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Phase separation and structural change accompanying the introduction of silver to arsenic trisulphide glass

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Glass–glass phase separation has been observed when melts of compositions $As_2S_3Ag_x$ ($x = 0.1, 0.25, 0.35, 0.4$ or 0.5) were cooled slowly to 210° C and annealed at this temperature. The two glass phases produced were an Ag-rich one (approximate compositon for $x = 0.4$, $As_2S_{3.4}Ag_{1.0}$) and an Ag-poor one ($As_2S_{2.7}Ag_{0.07}$). With increasing x value, Ag and S contents in the Ag-rich phase increased, and its composition approached that of trechmannite or smithite ($AgAsS_2$), whereas the Ag content of the Ag-poor phase changed little and only the S content decreased. A chemical-etching study of the phase-separated glasses was also made.

1. Introduction

The amorphous As–S–Ag system has been extensively investigated by many authors mainly from an interest in electronic processes [1] in non-crystalline materials or from aspects of electrical and optical applications (see for example [2]). It is now widely known that small amounts of silver cause a marked increase in the electrical conductivities of As_2S_3 glass [3, 4] and that when amorphous As_2S_3 surfaces coated with silver films are photo-irradiated, silver ions diffuse into its structure [5, 6]. A few attempts to grow some sulphide crystals by use of an As_2S_3 flux have also been made [7, 8]. In the present paper, we report the phase separation observed in silver-containing As_2S_3 glasses. Possible structural changes of them with increasing silver content and a chemical-etching procedure which enables detailed observation of the phase separation are also described.

2. Experimental procedure

Silver-containing glasses were synthesized from high purity elements, i.e. 99.9999% pure As, >99.999% pure S and 99.999% pure Ag according to the following procedure. The appropriate constitutents (for compositions of As_2S_3 and $As_2S_3Ag_x$ with $x = 0.1, 0.25, 0.35, 0.4$ and 0.5, of a total weight of about 12 g for each batch) were sealed in quartz tubes at about 10^{-5} Torr. After having been heated at 850° C (650° C for As_2S_3) for 10 h in a rocking furnace, these ampoules were allowed to cool to 210° C in the shut off furnace for 4 h, annealed at that temperature for 2 h and subsequently cooled slowly to room temperature in about 5 h. Arsenic was handled under an atmosphere of nitrogen in order to avoid air-oxidation of its surface.

The compositions of the phase separated glasses were determined by X-ray microanalysis of the carbon-evaporated glass surfaces. This analysis was carried out at a scanning speed of $400\,\mu m\,min^{-1}$ to avoid those changes in count with time which were encountered when one spot of the sample was continuously irradiated with the electron beam. These changes may be partly due to silver migration caused by the electron beam, since silver ions are generally mobile in silver-containing As–S glasses [9, 10]. A glass with the smithite or trechmannite composition ($AgAsS_2$) was used as a reference standard in the high silver concentration region. For the observation by scanning electron microscope, fractured surfaces of the glasses were chemical-etched by mixed solutions of 0.1 M NaOH (1 part) and 0.25 M $NaHCO_3$ (1 to 2 parts)

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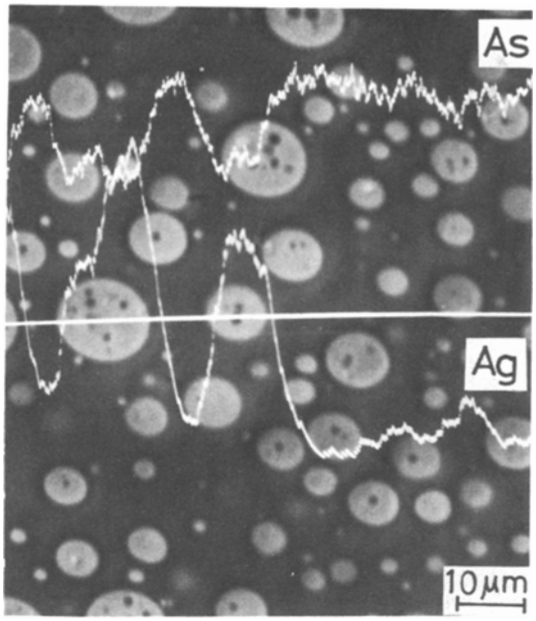

Figure 1 Ag and As concentration profiles along a line scan on the surfaces of the phase-separated glasses obtained from the $As_2S_3Ag_{0.4}$ melt. The X-ray intensities of Ag*Lα* and As*Lα* are shown in arbitrary units.

added with several drops (for each 50 ml of the mixed solutions) of 31% H_2O_2 at room temperature for 10 to 60 min, and then Pt films were sputtered on them.

