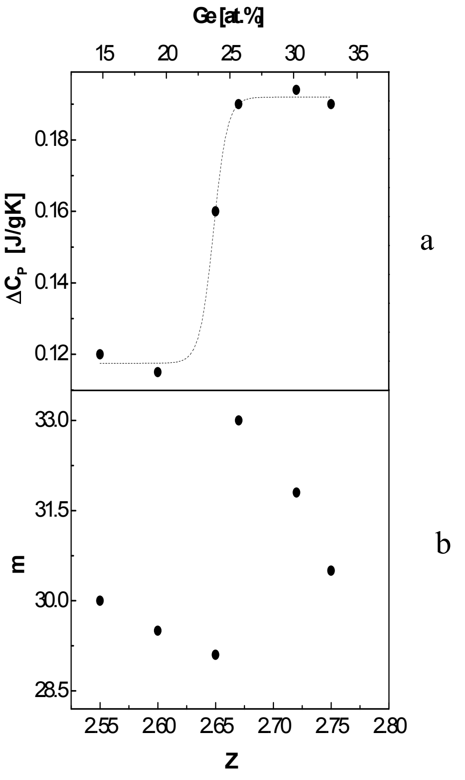

Fig. 4. Dependence of ΔC_p (a) and m (b) on Z for the glasses studied (DSC measurement).

4. Discussion

The average coordination number can be used as a good quantity to characterize the connectivity of a covalent network solid, given by the (8 – *N*) rule, where *N* is the number of the outer shell electrons in the corresponding atom. The observed peculiarities in the thermal properties of the present glasses at $Z \approx 2.67$ can be explained by the distribution of the chemical bonds in the frame of the COMN model [5]. It has been found [11] that the number heteropolar Ge-Se bonds increases at the expense of Sb-Se ones and at $Z > 2.67$ the latter disappear. The fraction of homopolar Sb-Sb bonds slightly increases up to $Z = 2.67$, after which Ge-Ge bonds appear. The presence of Ge-Ge bonds at $Z > 2.67$ leads to cross-linking, i.e. the covalent network undergoes a transition from a layer two-dimensional (2D) to a three-dimensional (3D) structure. According to Tichy and Ticha [8], this transition can be assisted by a chemical threshold at $Z = 2.67$ for the most stable composition and bonding arrangements with most negative formation energy.

5. Summary

The observed peculiarities in the variation of the glass transition and softening temperatures, coefficient of thermal expansion, specific heat capacity and glass fragility glasses from the $Ge_xSb_{40-x}Se_{60}$ family at a very narrow range of $Z = 2.65$-2.67 have been ascribed to structural rearrangements of the backbone Taking into account the medium range order, transition from molecular low-dimensional structure (2D) to a continuous cross-linked (3D) network occurs, which may be regarded as a topological one. This transition can be accompanied by chemical ordering effect as well. The obtained bond distribution of the chemical bond agrees with these structural changes dependent on the average coordination number.

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*Corresponding author: zoiv@abv.bg