Journal of Thermal Analysis, Vol. 52 (1998) 553-558

SOFTENING TEMPERATURE OF THE AMORPHOUS Cu–As–Se–I SYSTEM

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(Received July 17, 1996; in revised form May 14, 1997)

Abstract

A detailed characterization of softening temperatures of a series of samples of the amorphous Cu As Se I system is presented. Previous investigations showed that the most effective mode of erasing optical information stored in this complex quaternary system of chalcogenide amorphous semiconductors (ChAS) is a thermal treatment of the samples at temperatures close to their softening points.

On the basis of the results obtained using a range of thermal methods it was possible to determine the interval of the beginning of the softening process of the glass, as well as the coefficient of linear expansion of the samples before and after their softening.

Measurements of the temperature dependence of the thin film transparencies enabled the determination of softening temperatures of such types of samples of the investigated system, including the reversibility of the processes determining their transparency properties.

Keywords: amorphous chalcogenide, softening temperature, system Cu–As–Se–I

Introduction

As the samples of the investigated system contain selenium, they belong to the so-called chalcogenide amorphous systems (ChAS), whose physico-chemical properties are strongly dependent on the number and type of the elementary components involved. It is known that the variety of properties of such glasses is substantially enriched by introducing a third component [1, 2], whereas a fourth component expands their variety spectrum, and contributes especially to the changes in their mechanical characteristics [3, 4].

The importance of studying ChAS, in addition to the already known field of their application in special optical equipment, arises also from the clear indication of the possibility of using their photorecording properties. The fact that the introduction of Cu, Ag or Cd into a ChAS's brings about very large variations in the essential characteristics of photochromic glasses has prompted studies of the consequences of introducing copper into the pseudo-binary system As_2Se_3–AsI_3.

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The present report describes the results of thermal and optical investigations of the title system aiming at characterization of the processes of erasing optical information.

Experimental

Samples of the investigated system were synthesized and their films ($d \approx 1$ μm) prepared by evaporation according to known procedures [5, 6].

For determining the thermal characteristics and defining the range of existence of the amorphous phase a Paulik-Paulik-Erdey Derivatograph, type 1000 was used. Samples were heated in open ceramic crucibles in an air atmosphere, using Al_2O_3 as inert standard. The heating rate was 10 K min^{-1} and the mass of the samples was 100 mg.

DTA and DDTA measurements up to the temperature of sample decomposition in high vacuum were carried out on a laboratory-made apparatus, as described earlier [7]. The heating rate was 5 K min^{-1} and the mass of the glasses was 1 g.

DSC measurements were carried out on a DuPont calorimeter, type 910 in an air atmosphere. The range of thermal treatment was 290–770 K, the heating rate 10 K min^{-1} and the mass of the samples 7–10 mg. Dilatometric measurements in the range from room temperature up to 500 K use were made by a Perkin-Elmer TMA-7 instrument. Changes in sample length were measured with an accuracy of $\pm 10^{-4}$ mm, and the temperature changes with ±2 K. The rate of sample heating was 2 K min^{-1}.

The thermal treatment of thin films to study the reversibility of their properties was carried out using a special laboratory-made adapter, especially designed for the purpose of these experiments [8]. First, using a He–Ne laser beam (λ = 632.8 nm, p = 40 mW cm^{-2}) optical information was recorded at room temperature for each sample of the investigated system $Cu_x(As_{38.5}Se_{54}I_{7.5})_{100-x}$. Then, preserving carefully the experiment geometry, changes in transparency of thin films in a dynamic regime were monitored for radiation of the same wavelength but of low intensity, so that its effect on the material can be neglected. The necessary attenuation of the laser beam was achieved by putting absorption filters in front of the sample. The rate of sample heating and cooling was 10 K min^{-1}.

Results and discussion

In Fig. 1 are presented DTA curves for a series of glass samples of the system $Cu_x(As_{38.5}Se_{54}I_{7.5})_{100-x}$ (x = 0, 5, 10, 15, 20, 25 at%).

A general characteristic feature of the derivatographic behaviour of glasses of the type $Cu_x(As_{38.5}Se_{54}I_{7.5})_{100-x}$ is that their thermal treatment yields total sample decomposition and formation of the corresponding amount of copper oxides (Table 1). By analyzing the DTA curves for the whole series of samples (Fig. 1), the expected complexity of their patterns can be observed as a consequence of the increase in copper content.

