JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 4, April 2007, p. 825 - 827

Thermal coefficients of linear expansion of non-crystalline chalcogenides in the As-S-Ge-Er system

V. B. PETROVIĆ, S. R. LUKIĆ*, M. V. ŠILJEGOVIĆ, F. SKUBAN
Department of Physics, Faculty of Sciences, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia

The paper describes the results of a study of glasses of the type $[(As_2S_3)_x(GeS_2)_{1-x}]_{1-y}(Er_2S_3)_y$ for x=30 and 40 at % with Er =1 at % by the method of thermomechanical analysis. Values of the thermal coefficients of linear expansion in solid (α_g) and visco-plastic (α_ω) phase were determined. On the basis of results obtained using the mentioned methods, it was possible to determine the specific temperature of beginning of the softening process of the glass (T_g), as well as the temperature of the beginning of the deformation (T_ω). It was shown that the linear coefficients essentially depend on the glass system composition, i.e. on the fact wether structural network contains erbium. Specific temperatures are also functions of content of some components in material as it can be expected in disordered systems.

(Received November 2, 2006; accepted February 28, 2007)

Keywords: Chalcogenide glasses, Thermal coeffiicient, Glass-transition temperature, Glass deformation temperature

1. Introduction

Chalcogenide glasses contain one or more chalcogen elements: sulphur, selenium and tellurium in combination with other elements, namely from IV, V and VI group of the periodical table. In the last few years chalcogenide glasses are doped with rare-earth elements (RE). These glasses are very attractive for their optical transitions wich are used in many devices such as laser fibre amplifiers [1,2].

Application of chalcogenide glasess doped with RE depends on their mechanical properties. This paper presents the results of investigation the thermomechanical characteristics of chalcogenide glasess $(As_2S_3)_x(GeS_2)_{1-x}$, x=0.3 and 0.4 when they are doped with 1 at % Er in the Er_2S_3 form. The value of the thermal coefficient of linear expansion α and it's characteristic change in range of glass transformation could help in understanding of the internal structure of the glassy skeleton and the influence of some structural units on glassy stability.

2. Experimental

The investigated glasses were synthesized from high purity element components. The process was conducted according to a special program (Fig. 1) in cylindrical quartz ampoules evacuated at a pressure of 1×10^{-3} Pa. The ampoule's length was about 15 cm, it's diameter 15 mm and the wall thickness 2 mm, in order to withstand high pressures in ampulla during the synthesis. The synthesis was performed in a rocking furnace from the room temperature to the 1050 ℃ during 20 *h*.

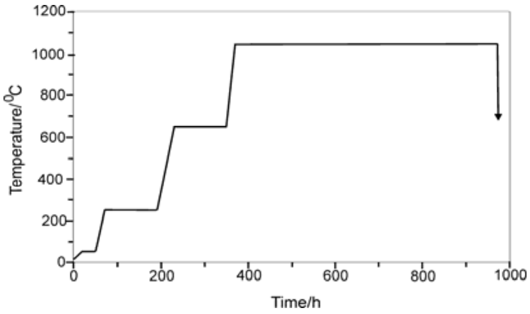

Fig 1. Diagram of process for obtaining glasses $[(As_2S_3)_x(GeS_2)_{1-x}]_{1-y}(Er_2S_3)_y$, Er =1% at %.

Amorphous character of samples was determined by iconoscopic technique in a polarization microscopy and by X-ray diffraction.

Dilatometric studies of amorphous samples $(As_2S_3)_{30}(GeS_2)_{70}$, $[(As_2S_3)_{30}(GeS_2)_{70}]_{1-y}(ErS_3)$y, $(As_2S_3)_{40}(GeS_2)_{60}$ and $[(As_2S_3)_{40}(GeS_2)_{60}]_{1-y}(Er\ S_3)_y$ with the concentration of Er 1 at % were carried out on a Perkin Elmer TMA7 analyzer in the range from the room temperature to the temperature on wich material starts to deform due its own mass. The samples were prepared in a form of parallelipiped (thickness was about 2 mm) by using abrasive powder and special holder. The changes in sample length were measured within accuracy of $\pm10^{-4}$ mm. The heating rate was $2\ ^\circ C\min^{-1}$ and the furnace was cooled using water. Measurements were carried out in the air atmosphere at loads of 10 mN.

3. Results and discussion

The results of measuring expansion of the samples $(As_2S_3)_{30}(GeS_2)_{70}$, $[(As_2S_3)_{30}(GeS_2)_{70}]_{1-y}(Er_2S_3)y$, $(As_2S_3)_{40}(GeS_2)_{60}$ and $[(As_2S_3)_{40}(GeS_2)_{60}]_{1-y}(Er_2\ S_3)y$ with the concentration of Er 1 at % are presented in Fig. 2.

