THERMOPHYSICAL AND STRUCTURAL PROPERTIES OF THE GLASS SYSTEM As—S—Ga

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Differential thermal analysis (DTA), powder X-ray analysis, and kinetics of crystallization were performed in a gallium doped As_2S_3 glass system. Partial crystallization of the separated phase indentified by X-ray analysis is due to the thermal treatment of samples with a Ga content at about 5 at % at a temperature $T_x \sim 255$ °C. The activation enthalpy of crystallization of this phase is 1.46 eV.

ТЕРМОФИЗИЧЕСКИЕ И СТРУКТУРНЫЕ СВОЙСТВА СТЕКЛООБРАЗНОЙ СИСТЕМЫ As—S—Ga

Для стеклообразной системы As_2S_3 с примесью галия проведены дифференциальный термический анализ (ДТА), порошковый рентгеноанализ и кинетика кристаллизации. Частичная кристаллизация сепарированной фазы, которую можно идентифицировать с помощью рентгеноанализа, возникает посредством термообработки образцов с содержанием галия порядка 5 ат% при температуре порядка 255° С. Активационная энтальпия кристаллизации этой фазы равна 1.46 эв.

I. INTRODUCTION

Doping model binary chalcogenide glasses (such as As_2S_3, As_2Se_3, etc.) by various impurities has principally two aims. The first is connected with the study of common problems of incorporation of impurities into such a model matrix and the corresponding response in the variation of physical and physicochemical parameters. The second tries to utilize the already existing basic knowledge for practical application, the choice of the dopant being already motivated by the kind of application. Let us note in this connection the realization of the reversible holographic optical record of information of high density performed on the basis of a binary As—Se system doped by either sulphur or germanium [1, 2].

The doping of the binary system As—S by gallium, investigated in this paper, is interesting from the viewpoint of the results obtained in our previous works [3, 4, 5]. It was shown there that the doping of the model glass system Ge_2S_3 by copper

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causes the formation of several glassy phases which can be transformed by proper thermal treatment, into the corresponding crystalline forms.

Gallium, used in this study as a dopant in As—S glass, reacts chemically both with arsenide and sulphur, the semiconductor of the GaAs type being especially widely applicable today. Therefore, our investigation aims to study the glass-forming region, to identify the formed phase, and to determine the thermal properties and crystallization kinetics of the $As_2S_3 + x$ at % Ga glass. Especially possibility of separating regions of different chemical types with a possible utilization led probably also other authors to the study of the influence of gallium on the changes of various properties of glassy systems with a substantial fraction of arsenic [6, 7, 8].

II. EXPERIMENTAL

The bulk glasses $As_2S_3 + x$ at % Ga were synthetized from high purity (99.999 %) elements in evacuated quartz ampoules with an internal diameter of 8 mm. The synthesis of this system (total amounts of elements being 3 g) was performed at a gradually increased temperature (up to 800 °C), the homogenization of the melt was carried out at this temperature for 5 hours in a rocking furnace. The quartz ampoule with the melt was then cooled down to room temperature by free quenching in air for $x < 5$ whilst, for $x \geq 5$, we use quartz ampoules of smaller diameters and the cooling was performed by immersing into water at 0 °C. The detailed description of the As—S system samples preparation is given in our previous paper [9].

The glass-forming limit for the samples prepared by free quenching in air is $x \sim 5$. According to the X-ray analysis the samples with $x = 5$ were glass-crystalline whilst concentrations $x < 5$ were characterized by a diffuse profile of the Debye—Sherer-gram. At concentrations $x \geq 5$ prepared in the smaller amounts (~ 200 mg) by rapid quenching in air the Debye—Sherer-gram exhibited the first indications of crystalline phase at concentrations from $x > 10$. With regard to the employed technology these data may be related to glass-forming limits.

The differential thermal analysis of the samples prepared in this way was performed by a commercial DU PONT device with a calorimetric DSC cell, in an inert gas flow (argon at 0.2 l/min), the temperature rise rate being 20 °C/min. The analyzed samples were in powdered form, weighing 20 mg, placed in aluminium pans, with sapphire as a reference sample. In order to test the reaction of our samples with the aluminium pan we performed several measurements under the same conditions, using, however, a specially adjusted quartz pan. Details concerning the calibration of the device are given in our previous paper [10].

