

THERMAL AND MECHANICAL PROPERTIES OF SOME THALLIUM-CONTAINING CHALCOGENIDES

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The results of differential thermal analysis (DTA) and differential scanning calorimetric (DSC) measurement as well as of measurements of the microhardness (H_k) on chalcogenide thin films and bulk samples from the systems As-S-Tl and Ge-S-Tl in wide range of concentrations are reported. The dependence of H_k on composition shows an increase in the hardness with the rise of the As and Ge content for the first two systems and a very large decrease in it when the Tl content increases. It is also found that the glass-transition temperature of bulk samples as well as thin films decreases when Tl content increases. No influence of the vacuum deposition conditions of thin films on the microhardness has been observed. It was shown that a correlation exists between the mechanical and thermal properties of the studied chalcogenide systems.

(Received October 7, 2003; accepted February 19, 2004)

Keywords: Chalcogenide glasses, DTA, DSC, Microhardness, Thallium chalcogenides

1. Introduction

The chalcogenide glasses are well-known infrared transmitting materials with pass bands, depending on composition, up to 10-20 μm . They have been employed as infrared filters, windows and fibers, and more recently have been investigated as potential materials for IR diffractive optical elements such as gratings and Fresnel lenses [1,2]. Amorphous thin chalcogenide films are prospective materials for nano-technology, for the photo-recording and radiation sensitive materials with very high optical resolution and very good optical properties. They are usable in optical switching, optical interconnections and optical sensing. Most of these applications are based on the wide variety of light-induced effects exhibited by these materials [3-6]. The properties of glass-systems as As-S, As-Se, Ge-Se and Ge-S were extensively studied. Nevertheless, for more complex multi-component systems the information is still insufficient. Addition of network formers or modifiers is expected to change the properties of glasses and to widen the scope of their applications.

DTA and DSC were used to determine the glass transition temperature (T_g) and the crystallization and melting temperatures of bulk chalcogenide glasses and measurements of the microhardness were carried out for the glass characterization [7-10]. In our previous paper [11,12] we have discussed the changes in the optical properties of thin As-S-Tl films and some data on the changes in their physicochemical properties were given.

The aim of this work is to present some new results on the thermal and mechanical properties of thin Tl-containing films, depending on the film composition and exposure to light.

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2. Experimental

Glasses from the systems $\text{As}_{1-x}\text{S}_{60}\text{Tl}_x$ and $(\text{As}_2\text{S}_3)_{1-x}\text{Tl}_x$ were prepared by direct synthesis from the elements with a purity of 99.999%, heated in an evacuated silica ampoule placed in an oven at 700 °C for 12 hours, while those from the system $(\text{GeS}_2)_{1-x}\text{Tl}_x$ ($x = 4, 6, 10$ or 15 at. %) at 970 °C for 14 hours with subsequent cooling in ice water. In order to achieve good homogenization of the chalcogenide glasses the oven was slowly rocked during the time the ampoule was at high temperature. Thin films were deposited at room temperature onto soda-lime glass, Si and BK-7 optical glass substrates by thermal evaporation of preliminary weighed powdered glassy material or by evaporation from a bigger quantity and stopping the process when the thickness needed is reached. The films were exposed to light from a halogen lamp with an intensity of 20 mW.cm⁻², for saturation times experimentally established for each composition. The composition of both bulk materials and thin films was determined in a scanning electron microscope with an X-ray microanalyzer (Jeol Superprobe 733).

Differential Scanning calorimeter (DSC) (Mettler DSC 12E) was used in non-isothermal regime for determination of the glass-transition temperature, T_g , of both bulk and thin As-S-Tl films using about 15 mg of powdered samples (thin films were scratched from the substrates). Measurements were performed in the temperature range 25-400 °C with heating rate 20 °C.min⁻¹. Samples were encapsulated in aluminum pans. DSC was used for determination of T_g because of higher instrument sensitivity comparing with DTA.

