Monatshefte für Chemie 120, 643—650 (1989)

Monatshefte für Chemie
Chemical Monthly

Glass Forming Region and Some Properties of the Glasses from the System Se—Te—Ag

Marga Mitkova[1,*] and **Zorka Boncheva-Mladenova**[2]

[1] Bulgarian Academy of Sciences, Central Laboratory of Optical Storage and Processing of Information, P.O. Box 95, Sofia 1113, Bulgaria
[2] Higher School of Chemical Technology and Engineering, Boul. Kl. Ochridski 8, Sofia 1156, Bulgaria

Summary. The glass forming region in the system Se—Te—Ag was determined, the presence of glassy phases was proved by electron microscope and X-ray analysis. The properties of the synthesized glasses (vitrification temperature, microhardness, density, molar volume, light transmission and electrical conductivity) were investigated and discussed in terms of their composition.

Keywords. Chalcogenide; Glass; Glass forming; Ternary system.

Glasbildungsgebiet und einige Eigenschaften der Gläser des Systems Se—Te—Ag

Zusammenfassung. Es wurde das Glasbildungsgebiet im System Se—Te—Ag bestimmt. Der glasartige Zustand der erhaltenen Phasen wird auf Grund röntgenographischer und elektronenmikroskopischer Untersuchungen nachgewiesen. Die Eigenschaften der erhaltenen Gläser (Transformationstemperatur, Mikrohärte, Dichte, Molvolumina, Lichttransmission und elektrische Leitfähigkeit) wurden untersucht und im Zusammenhang mit ihrer Zusammensetzung diskutiert.

Introduction

In recent years write-once optical storage products have been commercially introduced and a greater research effort has been devoted to reversible optical storage materials [1]. In many cases the write-erase effects are based on the crystal-amorphous phase transition. One of the main material for these purposes are Te-based films. The greatest disadvantage of these films is the humidity degradation which could be lessened by adding some stabilizing additives such as different metals, carbon and selenium [2–4], the last in a concentrations over 14% acting very favourably. There are no data in the literature concerning the influence of silver as dopant in chalcogenide systems. Silver diffuses very easily in the glassy chalcogenide matrix, bridging chalcogenide chains and thus the structure becomes more stable. In doing such investigations it is very important to know in which ranges of chalcogenide systems formation of stable glasses containing silver is possible and what their characteristic properties are.

The present paper gives a number of results concerning the glass forming region in the ternary Se—Te—Ag system and summarizes some data on the properties of the obtained glasses, which are of interest for their application as optical storage media.

The phase diagrams of the binary systems Ag—Te, Ag—Se and Se—Te which are parts of the investigated system are well known. In the first two systems there are eutectics, corresponding to 67 at% tellurium and 44.5 at% selenium, respectively [5]. The binary system Se—Te contains the glass forming chalcogen (Se) in combination with tellurium. The elements are isomorphous and therefore the phase diagram is very simple. It displays full solubility in the solid state [5]. The Raman spectra of the glassy alloys Se—Te near the pure selenium compositions indicate that tellurium enters more preferentially into copolymer chains and tends to reduce the Se_8 rings [6]. In this system glasses have been synthesized containing up to 28.57 at% Te [7]. Several glasses have been synthesized also in the Ag—Se system in which silver is up to 10 at%. At a silver content of 15 at% some microcrystals are already found in the glasses [8]. There are no data in the literature concerning glassforming in the Ag—Te system. Having in mind the considerably higher coordination of tellurium in comparison with other chalcogens, few glassy phases are to be expected in this system, excluding eventually the eutectics in the binary systems. It is well known that in many cases deep eutectics and complex compounds contribute to easy glass formation [9]. A suitable cooling rate is also important in the glass forming process [10].

Experimental

Experimental investigations for characterising the glass forming region in the studied system were carried out near to 100 at% Se and the eutectics in the binary systems. In the ternary system Se—Te—Ag a compound Ag_4SeTe is found to have diffuse X-ray maxima [11] indicating that a considerable part of the composition remained amorphous. This was the reason for exploring the possibility to synthesize this composition in the vitreous state.

