CHALCOGENIC GLASSES OF THE As$_2$Se$_x$ SYSTEM

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Investigation of structure of chalcogenic glasses in the As$_2$Se$_x$ $(2 < x < 3)$ system is described. An area between two points of the phase diagram, which correspond to stable As$_2$Se$_3$ and As$_2$Se$_2$ components, has been studied by electron microscopy, X-ray analysis, differential thermal analysis, and infrared spectroscopy. For glass of composition As$_2$Se$_{2.8}$ and to a greater extent for the As$_2$Se$_{2.44}$ glass, the droplet structure, which is interpreted as a phase area richer in crystalline As$_2$Se$_3$, has been found.

Many authors[1-5] have been lately concerned with structure of chalcogenic glasses of various composition. In all of these papers, structural changes after a thermal treatment of glasses have been particularly studied. To the As$_2$Se$_x$ system, studied by us, the As$_2$S$_x$ system is formally the most similar. The latter system was for $x < 3$ studied by Maruno and Noda[6] who likewise describe formation of the droplet structure which is connected with a separation of phases in a certain narrow area of glass composition. The system of chalcogenic glasses containing arsenic has been comprehensively described by Khvorostenko[7]. Nemilov and Petrovskii[8] calculated energetic parameters of viscosity and were able to prove existence of the As$_2$Se$_3$ and AsSe compounds. Dembovskii[9,10] prepared glasses of various As–Se composition, confirmed existence of the As$_2$Se$_3$ and AsSe compounds by determining dependences in the glass forming region, and anticipated existence of As$_2$Se$_5$ and As$_2$Se compounds. Later on, Dembovskii[11] studying crystallization of glasses in the Se–As$_2$Se$_3$ system showed that As$_2$Se$_3$ crystallizes more easily than AsSe. Dembovskii and Luzhnaya[12] examined phase diagram of the As–Se system by DTA and X-ray diffraction, and determined region of existence of the As$_2$Se$_3$ and AsSe compounds. A system of chalcogenic glasses As$_2$Se$_x$ $(1.07 < x < 18)$ was examined by Kohout, Vaško, and Wachtl[13]. By using electron microscopy they found the droplet structure for glasses of composition As$_2$Se$_x$ $(2 < x < 3)$.

The present paper includes results of a detailed study of chalcogenic As$_2$Se$_x$ glasses within a narrow range of composition $(2 < x < 3)$, electron microscopy, X-ray diffraction, and DTA being used as methods of investigation.

EXPERIMENTAL

Preparation of Samples

As starting material to prepare chalcogenic glasses of composition As_2Se_x ($2 < x < 3$), the As_2Se_2 glass was employed, prepared by synthesis from the elements, contamination of oxygen without using deoxidizing agents being prevented.

Quartz ampoules, which were cleaned by HF and heated at a temperature of $900-1000°C$ for 8 hours, were in all cases used for the synthesis. The starting elements As and Se were of 99.9999% purity; selenium was, in addition, redistilled under vacuum to remove last portions of SeO_2. As_2Se_2 was prepared in an ampoule, divided by a partition wall into two sections, in the following way: one part of the ampoule containing redistilled selenium was evacuated to a pressure of $1.33 . 10^{-2}$ Pa and sealed. Arsenic, which was after evacuation to $1.33 . 10^{-2}$ Pa freed of surface oxide layer by heating to a temperature bellow the distillation point of arsenic, was inserted into the other part of the ampoule which was sealed afterwards. After breaking the partition wall, arsenic was resublimed towards selenium; a temperature not higher than 500°C was employed. The part of the ampoule, containing pure selenium and arsenic, was sealed and put into a homogeneization rocking furnace. Synthesis of 350 g of As_2Se_2 was carried out for 12 hours at a temperature of 950°C. The other examined chalcogenic glasses of composition $As_2Se_{2.44}$, $As_2Se_{2.8}$, and As_2Se_3 were produced in the homogeneization furnace under following conditions: amount, temperature, and time of synthesis were 50 g, 750°C and 8 hours, respectively. In these cases, elementary selenium was added to the starting As_2Se_2 glass.

All the samples were produced in a form of small cylindric blocks of max. diameter 20 mm. Homogeneity of the samples thus prepared was examined by infrared defectoscopy on polished sections of the blocks. Composition of all the samples was checked by an electron microprobe, differences between the composition of the melt and weighed portions of the starting elements were negligible.

