On the Structure of Glasses in the System As-S
(The properties and structure of sulfide glasses Part III)

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1. Introduction
We have already reported that only As-S and S-S bonds exist in the binary glasses As-S as observed from the measurement of infrared absorption spectra and that the following three conclusions are obtained from the results of their molecular volume, molecular refraction, hardness, viscosity and solubility in CS₂:

(i) As=\text{S} bond seems not to exist in these glasses.

(ii) As-As bond exists in the glasses, the S content of which is lower than that of As₂S₃.

(iii) As their S contents become superior to that of As₂S₃, S begins to form the chain but when the S content is greater than that of As₂S₉₋₁₀, the ring may also be formed in addition to the formation of chain.

The structural analysis of crystalline arsenic trisulfide (orpiment) has been already attempted by the X-ray diffraction method. It is also known that the structure of As₂S₃ glass is almost similar to that of orpiment. However there have been few reports on the structural investigations of As-S glasses, the S content of which is lower or higher than that of As₂S₃.

In undertaking to establish the structural picture of glasses concerned, was investigated the structure of glasses in the system As-S by the X-ray diffraction method and thus a structural model was set up for clarifying the arrangement of As and S atoms in these glasses.

2. Experimentals and results
2.1 Glass preparation
A series of glasses were prepared by comelting elementary As and S (both with high purity) in definite proportions in evacuated sealed ampoules of pyrex type as described in the previous paper.

The following two groups of samples were prepared, the one group including As₂S₁₅, As₂S₁₂, As₂S₉, As₂S₇, As₂S₄, and As₂S₁₁, the other As₂S₁₇, and As₂S₁₈.

The sample pieces 15×20×3 mm were cut off from each of glasses prepared and then were ground with carborundum and polished with polishing powder ZrO₂.

2.2 X-ray diffraction study
2.2.1 X-ray intensity measurement
The scattering intensities of glasses were measured with a diffractometer (Rigaku Denki Co.) equipped with scintillation counter, amplifier and pulse height analyzer.

To obtain scattering intensities essentially due only to monochromatic X-ray, balanced filters were employed, the pair of filters being Ni-oil and Co₂O₃ powder plate for Cu-Kα, Zr-foil and Y₂O₃ powder plate for Mo-Kα, and the difference between the intensities measured with each of the filters were taken from 0.03 to 0.41 as a function of sin θ/2 for Cu-Kα, and from 0.31 to 0.80 for Mo-Kα, respectively. Both curves for Cu-Kα and Mo-Kα were combined together in the range 0.31 to 0.41.

Fig. 1. X-ray scattering intensity curve As₂Sₓ (x≥3).
Normalized intensities were obtained by correcting the observed intensities for polarization and then scaling them to the calculated scattering curves* in the range 0.70 to 0.80. These corrected intensities and the calculated total independent scattering curves are shown in Fig. 1 and 2.

**2.2.2 Radial distribution analysis**

These data represented in Fig. 2 were converted by the formalism of Warren to the radial distribution functions\(^7\). At this time, to avoid such error as the termination of series, the calculation was accomplished by applying an artificial temperature factor. In these calculations increments of 0.005 Å\(^{-1}\) in \(\sin \theta /\lambda\) were taken, and the distributions evaluated at 0.1 Å by an OKITAC 5090 C computer. The results are shown in Fig. 3.

On the other hand, the density of \(\text{As}_2\text{S}_3\) glass (3.14) is about 8% smaller than that of \(\text{As}_2\text{S}_3\) crystal (3.46) and this is mainly attributed to that the \(\text{As}_2\text{S}_3\) glass has an open structure.

The comparison of the results of the X-ray intensity of \(\text{As}_2\text{S}_3\) glass with that of \(\text{As}_2\text{S}_3\) crystal indicates that the distance (about 5 Å, \(\sin \theta /\lambda\approx 0.1\)) between layers in \(\text{As}_2\text{S}_3\) glass becomes wider than that (4.8 Å) of crystalline material. From these results, the following structural model can be considered (Fig. 4). In this model, \(\text{AsS}_\text{As}_3\) is represented as tetrahedron model and rings are formed consisting of six \(\text{AsS}_\text{As}_3\) tetrahedra but in the case of glass the rings sometimes may contain five or seven of these groups unlike the crystal.