Thirty samples, 10 g each, were synthesized in silica ampoules, evacuated to 10^{-3} Pa. The initial substance had semiconductor purity. The conditions for the synthesis involved slow heating to 1 273 K with a rate of 1.5 deg min^{-1}, the temperature being maintained constant for 6 h at 523 K and 733 K (near the melting points of selenium and tellurium, respectively). Heating at 1 273 K lasted for 6 h and was followed by slow cooling to 873 K. Vibration agitation for 2 h was applied at that temperature. It was established that the material was in the liquid state at that temperature, afterwards the samples were quenched in a mixture of water, ice and sodium chloride ensuring cooling rates of ca. 40 deg min^{-1}.

Electron microscope and X-ray investigations confirmed the glassy or crystalline state of the samples. The glass vitrification temperature (T_g) was determined by differential thermal analysis (DTA) of 2 g samples with grain diameters 0.25–0.4 mm at a heating rate of 10 deg min^{-1} in evacuated quartz vessels. The density was measured by a hydrostatic method in a medium of CH_2I_2. The microhardness was measured at an optimal loading of 20 g on well-polished glass samples. Since in the last two methods considerable scattering of results is to be expected, 50 measurements were taken for each sample and the average values, dispersion and standard deviation coefficients were calculated.

The electrical conductivity was estimated by the fourprobe method on finally polished flat samples.

Results and Discussion

Fig. 1 shows the glass forming region in the investigated system. The compositions and the properties of the samples in vitreous state are given in Table 1. As seen from Fig. 1 (eutectic compositions and compounds in the binary systems) the expectations of producing a vitreous phase from the three-component substance Ag_4SeTe were

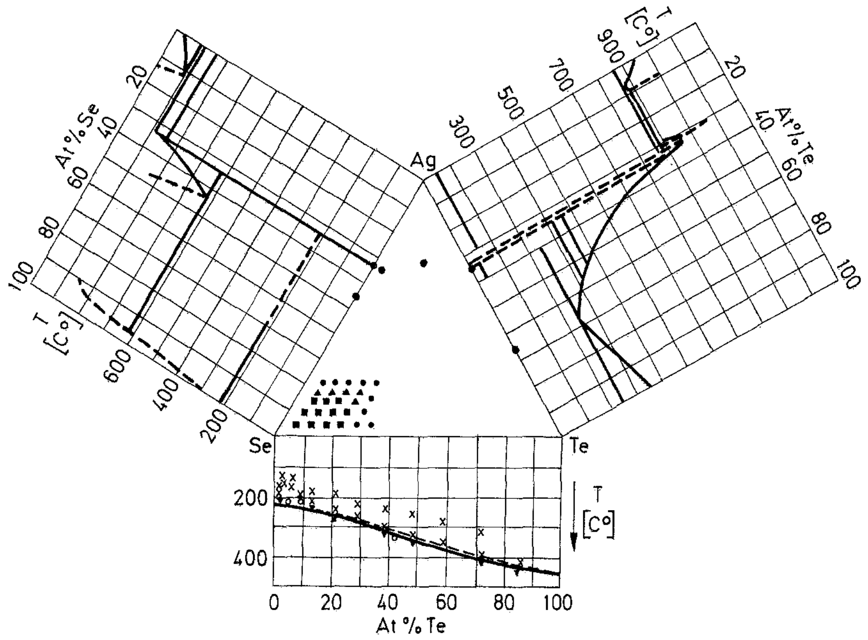

Fig. 1. Phase diagrams of the Se—Te, Se—Ag and Ag—Te systems and glass forming region in the Se—Te—Ag system: ■ vitreous phases; ▲ vitreous phases with microcrystals; ● crystal phases