Differential thermal analysis (DTA) (DTA03, R.M.I Electronic Measuring Instruments, CZ) was used for examination of glassy system $(\text{GeS}_2)_{1-x}\text{Tl}_x$ in non-isothermal regime in the temperature range 25-800 °C, heated with heating rate 20 °C.min⁻¹. Small quartz ampoules with powders (about 40 mg weight) were evacuated to 10⁻³ Pa and sealed. The calibration of DTA was made with the help of In, Al, Zn, Pb, and Sn. DTA was used this case for determination of crystallization and melting temperatures, which were expected above measuring range of DSC (400 °C). Pure Al₂O₃ was used as a standard in both cases.

The microhardness (H_k) was measured by a Knoop microindenter. The standard load of 3.75 g was used to produce impressions on each thin film ($\geq 1\mu\text{m}$). The length of the longer diagonal for each impression on the surface was measured. The hardness number H_k , was calculated using the formula

$$H_k = (14228.P/(d \times 0.4))^2,$$

where P is applied load in kilograms and d is the longer diagonal length in millimeters. Each observation was repeated at least ten times and the mean value of the hardness number was determined. The standard deviation was calculated and is shown as an error bar on the hardness bar.

3. Experimental results

3.1. Glass synthesis and element microanalysis

We synthesized chalcogenide glasses with the following compositions $\text{As}_{40-x}\text{S}_{60}\text{Tl}_x$, $(\text{GeS}_2)_{100-x}\text{Tl}_x$ and $(\text{As}_2\text{S}_3)_{100-x}\text{Tl}_x$ ($0 \leq x \leq 10$). The result of the X-ray microanalysis performed (Table 1) showed that the compositions of bulk samples are very close to the expected ones (≈ 1 at.%), while for thin layers some differences were obtained, due to different rate of evaporation of fragments presented in the bulk. This discrepancy was observed when the process was started from a bigger quantity of the powdered glass substance in the boat and was stopped when the needed thickness was reached. The bulk samples were subjected to X-ray and electron diffraction analysis, which confirmed that only amorphous phase, exists. Only $\text{As}_{45}\text{S}_{55}$ glass contained traces of a crystalline phase - As_4S_4 molecules.

3.2. DSC and DTA measurements

The main physical characteristics of the studied chalcogenide glasses are summarized in Table 2. Fig. 1 shows typical DSC curves of the measured bulk samples of $As_{40-x}S_{60}Tl_x$ glasses, while in Fig. 2 the DTA traces of bulk $(GeS_2)_{1-x}Tl_x$ ($0 \leq x \leq 15$) samples are shown. It is seen that T_g decreases when the Tl content increased. Increasing Tl content, breaks most probably the network of $AsS_{3/2}$ breaks which gives as a result into a decrease in both T_g and melting temperature. This behavior is similar to that observed recently [13], where the effect of thallium on the thermally induced structural changes in the As-Se-Tl system was investigated using DTA measurements. The decrease in the value of T_g with increasing thallium concentration may be due to a tendency for weaker bonding formation and hence lower stability in thallium-rich glasses. It is also shown that the value of the melting temperature of glasses decreases with increasing thallium content.

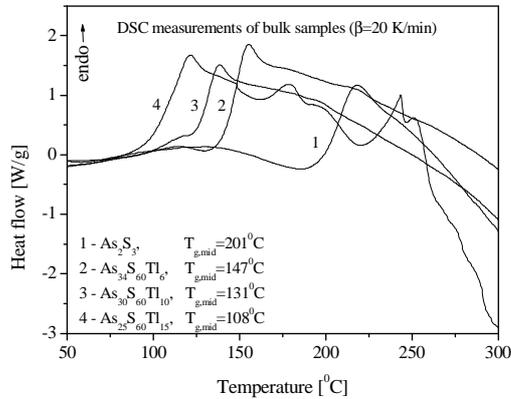
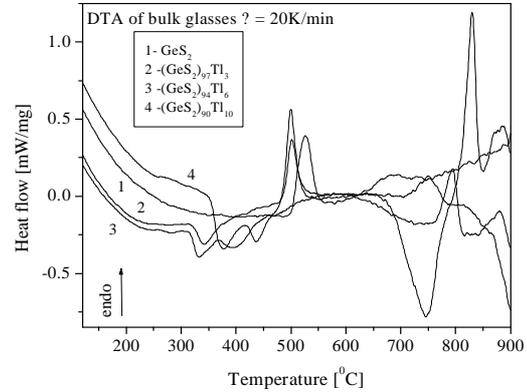
Table 1. Composition obtained from X-ray microanalysis for bulks and thin films investigated.