By assuming the structure of \(\text{As}_2\text{S}_3\) glass as the distorted structure of crystalline orpiment, we can interpret that the density is lower in glass than in crystal and that the distance between layers becomes wider in glass.

**3.2 On the structure of \(\text{As}_2\text{S}_{x>3}\) glasses**

In the intensity curves (Fig. 1), the first maximum, corresponding to interference between layers (\(\delta_{\text{def}}\) in the case of crystalline orpiment), appears almost not to change the position with the variation in composition from \(\text{As}_2\text{S}_3\) to \(\text{As}_2\text{S}_{12}\).
Therefore we may conclude that these glasses keep the layer structure and their layer distance is similar to that of As$_2$S$_3$ glass. Thus by setting up the structural model shown in Fig. 5*, it becomes clear that in the glasses with As$_2$S$_x$ to As$_2$S$_9$ composition, the ring type form of sulfur, S$_8$, cannot enter into the interstices of rings composed of As and S in their layer structure. However, when the S content is greater than that of As$_2$S$_9$, it becomes possible for S$_8$ to enter into the interstices. This agrees with the results obtained from the experiment on the solubility of these glasses to CS$_2$\(^2\)), i.e. the rings (S$_8$) begin to form in the glass when the S content is greater than that of As$_2$S$_8$-9.\(^5\) (Fig. 6). Moreover, it seems that S$_8$ does not enter into the layers of glass in such a way as in graphite. In the case of which the interlayer distance increases by the insertion of atoms and molecules. This suggests from X-ray diffraction patterns mentioned above, i.e. no increase of layer distance is observed with the increase of S content.

Otherwise, as described in the previous paper\(^3\), the variation of value for the activation energy of viscous flow changes abruptly around the range of the $x$ value of As$_2$S$_x$ is 8-10. This is attributed to that the mechanism for viscous flow changes in about As$_2$S$_{8-19}$ composition, and can be explained as follows.

The value for the activation energy of viscous flow in As$_2$S$_x$ is considerably large because of the break down of As–S bond required for viscous flow (Fig. 7). But its value decreases abruptly with the increase of S content. It is considered that the break down of S–S bond is likely to happen preferentially in addition to that of As–S bond. And in the range As$_2$S$_{8-19}$ and over, viscous flow is able to take place by S$_8$ ring transfer as well as the break down of S–S bond and, at this time, the interstices in which S$_8$ ring exists extend in size with the increase of S content. So S$_8$ ring transfer becomes easier and the activation energy monotonously decreases in the range As$_2$S$_{8-19}$ and over.

To sum up, the structure for the glasses of As$_2$S$_x$ (x<3) composition are as follows: With increasing S content above As$_2$S$_x$, S is likely to enter between As and As as the chain like form, but when the S content is greater than that in As$_2$S$_8$, ring type forms coexist with chain like forms and exist in the interstices of layer.

### 3.3 On the structure of As$_2$S$_x$ (x>3) glasses

On the results of radial distribution analysis
(Fig. 3), the first maximum for As$_2$S$_3$ glass is at about 2.25 Å and it is likely due to As–S pair, because its value is nearly the same as As–S bond length (2.245 Å) found in crystalline As$_2$S$_3$. However, as the S content is lower than that of As$_2$S$_3$, this first maximum shifts to a larger value (2.35 Å in As$_2$S$_{2.85}$ and 2.45 Å in As$_2$S$_{2.7}$). These results may be interpreted by assuming that S is eliminated from “some As–S–As linkages” and consequently “As–As bonds” are formed in the glasses. Adopting the value (2.49 Å) in the molecule As$_4$S$_4$ as As–As bond length, it would be expected that the first maximum shifts to a larger value with the decrease of S content, i.e. with the increase of As–As bond.

We find by considering from the structural model that, when As–As bonds begin to be formed in the layer structure, the deformation of layer (protuberance and strain) takes place here and there (Fig. 8) and then the thickness of layer of these glasses increases slightly compared with that of As$_2$S$_3$ glass.