Table 1. Properties of glasses in the system Se—Te—Ag

Sample no.	Composition [at%]			d [g/cm^3]	$H\mu$ [kg/mm^2]	$\bar{V}$ [cm^3/mol]	T_g [K]	T_c [K]
	Se	Te	Ag					
1	90	5	5	4.2_1	43.6_5	19.7_1	313	395
2	85	5	10	4.4_4	50.7_7	18.9_7	316	401
3	80	5	15	4.5_1	54.1_2	18.9_9	321	410
4	78	5	17	4.7_4	57.3_3	18.3_8	324	412
5	85	10	5	4.4_5	46.4_1	19.1_5	314	402
6	80	10	10	4.5_6	52.5_1	19.0_1	323	404
7	75	10	15	4.7_1	57.3_4	18.7_1	328	406
8	73	10	17	4.8_7	60.5_5	18.3_9	333	413
9	80	15	5	4.6_8	47.8_9	18.2_1	321	403
10	75	15	10	4.8_1	52.9_8	18.5_2	325	407
11	70	15	15	4.9_6	60.6_3	18.2_5	332	410
12	68	15	17	5.1_1	64.1_2	18.0_1	335	415
13	75	20	5	4.8_2	51.1_3	18.7_1	330	405
14	70	20	10	5.0_5	56.6_3	18.1_2	335	409
15	65	20	15	5.1_1	62.3_3	18.1_9	341	415
16	63	20	17	5.2_6	65.4_1	17.9_5	351	420

not justified at the cooling rate used. The glass forming region is concentrated in narrow boundaries close to 100 at% selenium and comprises concentrations of 38 at% tellurium and 17 at% silver. The glasses seem homogeneous. The presence of heavy atoms determines the lustre of the samples. They absorb in the visible region of the spectrum and are dark (almost black). Their transmittance increases by a wave length over 600 nm and depends on the composition (Fig. 2).

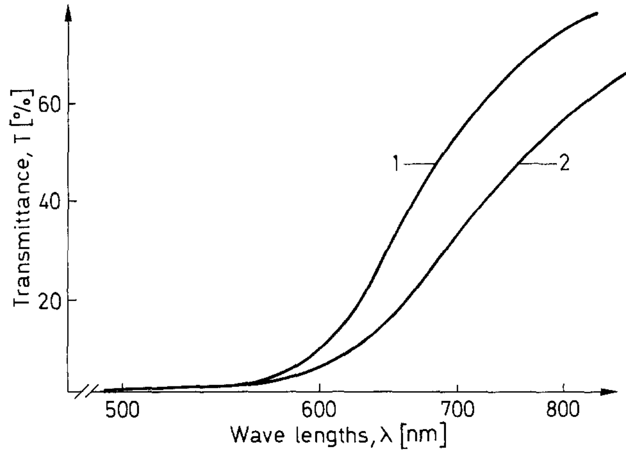

Fig. 2. Optical transmission spectra of samples with composition: curve 1: $Se_{90}Te_5Ag_5$; curve 2: $Se_{70}Te_{20}Ag_{10}$

Comparing the glass forming regions of the investigated system with that of the system Se—S—Ag [8], it must be pointed out that substitution of sulfur with tellurium in the ternary systems causes a decrease of the glass forming region, mainly concerning the content of the chalcogenide atom. This is in agreement with the generally accepted ideas that the strongly directed covalent bonds play an essential role in glass formation. In literature, tellurium is mentioned as a poor glass-former. This seems to be determined from its tendency to octahedral coordination similar to the distorted cubic lattice type NaCl. In the latter the ratio of the radii of the first and second coordination sphere is $r_2/r_1 = 1.199$, while in hexagonal selenium this ratio is $r_2/r_1 = 1.433$ [12]. The high coordination of tellurium is preserved in the molten state too and that is why the average coordination of vitreous tellurium is assumed to be approximately equal to 4.