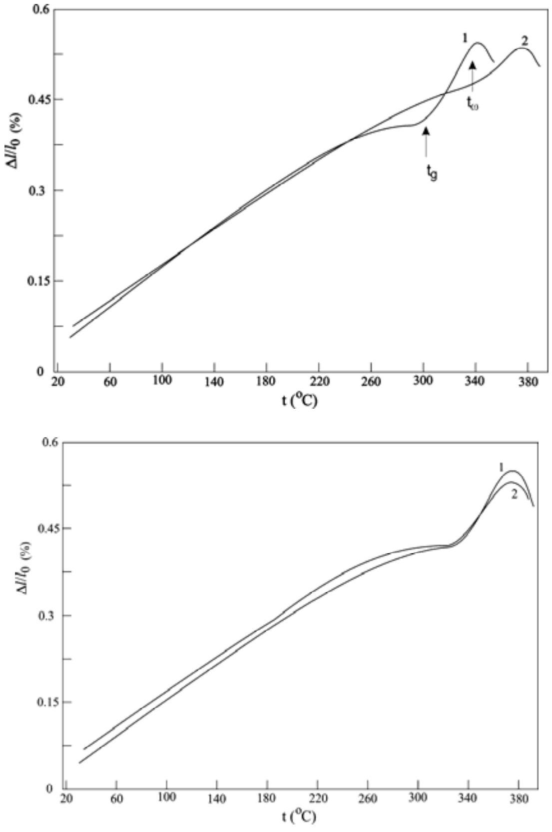

Fig. 2. Relative changes in the sample height of glasses: left: 1-$[(As_2S_3)_{30}(GeS_2)_{70}]_{1-y}(Er_2S_3)y$, 2-$(As_2S_3)_{30}(GeS_2)_{70}$, right: 1-$[(As_2S_3)_{40}(GeS_2)_{60}]_{1-y}(Er_2S_3)y$, 2-$As_2S_3)_{40}(GeS_2)_{60}$.

The thermal coefficients of linear expansion of solid and visco-plastic phase, α_g and α_l [3,4] respectively, were determined based on the slope of straight-line parts of the functional dependence of the relative changes in the sample height *vs*. temperature. The characteristic temperatures in area of phase transition, glass-transition temperature T_g and temperature of the beginning of deformation T_ω were also determined.

Derived results for T_g, T_ω, α_g and α_l of samples of composition $(As_2S_3)_{30}(GeS_2)_{70}$, $[(As_2S_3)_{30}(GeS_2)_{70}]_{1-y}(Er_2S_3)_y$,$(As_2S_3)_{40}(GeS_2)_{60}$ and $[(As_2S_3)_{40}(GeS_2)_{60}]_{1-y}(Er_2S_3)_y$ with the concentration of Er 1 at % including corresponding deviations are presented in Table 1.

It is known that in materials of this type, the chemical bonds inside structural units are covalent. These bonds are much stonger than intermolecular bonds between structural units so they are practically not influenced by the expansion. Thermal expansion of glass materials is caused by changes in lengthss of relatively weak intermolecular forces between the existing structural units. It is manifested in terms of relatively high values of thermal coefficients (Table 1).

Table 1. Characteristic temperatures and thermal coefficients of investigated glasses.

Sample	T_g (°C)	T_ω (°C)	α_g $\left(10^{-6}K^{-1}\right)$	α_l $(10^{-6}K^{-}$
$(As_2S_3)_{30}(GeS_2)_{70}$	348.4(8)	366.5(8)	15.0(3)	25.2(2)
$[(As_2S_3)_{30}(GeS_2)_{70}]_{1-y}$ $(Er_2S_3)y$ Er=1%	304 (1)	334 (1)	16.5(16)	43.2(11)
$(As_2S_3)_{40}(GeS_2)_{60}$	280.6 (4)	304.2 (4)	18.7(9)	49.7(9)
$[(As_2S_3)_{40}(GeS_2)_{60}]_{1-y}(Er_2S_3)y$ Er=1%	275.9 (15)	303.8 (15)	18.4(8)	39.8(4)

The thermal coefficients of linear expansion of solid phase α_g is caused by the increase of the mean distance between particles [5]. Values of α_g for $[(As_2S_3)_{30}(GeS_2)_{70}]_{1-y}$ $(Er_2S_3)_y$ and $[(As_2S_3)_{30}(GeS_2)_{70}$ are almost the same such as values for $[(As_2S_3)_{40}(GeS_2)_{60}]_{1-y}(Er_2S_3)_y$ and $(As_2S_3)_{40}(GeS_2)_{60}$ wich means that introduction of Er in this glasses doesn't have major influence on glass matrix.