Table 1 Softening points and contents (mass%) of copper oxides resulting after thermal treatment

Sample	T_g/K	Δm_{obs}	Δm_{calc}
$As_{38.5}Se_{54}I_{7.5}$	433	0	0
$Cu_5(As_{38.5}Se_{54}I_{7.5})_{95}$	438	7	5.27
$Cu_{10}(As_{38.5}Se_{54}I_{7.5})_{90}$	458	12	10.56
$Cu_{15}(As_{38.5}Se_{54}I_{7.5})_{85}$	458	19	15.85
$Cu_{20}(As_{38.5}Se_{54}I_{7.5})_{80}$	463	24	21.15
$Cu_{25}(As_{38.5}Se_{54}I_{7.5})_{75}$	473	28	26.46

Namely, with an increase in copper content in a given glass, the number of different structural units formed is constantly increasing, which culminates in the system $Cu_{25}(As_{38.5}Se_{54}I_{7.5})_{75}$ (Fig. 1), which is analogous to the situation in $Cu_x(As_2Se_3)_{1-x}$ [1].

The results of thermal treatment of the samples obtained by dynamic DDTA method are shown in Fig. 2. On the basis of the obtained DTA and DDTA curves it was possible to determine the temperature of softening (T_g), temperature of crystallization of particular structural units (T_{cr}) and the temperature of the beginning of melting of the crystalline forms (T_m). It can be noticed that the beginning of the softening process varies, and T_g shows an increase from 433 to 473 K with the increase in copper content (Table 1).

In Fig. 3 are presented DSC curves for the glass without Cu and for a sample representing the system with Cu. Analysis of the DSC curves permitted a more

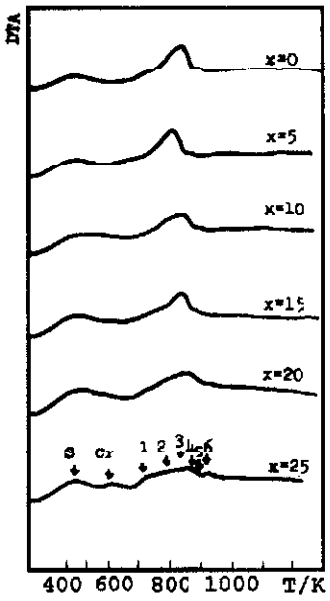

Fig. 1 DTA curves of samples of the $Cu_x(As_{38.5}Se_{54}I_{7.5})_{100-x}$ system

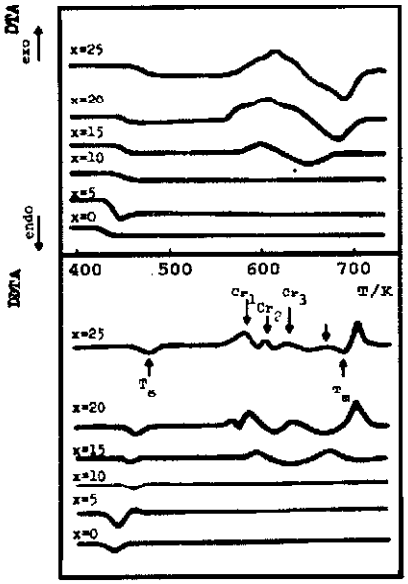

Fig. 2 DTA and DDTA curves of samples of the $Cu_x(As_{38.5}Se_{54}I_{7.5})_{100-x}$ system

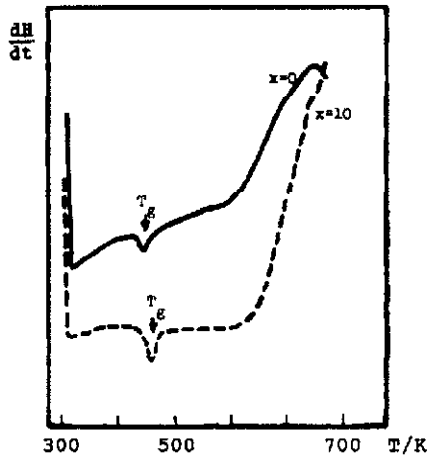

Fig. 3 DSC curves of samples with 0 and 10 at% Cu

precise characterization of the softening processes and determination of their quantitative parameters. It was established that the softening process for the sample without copper starts at 426.7 K whereas the temperature of 439.6 K can be considered as the softening point. This transformation is accompanied by an enthalpy change of 45.2 J kg^{-1}, i.e. 3.74 kJ mol^{-1}. For the sample with 10 at% Cu DSC analysis gave the temperature of the beginning of softening process of

