

STUDIES ON ARSENIC SULFIDE GLASS

BY SHIGERU MINOMURA, JIRO MATSUDA*, AND MASAHIRO ŌURA**

Introduction

Although the arsenic sulfide glass had already been well known, it is only of late that the artificial preparation and some properties have been reported for the purpose of getting optical materials in the infrared region^{1,2,3}.

In this work, the preparation, casting, and polishing of arsenic sulfide glass are investigated by the different methods, furthermore the transmission in the infrared region, the presence of stria and bubble, and the effect of adding sulfur on the stability of the glass are observed.

Preparation of the Sample Powder

Synthesis of arsenic trisulfide was done by following two methods: (1) the purification of commercial arsenic trisulfide, (2) the reaction of arsenic trioxide and hydrogen sulfide.

Commercial arsenic trisulfide contains some impurities, chiefly such as the oxides and the sulfides of heavy metals. It is dissolved in an alkaline solution, and the precipitate is obtained from the filtrate by adding hydrochloric acid. The precipitate obtained is again dissolved in an aqueous solution of sodium carbonate at 70°C and filtered. After the cooling, carbon dioxide is introduced in the filtrate while cooled with ice water, and then it is filtered. Dilute hydrochloric acid is added to the filtrate. The precipitate is collected by a glass filter, and it is washed with dilute hydrochloric acid, alcohol, then with carbon disulfide, and lastly with alcohol again which quickens the drying of the precipitate obtained. It is dried below 105°C for several hours, and rather voluminous yellow powder is obtained, and its apparent specific gravity is 2.7~2.8, being measured in the dilute hydrochloric acid saturated with purified arsenic trisulfide⁴. This is done by adding a little alcohol, since arsenic sulfide can hardly get wet. Dried yellow arsenic sulfide is distilled in a quartz tube of 5 cm in diameter at 600°C with flowing dried and oxygen-free nitrogen gas, and it is solidified separately in a red block of glass and in yellow powder, and the latter is

* Ehime University

** Horiba Instruments Inc.

1) R. Frerichs, *Phys. Rev.*, **78**, 643 (1950)

2) R. Frerichs, *J. Opt. Soc. Am.*, **43**, 1153 (1953)

3) F. W. Glaze, D. H. Blackburn, J. S. Osmalov, D. Hubbard, and M. H. Black, *J. Research Nat. Bur. Std.*, **59**, 83 (1957)

4) A. W. Mellor, *A. Comprehensive Treatise on Inorganic and Theoretical Chemistry*, IX, Longmans, London p. 273 (1928)

taken off. The emission spectra of the glass show that it contains a trace of Sn, Sb, Mg, and Mn as impurities.

In another method of preparation, commercial arsenic trioxide is used. The reagent is dissolved in an ammonical aqueous solution and filtered. The precipitate is obtained from the filtrate by adding dilute hydrochloric acid. After filtered, the residue is redissolved in conc. hydrochloric acid by warming, and diluted with distilled water. Hydrogen disulfide is introduced in this solution in the reaction vessel with a stirrer. This precipitated arsenic trisulfide is washed with dilute hydrochloric acid saturated with hydrogen sulfide, then with dilute hydrochloric acid and lastly with distilled water. The yield must not be more than 70% in order to prevent coprecipitation of impurities. This purified arsenic trisulfide is dried and distilled in the same way as the above process.

Preparation of the Glass

The arsenic sulfide glass is cast in the Pyrex glass vessel with flowing nitrogen gas. The schematic diagram of the casting is shown in Fig. 1. The red block of glass is heated in the

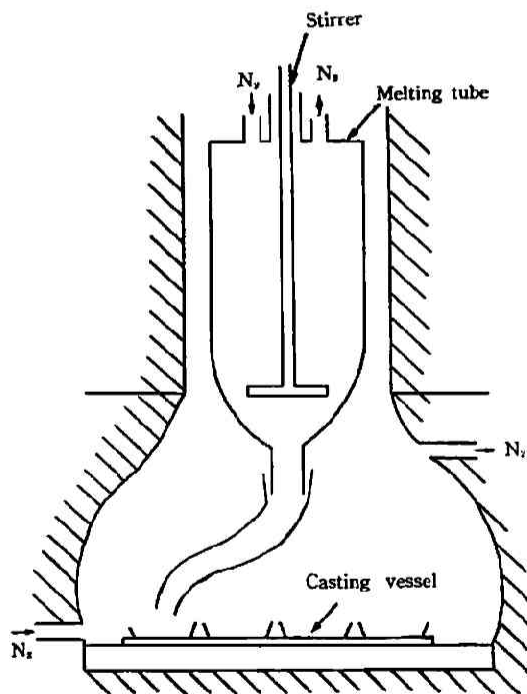


Fig. 1 Schematic diagram of the oven for casting of the arsenic sulfide glass

melting tube at 600°C for about an hour and the bubbles are driven off, and then the molten glass is stirred at 10 r. p. m. for 2 hours in order to homogenize it and to remove stria. The molten glass is flowed down into the casting vessels of 60 mm in diameter and 10 mm in depth. After annealed at 175°C for 12 hours, the glass is cooled slowly down to 105°C. The glass is polished roughly on the rotating grinder with Al_2O_3 of 500~1000 mesh and shaped to 30 mm in diameter and in the

variable thickness. Fine polishing is done with rouge on the soft pitch plate.