The powder X-ray analysis of samples immediately after preparation as well as after the corresponding heat treatment was performed with a commercial Phillips device (model PW 1049) by means of CuK_α radiation. The corresponding heat treatment was performed directly in a DSC cell of the DTA instrument in an argon atmosphere.

III. RESULTS AND DISCUSSION

Differential thermal analysis

The DTA thermograms of the prepared glassy and glass-crystalline samples are shown in Fig. 1. In a pure binary system ($x = 0$) the endothermic reaction in a temperature range close to 200 °C dominates in the thermogram, corresponding to the transition of this system to the liquid state (i.e. the transformation region). If we relate — as it is usually done — to the inflection point of this dependence the value of the so-called transformation temperature T_g, our measurements show that $T_g = 195$ °C. This value of T_g temperature is in good agreement with measurements of other authors (e.g. see [11]). A remarkable property of this glass system is, as follows from Fig. 1, the fact that it passes — contrary to other chalcogenide glasses — into the liquid state without a particular crystallization of any glassy phase. This is reflected in the course of the thermogram as an absence of any exothermic reaction.

As regards the values of the Ga dopant in the concentration range $x \sim 1$ the performed DTA shows that a small drop of T_g occurs, thus confirming the incorporation of Ga into the glassy As_2S_3 matrix as well as a lower stability of this more complex glass.

At higher amounts of the dopant ($x = 5$, Fig. 1) a clear decrease of T_g appears down to the value $T_g \sim 175$ °C with a simultaneous formation of a new exothermic transformation with a maximum at the temperature $T_k = 255$ °C and an endothermic transformation $T_{m1} = 295$ °C of this glass. With the highest amounts the Ga dopant ($x > 10$) in such a glass-crystalline material a new exotherm with $T_{m2} = 310$ °C is further developed.

The atmosphere in which they are performed plays an important role in these DTA measurements, as noted by Hrubý [12]. In order to demonstrate this fact also in our case, we performed some parallel DTA thermograms in air. Under such experimental conditions an origin of new transformations can be observed (e.g. formation of an exotherm at the T_k temperature, Fig. 1) corresponding to the oxidation of the material, and not having its origin in the transformations of the structure of the glassy material itself.

Fig. 2 shows DTA thermograms for $x = 5$, the curve 2 being measured at a slow cooling of the sample after the preceding measurement 1. It can be seen that the exothermic reaction at the temperature T_k has an irreversible character. This fact indicates that the transition of the system is that from the metastable state (induced by rapid quenching) to a state which is thermodynamically more stable. We shall

show in Sect. 3b that the samples which underwent such a heat treatment are characterized by the formation of new diffraction lines in the X-ray spectrum.

The existence of an exotherm at T_k conditioned by Ga doping (Fig. 1) can partly support picture of phase separation present in this glass. A definite confirma-
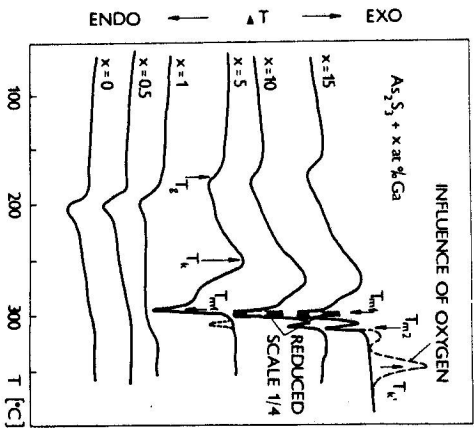
Fig. 1. DTA thermograms for the system As_2S_3 + x at.% Ga. Samples with $0<x<1$ and $x=5$ (dashed line) were obtained by free quenching in air, those with $5<x\leq15$ by quenching in water.
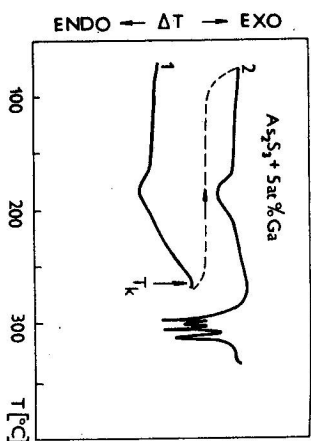Heating rate 20 °C/min., dose: 20 mg.