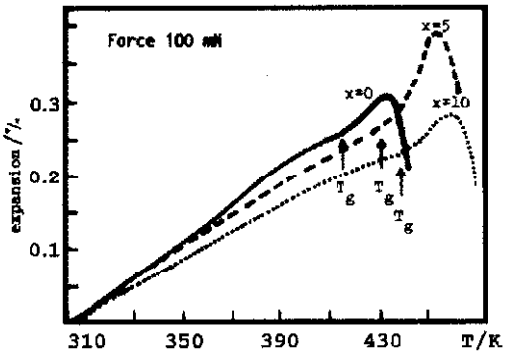

Fig. 4 Dilatometric curves of samples with 0, 5 and 10 at% Cu

446.5 K and T_g= 456.6 K, to which corresponds an enthalpy change of 49.2 J kg^{-1} (3.89 kJ mol^{-1}).

The beginning of glass softening was also detected by dilatometric measurements. Figure 4 shows the results of thermomechanical analysis, i.e. the relative changes of the length of the samples with 0, 5 and 10 at% Cu. It was established that the coefficient of linear expansion changes in the range of $24.6 \cdot 10^{-6}$ K^{-1} to $18.0 \cdot 10^{-6}$ K^{-1} before, and $84.0 \cdot 10^{-6}$ K^{-1} to $31 \cdot 10^{-6}$ K^{-1} after the softening point. The softening temperatures determined by this method were 415.5, 437 and 441 K for the samples with 0, 5 and 10 at% Cu, respectively.

In Fig. 5 are presented the temperature dependences of the relative transparencies τ_t/τ_{t_0}, where τ_t is the transparency of the thin film at the temperature t, and τ_{t_0} is its transparency at the initial (room) temperature. The results obtained by

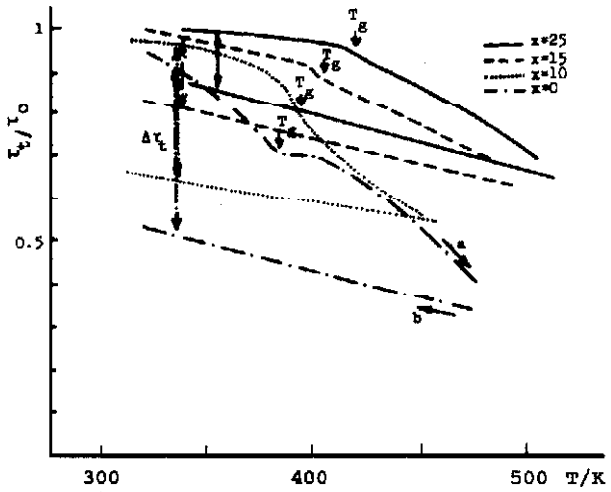

Fig. 5 Temperature dependence of the transparency of a thin film: curve a – changes obtained for temperature increase, curve b – changes obtained for temperature decrease

Table 2 Characteristics of the temperature depedence of thin film transparencies

Sample	T_g/K	$\Delta\tau_t$/%
$As_{38.5}Se_{54}I_{7.5}$	379	39
$Cu_{10}(As_{38.5}Se_{54}I_{7.5})_{90}$	387	32
$Cu_{15}(As_{38.5}Se_{54}I_{7.5})_{85}$	397	17
$Cu_{25}(As_{38.5}Se_{54}I_{7.5})_{75}$	418	14

measuring the temperature dependence of thin film transparencies enabled assessment of both T_g and the effectiveness of optical recording. Namely, at the temperature characterizing the softening process, there is a break in the slope of the curve $\tau_t/\tau_{t_0} = f(t)$ recorded for the process of sample heating. Table 2 contains the T_g values, as well as the values of $\Delta\tau_t$, indicating a change in the relative transparency at room temperature before and after sample heating, which is the measure of thin film transparency effectiveness.

Conclusions

Analytical characterization of non-crystalline solids and their thin films shows that:

It is generally necessary to use a combination of different analysis methods to characterize and determine the thermal stability of the materials in the bulk and thin film forms.

The determination of the softening temperature in bulk chalcogenide glasses by differential thermal analysis, derivative differential thermal analysis, dilatometry, and measurements of the temperature dependence of thin film transparencies, can contribute to a further improvement in the application of samples of the Cu–As–Se–I system as a medium for optical recording of information.

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