Electron Microscope Study of Surfaces

The surfaces of chalcogenic As_2Se_3, $As_2Se_{2.8}$, $As_2Se_{2.44}$, and As_2Se_2 glasses were examined by colloidal chromium-shadowed replicas which were taken from fresh fracture surfaces or natural surfaces of solidified melt. Electron microscope Tesla BS 513 or Phillips EM 300 were employed.

X-Ray Diffraction

In order to examine the structure of glasses, the Debye-Scherrer method adapted for planar samples was used. Both platelets produced by cutting fused blocks and samples of powdered material were studied. Radiation of CuK_α and photographic recording of the diffraction lines in chamber Chirana, 114 mm in diameter, were employed. This arrangement made it possible to record angles corresponding to values $d_{max} = 0.60$ nm. Photographic records of diffraction patterns were photometered by means of a very sensitive microdensitometer MK III CS, Joyce, Loebl & Co. Ltd., England.

Precision of readings was 0.1 mm, which for ϑ angles about 15° represents an error of determining $d \pm 0.001$ nm max.

DTA

Differential thermal analysis was accomplished on apparatures of our own construction, which were described by Rosický[14], Blažek and Endrýs[15], and Ederová[16]. The weighed portions of the

sample and standard (freshly heated Al_2O_3), which were placed in platinum crucibles, varied about 30 mg. The measurement was carried out in a flow of argon (0·8 l/min) at a heat rate of 5°C/min. A strip chart recorder EZ 2 was used to record the DTA curves.

Optic Homogeneity Study

Optic homogeneity of chalcogenic glasses of the As_2Se_x system was studied by infrared defecto-scopic methods[17], in particular by infrared microscope in normal and polarized light at wave-lengths within 1 and 1·2 μm.

RESULTS AND DISCUSSION

The photographs of surfaces of the As_2Se_x compounds are presented in Fig. 1–4.* Direct enlargement of all the photographs (colloidal replica shadowed with chromium) was 27 000, the abscissa in each figure indicates a distance of 1 μm.

In Fig. 1, the fracture surface of As_2Se_3 is illustrated. The surface has an imperceptible relief structure, the raster has its origin in shadowing with chromium. Fig. 2 shows the fracture surface of $As_2Se_{2.8}$, where the so-called droplet structure already appears. The number of droplets is, of course, much smaller than for $As_2Se_{2.44}$, which is shown in Fig. 3a and 3b, where the fracture surface of $As_2Se_{2.44}$ and surface of the solidified $As_2Se_{2.44}$ melt, respectively, are presented. In a fresh fracture surface, the droplet aggregates are more irregular and with sharper contours than regular eliptic droplets found in the solidified melt surface. Fig. 4 shows the fracture surface structure of the As_2Se_2 sample which has a more distinct structure than As_2Se_3, but where typical droplet aggregates which occurred in region $2 < x < 3$, cannot be found.

Results of the X-ray analysis of individual As_2Se_x compounds are summarized in Table I. Owing to the fact that in all cases compounds of vitreous character were involved, which contained only a very small amount of the crystalline component, merely position of the intensity maxima of three diffusion lines typical for vitreous components could be reliably determined by visual observations of the X-ray pattern. In photometric records of the X-ray patterns a greater number of small sharp peaks could be observed, whose positions correspond with a great precision to interplanar distances d of crystalline compounds As_2Se_3 for glasses having composition As_2Se_3, $As_2Se_{2.8}$, $As_2Se_{2.44}$, and of the crystalline As_2Se_2 compound for glass of composition As_2Se_2. Values of interplanar distances d for crystalline As_2Se_3 and As_2Se_2 were taken from the literature[18,19]. In order to check precision of the measurement, an X-ray pattern of a ground As_2Se_3 single crystal (As_2Se_2 single crystal was not available) was made, whose d values were read out both from the X-ray pattern directly and from its photometric record. As follows from Table I,

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* See insert facing page 2070.

