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THERMAL STABILITY OF THE AMORPHOUS SYSTEM $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$

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Abstract

Results of thermal investigations of the amorphous five-component chalcogenide system $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$ are presented. Differential thermal analysis (DTA), derivative differential thermal analysis (DDTA), and dilatometry were employed to determine the temperatures of softening and partial crystallization of the samples. Thermal treatment of the samples at 1000°C and recording of the corresponding thermogravimetric (TG) and derivative thermogravimetric (DTG) curves allowed an elucidation of the full mechanism of their decomposition, which proceeds via seven characteristic phase transitions.

Keywords: amorphous chalcogenide, system Ge-As-Se-S-I, thermal stability

Introduction

Samples of the investigated five-component system, which has stable physicochemical characteristics, were prepared by the appropriate technological procedure [1]. The samples exhibited high transparency in the visible and IR range of the spectrum. As a function of sample composition, the short-wave boundary of transparence in the visible range is observed even at 510 nm (for $x=0$), whereas the long-wave boundary is approximately constant for all the samples, at 12.5 μm [1], including the wavelength of the CO_2 laser (10.6 μm). Further, the temperature variation of the refractive indices of samples of a particular composition is small or negligible [2, 3], and thus a knowledge of the thermal properties is of great importance for the practical application of these samples.

Experimental

The DTA and thermogravimetric measurements (TG and DTG) were carried out on a Paulik-Paulik-Erdey derivatograph. Samples were heated in open ceramic crucibles in a static air atmosphere, using Al_2O_3 as reference material. 100 mg samples were investigated in the temperature range 20–1000°C, at a heating rate of 10 deg·min^{-1}.

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The DTA and DDTA measurements were carried out with a laboratory-made apparatus up to the temperature of sample decomposition in high vacuum, as described earlier [4].

For dilatometric measurements, a Perkin-Elmer TMA-7 instrument was used in the range from room temperature up to 240°C. Changes in sample length were measured with an accuracy of $\pm 10^{-4}$ mm, and the temperature changes with an accuracy of ±2 deg. The rate of sample heating was 2 deg/min.

Results and discussion

Figure 1 presents results of derivatographic analysis of the system $Ge_{20}As_{14}Se_{26}S_{26}I_{14}$ in the temperature range from 20 to 1000°C. It can be seen that there are no changes in the TG and DTG curves in the range 20–580°C,

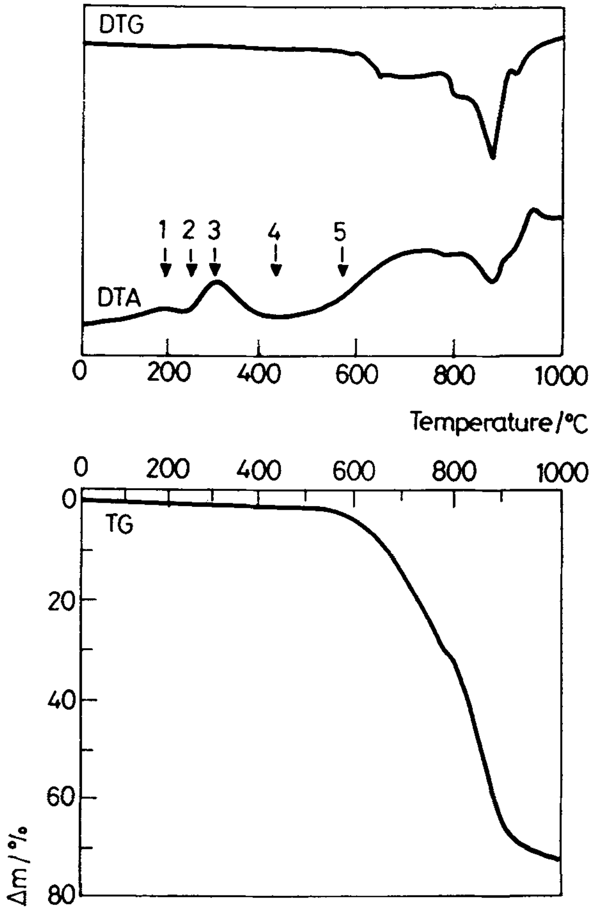

Fig. 1 TG, DTG and DTA curves of $Ge_{20}As_{14}Se_{26}S_{26}I_{14}$

whereas of DTA curve reveals five characteristic temperatures corresponding to the following effects:

(1) the beginning of glass softening at $t_g' = 160$°C;

(2) the range of softening preceding the start of partial crystallization, characterized by the temperature $t_g = 250$°C;

(3) the range of partial crystallization, characterized by the exothermic effect at the characteristic temperature $t_{cr} = 320$°C;

(4) the range of further softening of the amorphous base and melting of the crystalline products formed; and

(5) the beginning of thermal decomposition at $t_d = 580$°C, which represents the limit of thermal stability of the samples.