The X-ray investigations of samples in the glass forming region have diffractograms typical for amorphous materials (absence of sharp peaks with a rounded plateau, Fig. 3, curve 1). The samples containing crystal phase exhibit clearly marked crystallization peaks, those typical for Ag_2Se having the greatest intensities (Fig. 3, curve 2).

The electron microscope investigations proved clearly that glassy samples rich in selenium have a homogeneous structure (Fig. 4 a). On increasing the content of tellurium a tendency towards liquid phase separation is observed (Fig. 4 b). This process is probably connected with the relatively great dimensions of the tellurium atoms and their tendency to higher coordination. The phase separation in the melts is also influenced by the applied cooling conditions due to a non-equilibrial distribution of the primarily arising phases.

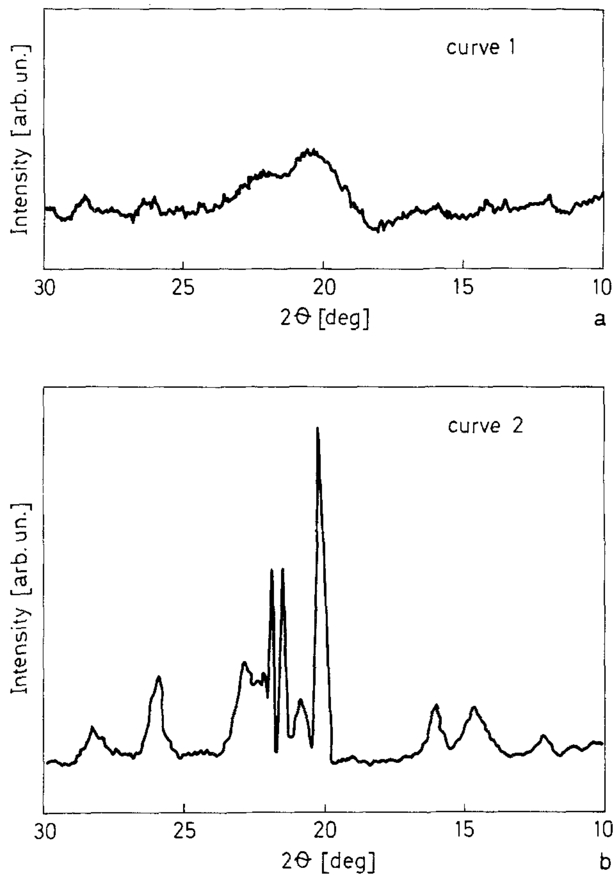

Fig. 3a, b. X-ray diffraction patterns of samples with composition: curve 1: $Se_{85}Te_5Ag_{10}$; curve 2: $Se_{68}Te_{15}Ag_{17}$

Despite the introduction of a relatively high-melting component (Ag), the vitrification temperature is very low (see Table 1), which is an indication for the low stability of the glasses. It depends on the composition of the substances and tends to go up when the content of tellurium and silver is increased, the influence of the latter being stronger. The change of the slope of the differential-thermal-analysis curve typical for the vitrification temperature is usually followed by a crystallization peak, the X-ray analysis indicates that it is Ag_2Se. This is to be expected bearing in mind its lower heat of formation (83.1 kJ/mol) compared with that of Ag_2Te (91.3 kJ/mol) and that it is the prevailing chemical composition in the system. The second small crystallization peak which occures in the last two samples listed in Table 1 was identified as corresponding to tellurium. With the increase of the selenium content the peaks of the melting endotherms become smaller which suggests that the degree of disorder becomes higher. When the silver and tellurium content is increased, the crystallization ability of the respective glassforming melts becomes higher which is suggested by the lowering the difference between the vitrification and crystallization temperature. It has maximal values for samples along the straight line connecting the point 100 at% Ag and $Se_{80}Te_{20}$. In these samples the crystallization peaks are steeper and the corresponding areas are greater.