Fig. 2. Irreversible exothermic transformation at the T_k temperature. $As_2S_3 + 5$ at.% Ga sample prepared by free quenching in air.

tion of this hypothesis from the viewpoint of the differential thermal analysis assumes an existence of transformation region corresponding to a separated non-crystalline phase (see e.g. [13]). However, this transformation region may be overlapped by existing thermal defects with a thermal colouring much more intense than the proposed endothermic reaction corresponding to the separated transformation region. The principle possible underlying such a mechanism was considered by Voldán [14].

We therefore tried to perform the transmission electron microscopy of the $As_2S_3 + 5$ at.% Ga glass, which enables a very selective resolution of various atomic configurations differing by their electron density from the surrounding matrix. In connection with the corresponding differential thermal analysis these findings are assumed to be a sufficient proof of the existence of phase separation in the glass basis of all the available data from literature [15]. However, it was not possible to perform such observations due to high evaporation of the material while interacting with the beam of the impinging electrons.

On the basis of our differential thermal analysis (and taking into account the powder X-ray analysis) we can conclude that in As_2S_3 glass systems with $x\geq5$ are characterized by the formation of such structural forms which crystallize at the T_k temperature and their melting point is T_{m1}. The existence of an endotherm with
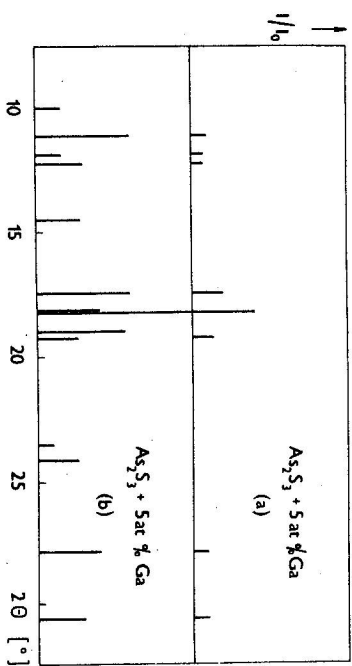
Fig. 3. Schematical X-ray diffraction records a) As_2S_3 sample + 5 at.% Ga quenched in air, b) the same sample after heat treatment at the T_k temperature.

a peak at T_{m2} is characteristic for all glass-crystalline samples and, obviously, it is related to the presence of the crystalline phase occurring in the material. In order to find a correspondence between the existing literature data and the values obtained in our experiments we tried next to analyze the originating phase of the glass-crystalline system.

Powder X-ray analysis

In Fig. 3 some schematic diffraction records of powdered $As_2S_3 + 5$ at.% Ga samples are shown, where (a) corresponds to a sample prepared by free quenching in air, (b) the sample underwent heat treatment at the T_k temperature. The X-ray diffraction diagrams of samples of a similar composition prepared by quenching in water had diffused profiles. The glass-crystalline sample according to the record from Fig. 3 was characterized by endotherms at the T_{m1} and T_{m2} temperatures.

We tried to carry out phase separation of the obtained spectra on the basis of data existing up to 1971 [16]. We took into account the possible formation of all binary (As—S, As—Ga, Ga—S) and ternary (As—S—Ga) compounds, however, we did not succeed to index crystalline phase of corresponding compositions on the basis of all the available data from literature.

On the basis of our previous experience with the glass system As_2S, with $y<3$ we may, however, conclude that the glassy phase crystallizing at T_k has a ternary

IV. CONCLUSIONS

(a) The doping of the As_2S_3 glass by gallium causes a decrease of the transformation region of this glass as well as pronounced changes (origin of new endo- and exothermic transformations) in the DTA thermograms.

(b) For the glass $As_2S_3 + T$ at % Ga the exothermic reaction at $T_x = 255\,°C$ is surpassed by the formation of a crystalline modification with a probably ternary composition.

(c) The crystallization activation enthalpy of this phase is 1.46 eV.

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