The thermal coefficients of linear expansion of visco-plastic phase α_l can be represented as: $\alpha_l = \alpha_g + \Delta\alpha$

$\Delta\alpha$ is consequent of gradual laceration of chemical bond in glasses in range of short ordering and increase of their mobility [6]. α_l for $[(As_2S_3)_{30}(GeS_2)_{70}]_{1-y}(Er_2S_3)y$ is much higher then α_l for $(As_2S_3)_{30}(GeS_2)_{70}$ wich means that chemical bonds are much weaker as the whole network when this glass contains Er. On the other hand, α_l for $[(As_2S_3)_{40}(GeS_2)_{60}]_{1-y}(Er_2\ S_3)y$ is quite lower then α_l for $(As_2S_3)_{40}(GeS_2)_{60}$ and in this system chemical bonds are much stronger when it contains Er.

It can be concluded that the values of coefficient α for investigated samples (Table 1) are in the range of characteristic values for chalcogenide glasses [7].

Incorporation of Er leads to the decrease of the characteristic temperatures T_g and T_ω for glass $(As_2S_3)_{30}(GeS_2)_{70}$ (Table 1), while in case of glass $(As_2S_3)_{40}(GeS_2)_{60}$, infuence of Er is not so significant.

After several days of storage the glasses develop mechanical stresses that leads to specific fractures (Fig. 3). It seems that Er distribution in this glass changes. Similar results have been obtained by other authors [8].

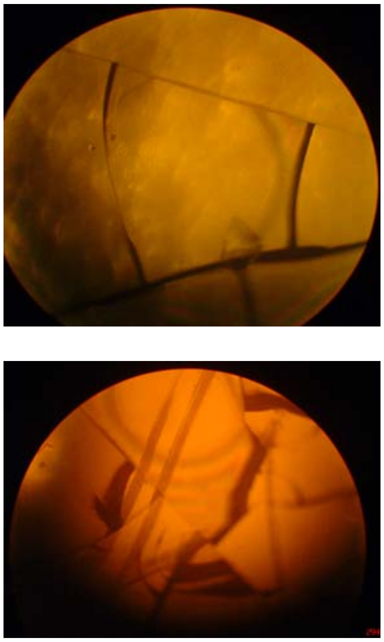

Fig. 3. Picture of glasses $[(As_2S_3)_{30}(GeS_2)_{70}]_{1-y}(Er_2S_3)y$ (left) and $[(As_2S_3)_{40}(GeS_2)_{60}]_{1-y}$ $(Er_2S_3)y$ (right), Er = 1 at %, obtained by optical microscopy.

4. Conclusion

It was shown that the glass-transition temperature and the temperature of beginning of glass deformation show a decrease with Er content in the $(As_2S_3)_{30}(GeS_2)_{70}$ for 44 °C and 33 °C respectively. In case of glass $(As_2S_3)_{40}(GeS_2)_{60}$ tha infuence of Er is not significant.

At the same time thermal coefficients of linear expansion of solid phase α_g are almost the same for both pairs of samples, wich means that introduction of Er in this glasses doesn't have a major influence on glassy matrix. On the other hand, thermal coefficients of linear expansion of visco-plastic phase α_l is higher in first case and lower in second, wich indicates some strength of the chemical bonds.

It was shown that glasses with the concentration of Er of 1% develop mechanical stress, and, possibly, nonuniform distribution of Er.

Acknowledgement

This work was supported by Provincial Sekretariat of Science and Tehnological Development, Project "Tehnology of obtaining and characterization of dissordered semiconductors".

References

[1] D. Lezal, J. Pedikova, J. Zavadil, Chalcogenide Letters, **1**(1), 11 (2004).
[2] D. Lezal, J. Optoelectron. Adv. Materials **5**(1), 23 (2003).
[3] D. M.Petrović, F. Skuban, S. R. Lukić, M. M. Garić, S. J. Skuban, Funct. Mater. **6**, 478 (1999) .
[4] F. Skuban, D. M.Petrović, S. R. Lukić, M. M. Garić, I. O. Guth, J. Ther. Anal. Cal., **59** 877 (2000)
[5] D. S. Sanditov, G. M. Bartenev, Phys. Prop. of Disord. Struct. Nauka, Novosibirsk, 1982.
[6] D. S. Sanditov, V. V. Mantatov, Fiz. i Him. Stekla (russ.), **10**(1), 37 (1984).
[7] A. Feltz, Amorphe und Glasartige Anorganische Festkoerper, Akademie-Verlag, Berlin
[8] D. Lezal, J. Pedlikova, J. Zavadil, P. Kostka, M. Poulain, "Journal of Non-Crystalline Solids", 47-52 (2003).

---

[*] Corresponding author: svetdrag@im.ns.ac.yu