Figure 2 depicts DTA, TG and DTG curves of the samples $Ge_{20}As_{14}S_{52}I_{14}$ and $Ge_{20}As_{14}Se_{52}I_{14}$, as the two extremal compositions of the investigated system, up to the temperatures of their decomposition. The characteristic temperatures on the curves are denoted by arrows.

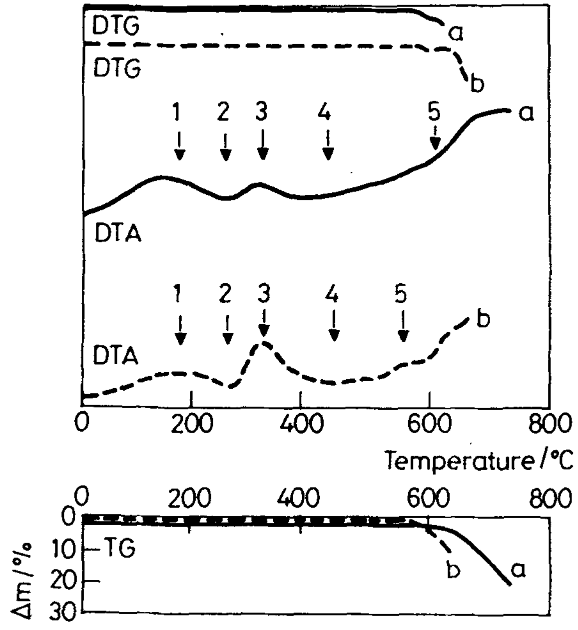

Fig. 2 TG, DTG and DTA curves of the samples. a - $Ge_{20}As_{14}Se_{26}I_{14}$; b - $Ge_{20}As_{14}S_{26}I_{14}$

The above characteristic temperatures for all three investigated samples are presented in Table 1. It may be noted that the characteristic points representing the beginnings of particular phase transitions for the present five-component system coincide with the corresponding temperatures for that four-component

Table 1

Glass	Temperature / °C			
	t'_g	t_g	t_{cr}	t_d
$Ge_{20}As_{14}S_{52}I_{14}$	155	245	315	540
$Ge_{20}As_{14}Se_{26}S_{26}I_{14}$	160	250	320	580
$Ge_{20}As_{14}Se_{52}I_{14}$	180	270	340	600

system in which the given process takes place at a lower temperature. This indicates that the structural characteristics of the quaternary system, at least in part, are preserved in the five-component system.

Figure 3 presents DTA (a and b) and DDTA (a' and b') curves of the samples treated in vacuum. Curves a and a' refer to the sample $Ge_{20}As_{14}Se_{26}S_{26}I_{14}$, while curves b and b' correspond to the sample $Ge_{20}As_{14}Se_{52}I_{14}$. Curves a and a' exhibit two endothermic and one exothermic effects, with characteristic softening temperatures of $t_{g1}=125$°C and $t_{g2}=250$°C, and the temperature of crystallization $t_{cr}=345$°C. The appearance of two softening temperatures is an indication of the complex character of the glass softening processes, which was noted earlier for sulphide glasses with the sulphur concentration exceeding the stoichiometric ratio [5]. Some differences in the characteristic temperatures determined from the DTA curves (Figs 1 and 2) and the DDTA curves (Fig. 3) can be ascribed to the differences in the experimental methods employed.

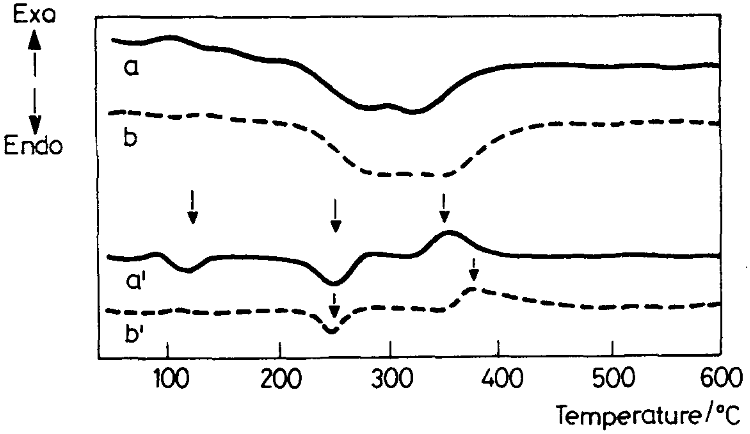

Fig. 3 DTA (a,b) and DDTA (a',b') curves of the samples: a - $Ge_{20}As_{14}Se_{26}S_{26}I_{14}$; b - $Ge_{20}As_{14}Se_{52}I_{14}$

The beginning of glass softening was also observed in the dilatometric curves. Figure 4 demonstrates the relative change in length for the sample

$Ge_{20}As_{14}Se_{18}S_{34}I_{14}$. The measured temperature coefficient of linear thermal expansion is $26.3\times10^{-6}deg^{-1}$ up to the softening temperature ($t_g\approx180°C$), and $45.3\times10^{-6}deg^{-1}$ above this temperature.