Table I

Values of Interplanar Distance d (nm)

Tabulated		Found					Tabulated	
As_2Se_3 ref.[18]	As_2Se_3 ref.[19]	As_2Se_3 single crystal	As_2Se_3 glass	$As_2Se_{2.8}$ glass	$As_2Se_{2.44}$ glass	As_2Se_2 glass	As_4Se_4 acc.[18]	AsSe acc.[19]
								0·775
						0·703	0·697	
						0·622	0·621	
						0·582	0·581	
						0·558	0·556	
								0·546
0·519		0·538	0·510	0·530				
0·498		0·497			0·493			
	0·487							
						0·474	0·472	
								0·464
0·405		0·405					0·419	0·419
0·395		0·396	0·392	0·396				
						0·385	0·383	
0·376		0·376	0·371	0·371				
						0·349	0·347	
0·326		0·327				0·324	0·325	0·325
0·314		0·314	0·313	0·317		0·314	0·314	0·313
						0·301	0·301	0·300
0·295			0·294		0·296	0·294	0·294	0·294
0·291		0·292	0·289					
0·287	0·286			0·287	0·285		0·286	0·287
0·282		0·282	0·280	0·280	0·280	0·280	0·279	0·279
								0·277
0·262		0·262	0·263		0·262			
						0·258	0·258	0·260
0·255	0·251	0·255	0·256					
0·249		0·249	0·248	0·250				
						0·246	0·246	0·246
0·241		0·241	0·243					0·241
0·235			0·236			0·235	0·236	0·234
						0·231	0·231	0·230
						0·226	0·225	0·224
0·218			0·218			0·218	0·218	0·219
0·212	0·208	0·212			0·211	0·211		
0·195	0·196	0·196	0·195	0·196	0·196			1·196
						0·186	0·185	0·184
0·181		0·181	0·181					0·182

TABLE I
(Continued)

Tabulated		Found					Tabulated	
As_2Se_3 ref.[18]	As_2Se_3 ref.[19]	As_2Se_3 single crystal	As_2Se_3 glass	$As_2Se_{2.8}$ glass	$As_2Se_{2.44}$ glass	As_2Se_2 glass	As_4Se_4 acc.[18]	AsSe acc.[19]
0·178	0·178		0·178	0·179	0·179	0·179		0·178
	0·175					0·176		0·176
0·172		0·172	0·172	0·172	0·173			
						0·169		0·167
						0·165		0·166
								0·161
0·153	0·152	0·152	0·152	0·152	0·152			

there are great differences between tabular values presented in different literature sources. Because of the fact that within the limits of precision of our determination of d on a As_2Se_3 single crystal the values found are in good accordance with tabular values given in ref.[18], we consider these values more reliable than those in ref.[19]. By comparing d values found for powdered glass and glass in the form of plates $(0.5 - 1 \text{ mm thick})$ these values have been found not to differ within the limits of precision of the determination.

Fig. 5 shows, as an example of photometric records, a record of the X-ray pattern of the $As_2Se_{2.44}$ glass. In addition to three diffusion maxima roughly corresponding to $\vartheta = 8°30'$, $15°45'$, and $27°00'$ angles, low sharp peaks, which correspond by their position to interplanar d distances of crystalline As_2Se_3 are distinct in the figure. Curves of differential thermal analysis are graphically presented in Fig. 6. A distinct endothermic effect of glass Tg transformation is present in thermograms of all the samples; moreover, curves of As_2Se_2 and As_2Se_3 samples (their crystalline form is well-known) exhibit exothermic effects Tk which can be assigned to glass recrystallization after which endothermic melting effects Tt of produced crystalline phase follow. The $As_2Se_{2.44}$ and $As_2Se_{2.8}$ samples have a consistent course (from the viewpoint of the DTA results); little endothermic effect of the $As_2Se_{2.8}$ sample at a temperature of 370°C belongs to the melting of crystalline As_2Se_3 which is in this sample obviously produced by heat treatment. Endothermic effect could not be found at 370°C for $As_2Se_{2.44}$, which may be explained by the fact that the portion of crystalline As_2Se_3 is so small that it practically varies within the sensitivity limit of DTA. Temperatures belonging to the effects of glass transformation, crystalli-
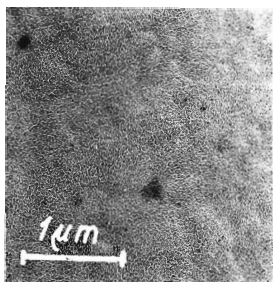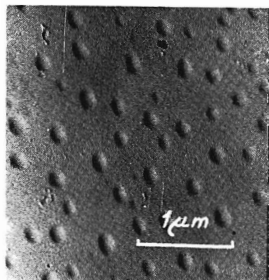
1
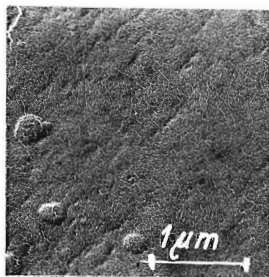
2
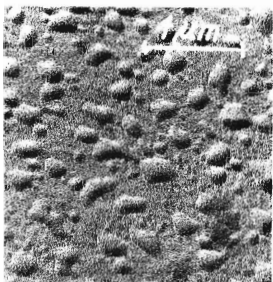
3a

3b

4

FIG. 1
Surface of As$_2$Se$_3$, Fracture Surface

FIG. 2
Surface of As$_2$Se$_{2.8}$, Fracture Surface

FIG. 3
Surface of As$_2$Se$_{2.44}$
  a) fracture surface; b) surface of solidified melt.