Composition	Expected composition	Derermined compositions	
		Bulks	Thin films
As_2S_4	$As_{33}S_{67}$	$As_{33.8}S_{66.2}$	$As_{33.6}S_{66.4}$
As_2S_3	$As_{40}S_{60}$	$As_{39.1}S_{60.9}$	$As_{41}S_{59}$
$(As_2S_3)_{97}Tl_3$	$As_{39}S_{58}Tl_3$	$As_{38.8}S_{59.5}Tl_{1.7}$	$As_{43}S_{54.6}Tl_{2.4}$
$(As_2S_3)_{94}Tl_6$	$As_{38}S_{56}Tl_6$	$As_{37}S_{57}Tl_6$	$As_{41}S_{54}Tl_5$
$(As_2S_3)_{90}Tl_{10}$	$As_{36}S_{54}Tl_{10}$	$As_{37.8}S_{53.5}Tl_{8.7}$	$As_{34}S_{53}Tl_{13}$
GeS_2	$Ge_{33}S_{67}$	$Ge_{34}S_{66}$	$Ge_{35.1}S_{64.9}$
$(GeS_2)_{94}Tl_6$	$Ge_{31}S_{63}Tl_6$	$Ge_{30.5}S_{62.5}Tl_{7.0}$	$Ge_{37.1}S_{60.2}Tl_{2.7}$
$(GeS_2)_{90}Tl_{10}$	$Ge_{30}S_{60}Tl_{10}$	$Ge_{26.8}S_{64.2}Tl_{9.0}$	$Ge_{32.4}S_{62.9}Tl_{4.7}$

Table 2. Physical characteristics of some Tl-containing chalcogenide bulk samples and thin films.

Composition	E_g (eV)		T_g (°C)		H_k (kgf.mm ⁻²)	
	Unexp	Exp.	Bulk samples	Thin films	Unexp.	Exposed
As_2S_3	2.39	2.37	203	195	120	145
$(As_2S_3)_{97}Tl_3$	2.38	2.37	172	170	100	125
$(As_2S_3)_{94}Tl_6$	2.35	2.34	160	158	90	110
$(As_2S_3)_{90}Tl_{10}$	2.16	2.14	151	142	80	100
$(As_2S_3)_{85}Tl_{15}$			135	129	70	85
GeS_2	2.53	2.82	513	430	330	535
$(GeS_2)_{97}Tl_3$	2.29	2.33	283	348	280	375
$(GeS_2)_{94}Tl_6$	2.23	2.24	277	330	235	315
$(GeS_2)_{90}Tl_{10}$	2.34	2.39	265	306	215	280

According to Vorobjov et al. [14], when Tl - concentration in the As-S-Tl system increases, the network connection of $AsS_{3/2}$ pyramids disrupts which results in decreasing the melting temperature of crystals and as a result T_g of Tl-containing glasses decreases, comparing with As_2S_3 glass. There are three glass-forming regions in the system As-S-Tl corresponding to the binary systems As_2S_3 , As_4S_3 , Tl_2S_5 and Tl_2S_3 . All these glasses have very different properties.

Fig. 1. DSC curves of bulk $As_{40-x}S_{60}Tl_x$ samples.Fig. 2. DTA curves of bulk $(GeS_2)_{1-x}Tl_x$ samples.

Results of DTA measurements of GeS_2 bulk glasses doped by thallium are shown in Fig. 2. It is seen that thallium reduces significantly T_g from 513 °C for pure GeS_2 down to 265 °C (heating rate 20 C min⁻¹) for the composition $(GeS_2)_{90}Tl_{10}$. For all studied glasses we observed two crystallization temperatures (the second crystallization for Tl-content of 3 at.% is very weak) as well as two melting temperatures due to the formation of several crystalline phases.