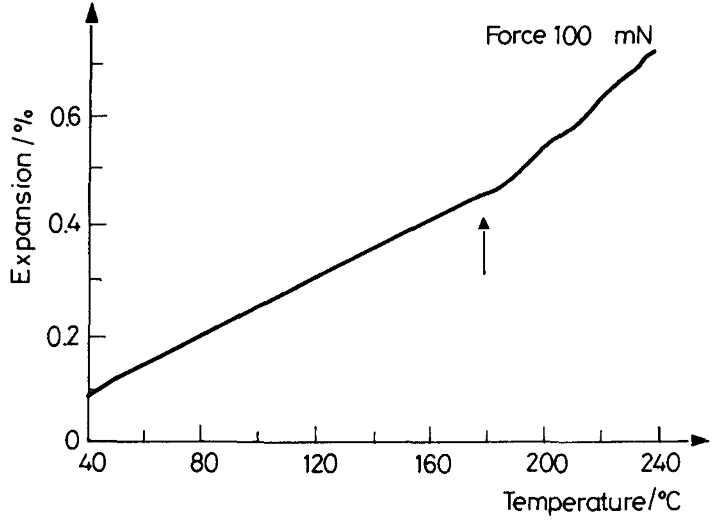

Fig. 4 Dilatometric curve of sample $Ge_{20}As_{14}Se_{18}S_{34}I_{14}$

Table 2

N°	Δt / °C	Δm / %		
		obs	calc	
1.	580–620	2	1.55 (GeS, GeSe)	
2.	620–805	30	27.89 ($9GeS_2$, $9GeSe_2$) 10.80 ($2As_2Se_3$)	40.24–8.93 (20 O_2)= =31.31
3.	805–830	5	6.88 ($2As_2Se_3$)	
4.	830–885	26	25.44 ($4AsI_3$)	
5.	885–915	3	3.26 (AsSI)	
6.	915–925	3	3.92 (AsSeI)	
7.	925–980	2		
Total		71	70.81	
Residue		29	29.19 (20 GeO_2)	

The temperature interval which includes the thermal decomposition of the sample $Ge_{20}As_{14}Se_{26}S_{26}I_{14}$ starts from 580°C and ends at 980°C (Fig. 1). The shapes of the TG, DTG and DTA curves in this temperature range indicate the very complex nature of the decomposition process and, at the same time, the complexity of the glass composition. The TG and DTG curves allowed determination of the temperature intervals in which particular decomposition processes take place, whereas the extrema on the DTA curves indicate whether these changes are exothermic or endothermic. These data (Table 2) were the basis for postulating the molecular composition of the glass:

$$Ge_{20}As_{14}Se_{26}S_{26}I_{14} \rightarrow$$

$$2\ As_2S_3 + 2\ As_2Se_3 + AsSI + AsSeI + 4AsI_3 + 9\ GeS_2 + 9\ GeSe_2 + GeS + GeSe$$

On the basis of this chemical composition, it was possible to calculate the contents of particular molecules in mass percent. These data are included in Table 2, together with the experimentally determined percentage mass losses of the sample. In the first temperature interval, from 580°C to 620°C, the mass loss was 2%, which could be ascribed to the dissociation of the molecules GeS and GeSe, with emission of S and Se to the atmosphere. In the subsequent temperature interval, the dissociation of the molecules GeS_2 and $GeSe_2$ takes place with simultaneous elimination of an As_2Se_3 molecule. The dissociation of GeS_2 and $GeSe_2$ proceeds simultaneously with the oxidation of Ge, which takes place in air at 600–700°C. The mass loss calculated for the given decomposition process, corrected for the percentage mass increase due to the oxidation of germanium, agrees well with the experimentally determined value ($31.31\%_{calc} \approx 32\%_{obs}$). In this temperature interval, the shape of the DTA curve suggests the occurrence of a mild exothermic process that can be ascribed to oxidation of germanium. The further decomposition proceeds according to the sequence presented in the Table, which reveals the relatively good agreement of the experimentally determined and calculated mass losses. The mass of the residue after decomposition 29%, agrees well with the value calculated for GeO_2 (29.19%).

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Zusammenfassung — Chalkogenidsystemes $Ge_{20}As_{14}(Se_xS_{1-x})_{52}I_{14}$ dargelegt. DTA, DDTA und Dilatometrie wurden zur Bestimmung des Erweichungspunktes und der Temperatur für eine partielle Kristallisation der Proben eingesetzt. Thermische Behandlung bei 1000°C und die Aufzeichnung der entsprechenden TG- und DTG-Kurven erlaubte es, ihren über sieben charakteristische Phasenumwandlungen verlaufenden Zersetzungsmechanismus voll zu klären.