FIG. 4
Surface of As$_2$Se$_2$, Fracture Surface

zation, or melting are given in Table II. The values presented have been achieved as point of intersection of a zero line with descending branch of the endothermic effect, or with ascending branch of the exothermic effect.

It was not possible to prove by means of infrared defectoscopy presence of optical inhomogeneities which give evidence of the glass structure. In the studied region of the glass composition, macrodefects described in[17] were not found and the droplet structure, found by electron microscopy, has its size deeply under the resolving power of the infrared microscope.

Results achieved by electron microscopy referred in[13] pointed out existence of the droplet structure for $As_2Se_{2.44}$ and to a smaller extent even for $As_2Se_{2.8}$. This structure is similar to that described by Maruno and Noda[6] who interpret it for $As_2S_{2.55}$ as As_2S_2 crystals proved by X-ray diffraction and DTA curves. Results of the X-ray analysis showed that found values of interplanar distances d correspond to a crystalline portion of As_2Se_3 for As_2Se_3, $As_2Se_{2.8}$, and $As_2Se_{2.44}$
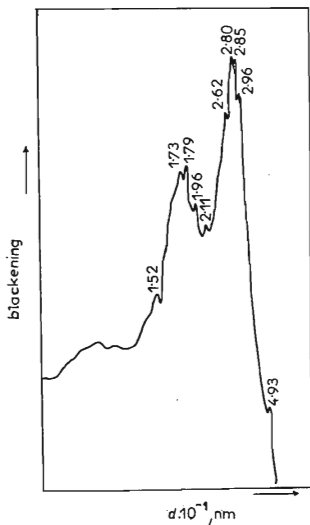
FIG. 5

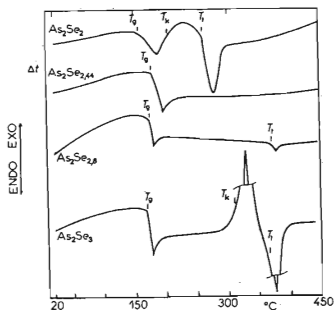Photometric Record of Diffraction Pattern of the $As_2Se_{2.44}$ Glass

FIG. 6

DTA Curves of As_2Se_2, $As_2Se_{2.44}$, $As_2Se_{2.8}$ and As_2Se_3

Sample	T_g	T_k	T_t	Sample	T_g	T_k	T_t
As_2Se_2	154	201	268	$As_2Se_{2,8}$	171	—	370
$As_2Se_{2,44}$	172	—	—	As_2Se_3	171	320	370

glasses, and to the crystalline portion of AsSe (As_4Se_4) for the As_2Se_2 glass respectively, and are in better accordance with the values given in[18] than with those mentioned in[19]. This accordance appeared more markedly for the d values obtained by measuring diffraction lines of ground As_2Se_3 single crystal. Likewise results achieved by DTA confirmed existence of crystalline As_2Se_3 in some glasses under investigation.

Dembovskii[10] showed that crystallization of the Se–As_2Se_3 glasses takes place very slowly. A complete crystallization occurred merely with pure Se and the As_2Se_3 and AsSe compounds, AsSe crystallizing more slowly than As_2Se_3.

These results lead us to a conclusion that in our case the droplet aggregates may be interpreted as regions richer in crystalline As_2Se_3. In the $As_2Se_{2,44}$ glass (and obviously within the whole region close to this composition — the range of this region has not been examined as yet) separation of phases took place; one phase is richer in As_2Se_2, the other one in As_2Se_3, which are stable components of the As_2Se_x system. The droplet aggregates are probably formed just from the phase richer in As_2Se_3.

It may be assumed that further results, particularly more distinct endo- or exo-effects, could be achieved by a long-time tempering of glasses, which should lead to an increase of the portion of the crystalline phase.

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