3.3. Measurement of the microhardness of thin layers

We have measured the microhardness of thin layers from the systems $(As_2S_3)_{1-x}As_{40-x}S_{60}Tl_x$ and $(GeS_2)_{1-x}Tl_x$ ($0 \leq x \leq 15$) deposited by thermal evaporation with and without residue in the boat at different rate of evaporation. Fig. 3 shows the dependence of the microhardness of unexposed and exposed thin $As_{40-x}S_{60}Tl_x$ films deposited without and with a residue in the boat. The values of the microhardness of unexposed and exposed thin $(As_2S_3)_{1-x}Tl_x$ films deposited at different rate of evaporation are displayed in Fig. 4. It is seen that the conditions of evaporation do not influence the mechanical properties of layers from the studied systems.

In both cases the addition of Tl leads to a decrease in the microhardness. After exposure the values of the microhardness increase by about 20-30 % owing to the structural changes in the layers. The comparison of the first two curves (1 and 2) from Fig. 3 shows that the values of the microhardness are determined mainly by the quantity of As and Tl in the samples while conditions of the film deposition do not influence significantly the H_k values.

The same dependence of the microhardness on the Tl content was observed for thin films from the system $(GeS_2)_{1-x}Tl_x$ ($0 \leq x \leq 15$) (Fig. 4). It is seen that the most ordered are as-deposited thin As_2S_3 and GeS_2 layers. After adding thallium the system becomes less ordered.

4. Discussion

The as-deposited thin films from the system As_xS_{100-x} are a heterogeneous mixture of structural units of the type As_2S_3 , As_4S_3 , As_4S_4 , As_4S_8 , As_4 , S_8 and they contain some homopolar bonds (As-As, S-S). The presence of As_4S_4 molecules is responsible for the appearance of peaks at 375 and 336 cm⁻¹ in the infrared spectra, and the AsS_3 pyramids for the peak at 310 cm⁻¹. During illumination, polymer destructive changes occur leading to the weakening of some bonds and to strengthening of others [15,16]. The irreversible changes occurring after exposure of as-deposited films are accompanied by a density increase of the As-S bonds and subsequent photopolymerization process of As_4S_6 molecules. This leads to an increase in the refractive index and considerable changes in the absorption peaks at 375 and 308 cm⁻¹ obtained by infrared spectroscopy.

The structure of as-deposited films from the system As-S-Tl is more complicated because new structural units, as TlAsS_2 , Tl_3AsS_3 and others, could be formed. The existence of photoinduced structural changes in As-S-Tl chalcogenide films is supported by changes in their optical properties.

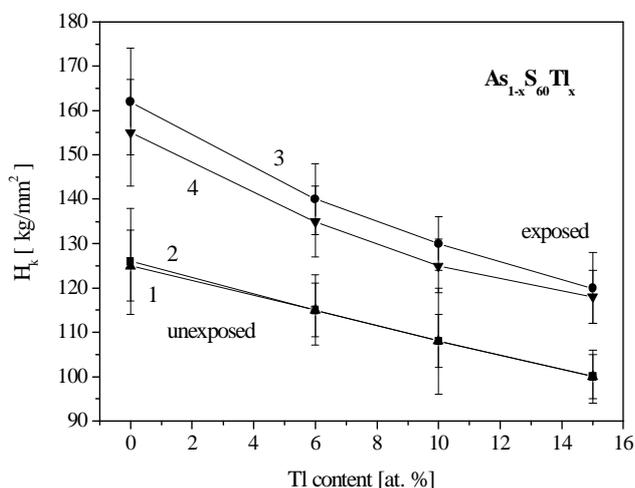


Fig. 3. Dependence of the microhardness on the Tl – content for unexposed and exposed thin $\text{As}_{40-x}\text{S}_{60}\text{Tl}_x$ films deposited without (1, 3) and with (2, 4) a residue in the boat.