3. Results

X-ray diffraction measurements of all the powdered samples obtained for $x \leqq 0.4$ showed no peaks, but for $x = 0.5$ a few peaks have been observed, which indicates the presence of small amounts of crystallites which are probably trechmannite, $AgAsS_2$.

Fig. 1 shows concentration profiles for As and Ag along a line scan of the $x = 0.4$ glass. It can be seen that Ag-rich and Ag-poor phases coexist. Tiny domains found in most of the large round domains are believed to have chemical compositions similar to those of the Ag poor phase. When more Ag was introduced ($x = 0.5$), the Ag-poor domains became to be surrounded by the Ag rich ones. From X-ray microanalysis of the phase-separated glasses for $x = 0.4$, the composition of the Ag-rich phase was found to be $As_2S_{3.4 \pm 0.2}Ag_{1.0 \pm 0.1}$, whereas that of the Ag-poor phase was $As_2S_{2.7 \pm 0.2}Ag_{0.07 \pm 0.01}$. On the other hand, the compositions of the two phases for $x = 0.5$ are represented by $As_2S_{3.5 \pm 0.2}Ag_{1.2 \pm 0.1}$ and $As_2S_{2.6 \pm 0.2}Ag_{0.07 \pm 0.01}$, respectively. For $x \leqslant 0.35$, the Ag rich domains were too small to carry out X-ray microanalysis. Mean diameters of the Ag-rich domains for $x = 0.1$, 0.25, and 0.4 were about 0.1, 0.7 and 7 µm,, respectively. The diameters of the Ag-rich domains for $x = 0.4$ ranged from about 1 to 30 µm, and those of the Ag-poor domains for $x = 0.5$ ranged from about 1 to 80 µm (the quantitative analysis of domains with small values of diameter was impossible because of the fast line scan).

Fig. 2 shows the surface structure obtained by etching the fractured surface of the specimen for $x = 0.25$. The Ag-poor domains dissolved select-

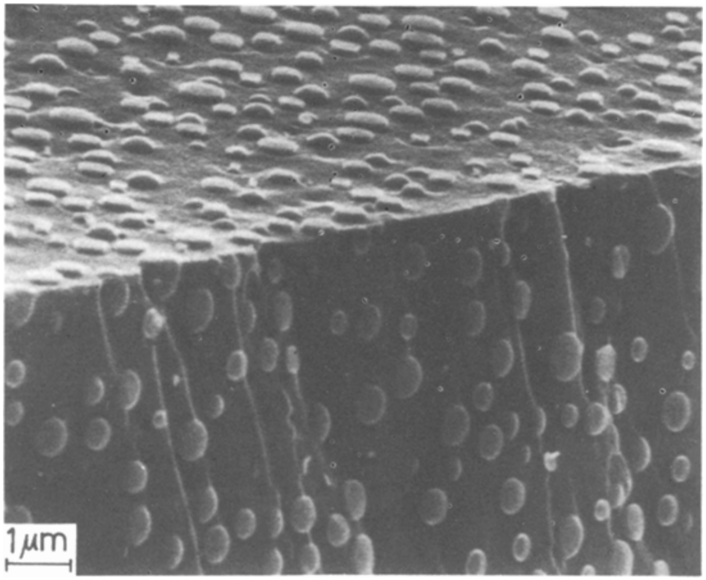

Figure 2 Surface structure obtained by chemical-etching of the phase separated glass for $x = 0.25$, showing silver-rich droplets. Fractured surfaces were treated at room temperature for 1 h with 25 ml of 0.1 M NaOH and 25 ml of 0.1 M $NaHCO_3$ solutions added with several drops of 31% H_2O_2.

ively, and the rich domains were found to be spherical in shape.