The density of the vitreous phases increases at higher tellurium and silver concentrations although this change is in narrow limits (see Table 1). The

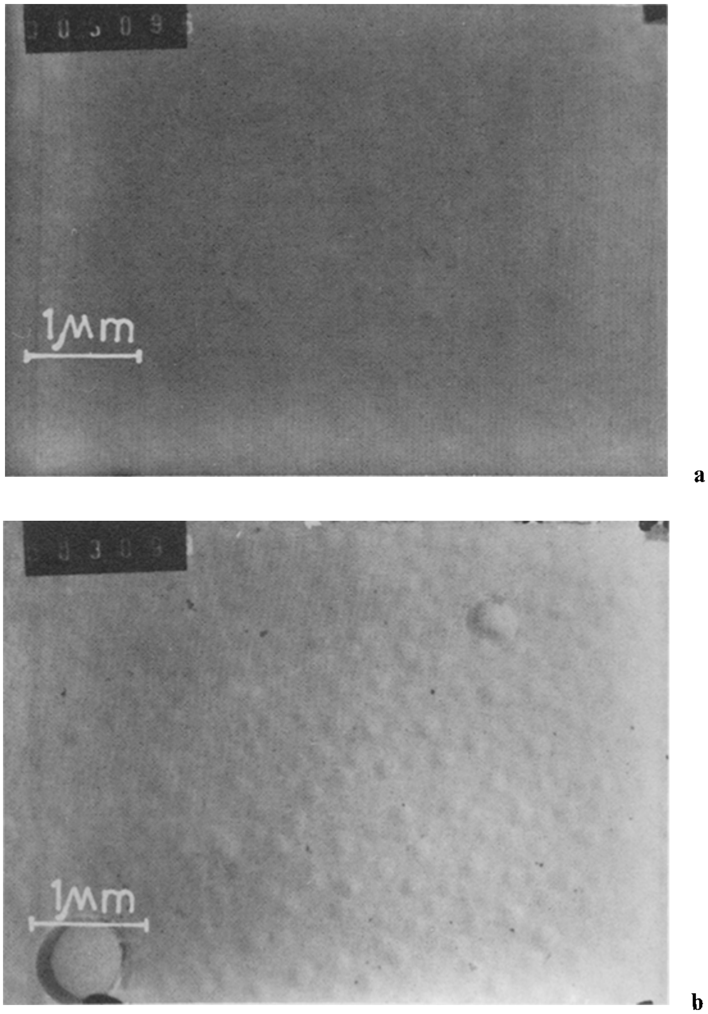

Fig. 4 a, b. Electron microscope photographs of samples with composition: **a**: $Se_{85}Te_5Ag_{10}$; **b**: $Se_{75}Te_{15}Ag_{10}$

microhardness of the samples also rises with the increase in the concentration of these two elements. The influence of silver and tellurium in causing a density and microhardness increase evidently is connected with the densification of the chalcogenide structure due to inclusion of short tellurium chains. Of significance is also the greater coordination number of tellurium and the chalcogen chains bridging by silver atoms.

The measurements of electrical conductivity were accomplished starting at the temperature of liquid nitrogen and going up to 300 K. Up to 180 K the temperature course of the conductivity (in logarithmic coordinates) is non-linear which indicates that the conductivity has a complicated character. At higher temperature the relationship $\ln \sigma = f(T)$ is linear which means that the conduction mechanism is only of one type. The conductivity values at room temperature are presented as a function of the conductivity activation energy in Fig. 5. The errror limits of the calculation are ± 0.2 for the logarithmic law for the electric conductivity and ± 0.05 eV for this