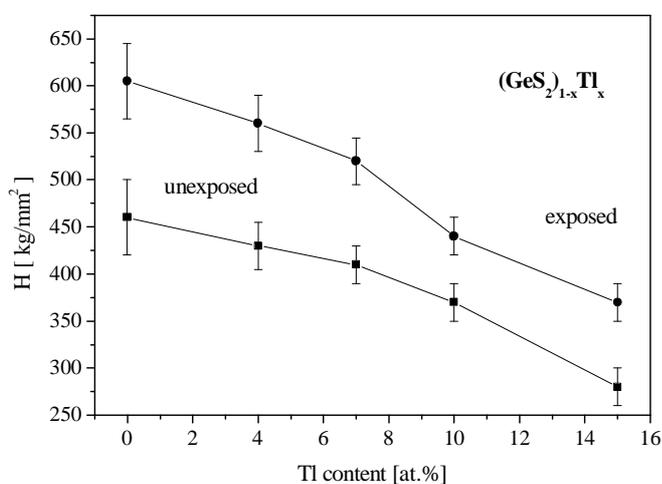


Fig. 4. Dependence of the microhardness on the Tl-content for unexposed and exposed thin $(\text{GeS}_2)_{1-x}\text{Tl}_x$ films.

The addition of Tl to arsenic sulfide leads to the increase in the refractive index and decrease in E_g and to the creation of localized states in the band-gap. The addition of Tl to As_2S_3 results in a considerable decrease in the microhardness of thin films. After illumination it increases by 20 %. This phenomenon could be explained by changes in the structure and the coordination number of layers [12].

As firstly suggested by Heo et al. [17] from the analysis of the core level X-ray photoelectron spectra the Tl atoms are expected to break some As-S-As bridges present in As_2S_3 matrix which leads to formation of some terminal As-S bonds and a creation of Tl-S bonds. Because of the more ionic character of the Tl-S bonds compared with the As-S bonds, two types of S atoms must be distinguished: (i) the bridging sulfur atoms S_b occurring in As- S_b -As bridges and (ii) the non-bridging

sulfur atoms in As-S_{nb}-Tl bridges [18,19]. It means that the addition of a small amount of Tl atoms to As₂S₃ strongly modifies the covalent network forming inhomogeneities and/or creating some covalent fragments linked by weak interactions which strongly modify both the optical band gap and the glass transition temperature. The short-range order is only slightly modified because of small Tl concentration in the samples.

It is seen from DTA measurements of GeS₂ bulk glasses doped by thallium (Fig. 2) that thallium reduces very strongly T_g from 513 °C for pure GeS₂ down to 265 °C (heating rate 20 C min⁻¹) for the composition (GeS₂)₉₀Tl₁₀. We observed two crystallization temperatures (the second crystallization for Tl-content x = 3 at. % is very weak) as well as two melting temperatures in all the cases. Three compounds, Tl₂Ge₂S₅, Tl₂GeS₃ and Tl₄GeS₄ could be formed in the system Ge-S-Tl, which have melting temperatures 853, 770 and 668 K, respectively [20, 21]. In [22] the presence of the following structural units in the Ge-S-Tl glasses is allowed: GeS_{4/2}, Tl⁺S⁻GeS_{3/2} and Tl⁺S⁻GeS_{2/2}S⁺Tl⁺. A statistical disordered distribution of these elements was observed in the whole glass-forming region. The addition of Tl₂S to GeS₂ gives rise to the state changes of Ge atoms in Ge-S-Tl glasses compared with the pure GeS₂ crystals. The increase in the quantity of Tl and S atoms in the system studied could be used as an explanation of the decrease in T_g and Hk of both bulk samples and thin films (Table 2). Unfortunately, weak sensitivity of DTA for T_g determination does not allow to estimate more precisely the T_g values. The more sensitive DSC method will be used later for determination of T_g of thin Ge-containing chalcogenide thin films.