4. Discussion

Trechmannite [11] and smithite [12], both of which are represented by $AgAsS_2$ (i.e., $As_2S_4Ag_2$), proustite [13] and xanthoconite [14], Ag_3AsS_3, are known as crystalline phases in the Ag–As–S ternary system [15]. The present results of X-ray microanalysis, although they involve experimental errors in some degree, indicate that, as more Ag is introduced, the composition of the Ag-rich phase approaches that of trechmannite or smithite, whereas in the Ag-poor phase, the Ag content changes little and only the S content decreases.

Although there are considerable discrepancies between the glass-forming regions, obtained by melt-quenching [16, 17], so far reported for the As–S–Ag system, these regions are both spread around the compositions of the Ag-rich phases observed in the present study, and the Ag-poor phase for $x = 0.4$ and 0.5 lie near the boundary of the regions.

Orpiment (crystalline As_2S_3) [18] has a layered structure composed of $(AsS_{3/2})_n$ layers each of which can be regarded as consisting essentially of As_6S_{12} rings (or groups) (see Fig. 3). It is generally believed that As_2S_3 glass has a layer structure similar to that in orpiment but it is a distorted and open structure and that the rings may sometimes contain five or seven as $AsS_{3/2}$ tetrahedra [19, 20]. The main structural units which constitute trechmannite and smithite are As_3S_6 groups as schematically shown in Fig. 4. In these minerals, the As_3S_6 groups are connected to one another with Ag^+ ions [11, 12]. In proustite and xanthoconite, the structural unit is AsS_3 pyramids [13, 14]. On the other hand, As–As bonds are formed in glasses, As_2S_y with $y < 3$ [19].

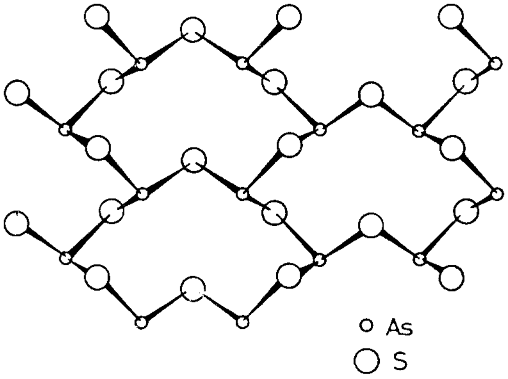

Figure 3 Layer in the structure of orpiment (crystalline As_2S_3) (projection on (0 1 0)).

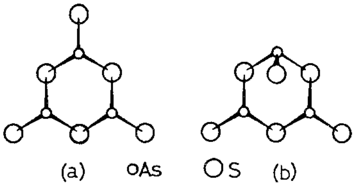

Figure 4 As_3S_6 group in $AgAsS_2$ crystals; (a) trechmannite, (b) smithite.

In the low Ag concentration region (probably, $x \lesssim 0.1$) intercalation of silver is generally believed to be taking place. Therefore, by reference to the features of the crystal and glass structures described above, we can deduce the most possible structural change within the present Ag concentration range as follows. As more Ag is introduced to As_2S_3 glasses under the condition of the present final heat treatment, the $(AsS_{3/2})_n$ layer structure, similar to that in orpiment, disintegrates with both the formation of As_2S_y $(y < 3)$ networks containing small amounts of Ag, and of As_nS_{2n} groups (n is an integer and is considered to decrease from, on the average, about 6 to 3 with increasing silver content) which are connected to one another with Ag^+ ions or directly.

5. Conclusion

When melts of the composition $As_2S_3Ag_x$ $(0.1 \leqq x \leqq 0.5)$ were subjected to the final heat treatment of slow-cooling and annealing, they separated into the Ag-rich and Ag-poor glasses. The former is considered to consist essentially of As_nS_{2n} groups (the mean value of n being less than 6) connected one another with Ag^+ ions and the latter As_2S_y $(y < 3)$ networks containing small amounts of silver.

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