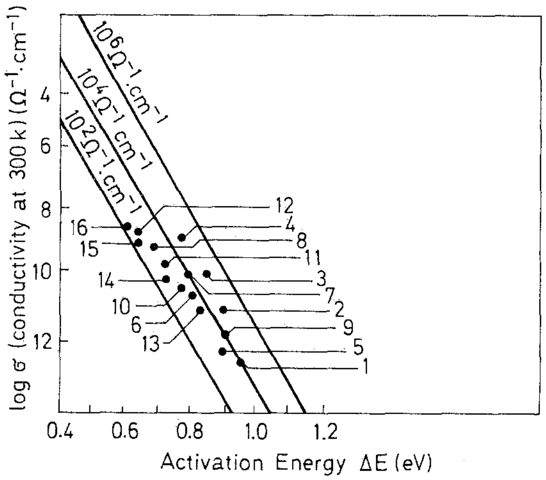

Fig. 5. Room temperature conductivity of glasses as a function of the conductivity activation energy; the slopes of lines are $-1/300\,\mathrm{K}$; their intercepts are σ_0

activation energy. The electric conductivity and activation energy are in limits typical for chalcogenide glasses. Their values depend to a certain degree on the compositions, primary on the silver content, but no substantial differences are observed. The influence of silver on the conductivity of chalcogenide glasses has been discussed by a number of authors. Kolomietz et al. [13] suggest that silver causes a increase of the charged donors in As_2Se_3 doped with silver. Arai et al. [14] believe that silver combines immediately into Ag_2Se. Kastner and Fritzsche [15, 16] have discussed the effect of foreign additives on the density of valence-alteration defects in lone-pair amorphous semiconductors. It has been pointed out that although the addition of small concentrations of metal additives to chalcogenide glasses can change the density of valence-alteration pairs, the effect may be much smaller than expected. Some parts of the silver added in the glasses can dissociate into positive ions, compensated by charge dangling bonds (D^- or C_1^-) described by the reaction:

$$Ag + C_2^0 = Ag^+ + C_1^- .$$

The negative effective correlation energy of the defect centers and their interconnection property are normally interpreted as predicting a pinned Fermi level E_F even in the presence of charge dopant [16, 17]. This might be the reason for the narrow limits in which the electrical properties change for the glass systems investigated in the present study.

References

[1] Takenaga M., Mikoda M. (1984) In: Hamakawa Y. (ed.) JARECT 16, Amorphous Semiconductor Technologies and Devices. Ohmsha, Tokyo; North-Holland, Amsterdam, p. 266

[2] Terao M., Horigome S., Shigematsu K., Miyauchi Y., Nakazawa M. (1982) SPIE **382**: 276

[3] Unno Y., Goto K. (1983) Technical Digest of Topical Meeting on Optical Data Storage. MB2, Incline Village, Nevada

[4] Terao M., Shigematsu K., Ojima M., Taniguchi T., Horigome S., Yonezawa S. (1979) J. Appl. Phys. **50**: 6881

[5] Hansen M., Anderko K. (1958) Constitution of Binary Alloys. McGraw-Hill, New York

[6] Wart A. T. (1970) J. Phys. Chem. **74**: 4110

[7] Abou el Ela A. H., Elmously M. K., Abdu K. S. (1980) J. Mat. Sci. **15**: 871

[8] Tsaneva K., Bontschewa-Mladenowa Z. (1978) Monatsh. Chem. **109**: 911

[9] Dembovsky S. A. (1978) Phys. and Chem. of Glasses **4**: 522 (in Russian)

[10] Dembovsky S. A., Chechetkina E. A. (1982) Mat. Res. Bul. **17**: 1531

[11] Bontschewa-Mladenowa Z., Vassilev V. (1984) J. Therm. Anal. **29**: 523

[12] Krebs H. (1958) Angew. Chem. **70**: 615

[13] Kolomietz B. T., Lebedev E. A., Rogachev N. A. (1974) Phys. Techn. Semicond. **8**: 545 (in Russian)

[14] Arai K., Kuwahata T., Namikawa H., Saito S. (1972) Jap. J. Appl. Phys. **11**: 1080

[15] Fritzsche H., Kastner M. (1978) Phil. Mag. **B37**: 285

[16] Fritzsche H., Gaczi P. J., Kastner M. (1978) Phil. Mag. **B37**: 593

[17] Adler D. (1982) Sol. Energy Mat. **8**: 53

Received February 22, 1988. Accepted October 27, 1988