5. Conclusions

Chalcogenide glasses from the systems As-S-Tl and Ge-S-Tl were synthesized and their actual chemical composition has been determined. The effect of thallium on the thermal and mechanical properties of bulk samples and thin films was investigated by DSC and DTA measurements. A correlation between the compositional dependence of the microhardness and glass-transition temperature of As-containing glasses was found. The thin film illumination causes an increase in the microhardness of the layers due to structure densification.

Addition of thallium into the GeS₂ glass decreases significantly the glass-transition temperatures. In Ge-S-Tl bulk glassy systems two crystallization and two melting states were found which could be connected with the existence of two phases in the glasses. The above mentioned Ge-S-Tl system is new and very interesting system and it will be the subject of our further research.

References

- [1] A. Zakery, P. J. S. Ewen, C. W. Singer, A. Zekak, A. E. Owen, *J. Non-Cryst. Solids* **137&138**, 1333 (1991).
- [2] C. W. Slinger, A. Zakery, P. J. S. Ewen, *Applied Optics* **31**, 2490 (1992).
- [3] P. J. S. Ewen, A. E. Owen. *High Performance Glasses*, Eds. M. Cable and J. M. Parker, Blackie, London, 1992, pp. 287-309.
- [4] G. Pfeiffer, M. A. Paesler, S. C. Agarwal, *J. Non-Cryst. Solids* **130**, 111 (1991).
- [5] A. Kolobov, S. R. Elliott, *Advances in Physics* **40**, 625 (1991).
- [6] S. R. Elliott, *Materials Science and Technology, A Comprehensive Treatment*, Ed. by R. W. Cahn, P. Haasen, E. J. Kramer, v.9, *Glasses and amorphous Materials*, p. 376.
- [7] A. Elshafie, *J. Phys. D: Appl. Phys.* **29**, 991 (1966).
- [8] E. Cernoskova, Z. G. Ivanova, V. Pamukchieva, *Termochimica Acta* **316**, 97 (1998).
- [9] E. Cernoskova, J. Holubova, Z. Cernosek, *J. Thermal Analysis and Chemistry* **56**, 423 (1999).
- [10] Z. G. Ivanova, E. Cernoskova, V. Pamukchieva, J. Shanilova, *Termochimica Acta* **345**, 13 (2000).
- [11] K. Petkov, R. Todorov, D. Kozhuharova, L. Tichy, E. Cernoskova, P. J. S. Ewen, to be published.
- [12] R. Todorov, K. Petkov, *J. Optoelectron. Adv. Mater.* **3**, 311 (2001).
- [13] M. F. Kotkata, M. H. El-Fouly, S. A. Fayek, *J. Mater. Sci.* **25**, 2917 (1990).

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- [14] Ju. I. Vorobjov, N. G. Velikova, V. V. Kirilenko, *Izv. AN SSSR, Inorganic Materials* **27**, 2254 (1991).
- [15] U. Strom, T. P. Martin, *Solid State Commun.* **29**, 527 (1979).
- [16] K. Petkov, M. Vlcek, M. Frumar, *J. Mat. Sci.* **27**, 3281 (1992).
- [17] J. Heo, J. S. Sanghera, J. D. Mac-Kenzie, *J. Non-Cryst. Solids* **101**, 23 (1988).
- [18] R. M. Almeda, H. Nasu, J. Heo, J. D. Mackenzie, *J. Mat. Sci. Lett.* **6**, 701 (1987).
- [19] J.-M. Durand, P. E. Lippens, J. Oliver-Fourcade, J.-C. Jumas, M. Womes, *J. Non-Cryst. Solids* **194**, 109 (1996).
- [20] N. D. Axenov, L. L. Makarov, *Phys. Chem. Glasses (Russian)* **19**, 256 (1993).
- [21] G. Z. Vinogradova, in: "Glass-forming and phase equilibrium in chalcogenide systems", Nauka, Moscow, 1984, p. 86.
- [22] H. M. El-Laban, M. C. Gutenev, L. A. Bajdakov, *J. Inorg. Mat. (Russian)* **23**, 2061 (1987).