On the other hand, the position of the first maximum on the X-ray intensity curve is 0.1 in sin $\theta$/λ for As$_2$S$_3$ glass, but it shifts to 0.095 for As$_2$S$_{2.85}$ and As$_2$S$_{2.7}$ glasses. This means that the distance between layers changes from 5 Å to 5.19 Å and this agrees with the information obtained by the structural model.

By the way the hypothesis of the existence of As–As bond in the glass makes easy to understand the following properties. The activation energy for viscous flow and the hardeness$^5$ (Fig. 7, 9) show the maximum value in As$_2$S$_3$ composition and its value decreases accordingly as the S content increases or decreases. This is attributed by the appearance of As–As bond in the glass the strength of which (32.1 kcal/mol)$^{11}$ is almost the same as S–S bond strength (33.4 ± 4.8 kcal/mol)$^{10}$ for the chain like type sulfur and these values are lower than that of As–S bond strength (61 kcal/mol)$^{10}$.

Since the absorption band due to As$_4$S$_4$ molecule was not observed in the infrared spectra as mentioned in the previous paper$^3$, it seems that if As–As bond exists in the glass, it could never exist in such form as As$_4$S$_4$ molecule.

As mentioned above, the glass structure for As$_x$ S$_{3(x<3)}$ composition is a layer structure similar to As$_2$S$_3$ glass and with decreasing S content, that is, with the elimination of S between As and As of “a $\gamma$As–S–As$\gamma$ linkage”, “a $\gamma$As–As$\gamma$ bond” begins to be formed and the formation of As–As bonds lead to the deformation of layer structure which gives rise to expansion of the distance between layers.

4. Conclusions

As S–S binary glasses with various compositions were prepared and X-ray intensity curves for these glasses were measured by X-ray diffraction techniques and the radial distribution analysis, if necessary, was adopted. On the other hand, the structural models for As–S glasses were proposed by setting up molecular model.

Consequently the following conclusions were deduced.

(i) The structure of As$_2$S$_3$ glass is a layer structure similar to that in orpiment but a distorted and open structure.

(ii) The glasses with As$_x$ S$_{3(x>3)}$ composition keep the layer structure, too. With increasing S content above As$_2$S$_3$, S exists as $\{S\}_n$ chain between As and As, but when the S content is greater than that in As$_2$S$_{2.85}$, both chain-like and ring type forms co-exist.

(iii) The glasses of As$_x$S$_{3(x<3)}$ composition also have the layer structure. With decreasing S content below As$_2$S$_{2.7}$, S between As and As is eliminated and As–As bonds are formed. Consequently the deformation of layer occurs and the expansion of the layer distance was observed.
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As-S系ガラスの構造について
(硫化物ガラスの物性と構造, III)

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AsとSとの割合を様々な変えたAs-S系ガラスをつくり、X線回折法によりその強度分布曲線を得た。必要な場合にはさらに動的分布解析を行なった。一方で原子形を組み立てて、As-S系ガラスの構造模型をつくった。
これらの結果から、As$_2$S₃組成のガラスは硫黄の結晶構造と似ている層状構造を持つが、すさまじくかなり多乱れた構造であると考えられる。As$_2$S₃より層状構造を持っていて、As$_2$S₃組成より硫黄が増すにしたがって硫黄はAsとAsとの間にと考えられる。As$_2$S₃以上になると硫黄の同化と同時にS₁環ができてくると考えられる。また、As$_2$S$_{1+x}$より層状構造を持っていて、As$_2$S₃組成より硫黄が減少するとしたがって、AsとAsとの間の硫黄がとれて、As-As結合が生じる。それにとなって層がびずみ、層間隔が広がるようになると考えられる。

上に述べた構造を考えると前報で得られたガラスの硬度測定、粘度測定の結果や、CS₂によるガラスの溶出実験の結果が非常に説明できる。

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高炉水砕スラグの定量およびセメント中のスラグの水和反応速度に関する研究

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Studies on a Method to Determine the Amount of Granulated Blastfurnace Slag and the Rate of Hydration of Slag in Cements

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A method of quantitative determination of granulated blastfurnace slag not only in unhydrated slag cement but also in hydrated paste as an unreacted part was established by