Light Transmission

Fig. 2 shows the transmissions of arsenic sulfide glasses with the variable thickness in the infrared

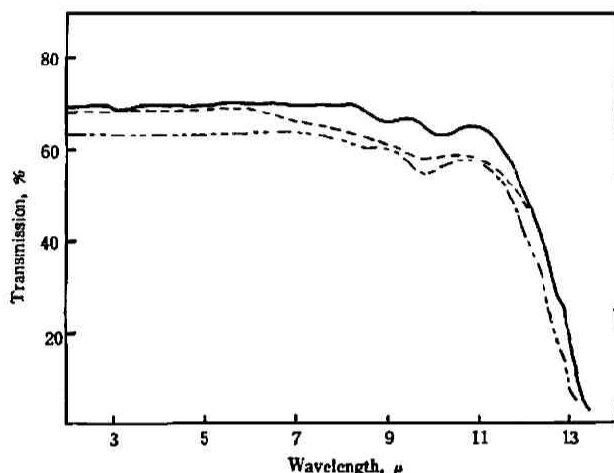


Fig. 2 Transmission of As_2S_3 glass with the variable thickness in the infrared region

— 1 mm in thickness
 ---- 2 mm in thickness
 - · - 4 mm in thickness

region determined using a Perkin Elmer Model 21 spectrometer with a NaCl prism. For the glass of 1 mm in thickness, the transmission is about 70% between 1 and 8μ , and decreases to 60% at 11μ . Beyond 12μ it is suddenly lowered and reduced to a few per cent at 13μ . Many samples show monotoneous transmission curves, but some show the weak absorptions at 3 and 6.4μ being due to the gases included in the arsenic sulfide glass.

Quantitative analysis of arsenic is done by Levoll's method⁵⁾, and that of sulfur, by Escka's

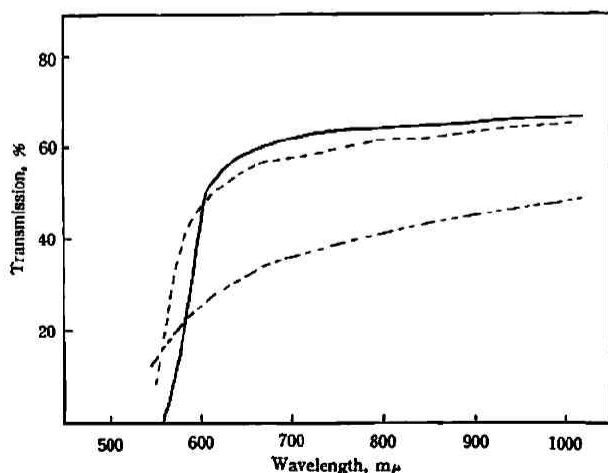


Fig. 3 Transmission of As_2S_3 glass of 1 mm in thickness

— As_2S_3 glass
 ---- 40% sulfur
 - · - 60% sulfur

5) F. Treadwell and W. Hall, *Analytical Chemistry*, II, Chapman and Hall, p. 317 (1937)

method⁶⁾.

As the result of the analysis, arsenic sulfide glass is found to be almost perfectly composed of two atoms of arsenic and three atoms of sulfur, that is, the glass is arsenic trisulfide As_2S_3 itself, and does not contain free sulfur, free arsenic, and other sorts of arsenic sulfides, *e. g.* As_2S_2 , As_2S_5 as network former. Fig. 3 shows the transmission curves in the visible region. Arsenic trisulfide glasses containing different amounts of sulfur are prepared. As the sulfur content increases, the transmission decreases beyond $600\text{m}\mu$, but increases at about $550\text{m}\mu$, and the glass becomes more and more yellow.

These glasses are stuck on slide glasses with Canada balsam and polished to thin layers with alumina. They are observed with a polarizing microscope and recrystallization of sulfur can not be detected after one month even in the glass containing 60% sulfur.

Strain and Homogeneity

In most of arsenic trisulfide glasses the homogeneity was good and no internal strain was found. But in a few part of the samples the inhomogeneity and many tiny bubbles were found. The inhomogeneity of the glasses was caused by inflow of the sublimate into the melt from the inner wall of a crucible. The inflow of the sublimate was prevented by using shallow crucibles. The tiny bubbles aggregate and settle down at the bottom of the melt during heating at 600°C for an hour.

Considerations

For the preparation of pure arsenic trisulfide, the synthesis from hydrogen sulfide and arsenious oxide seems to be the more favourable of the two methods in this work in respect of economization and techniques.

Although As_2S_3 glass has some defects, such as brittleness or lower melting point, it has a good transparency to the longer range of infrared as compared with the other oxide glasses^{7,8)}. With the glass of 1 mm in thickness, about 70% is the maximum value of transmission, and the loss seems to be chiefly caused by the surface reflection because the index of refraction is very high, *e. g.* 2.5 at 0.589μ ⁹⁾. If the absorption of this glass is zero and the index is used as 2.5, transmission is calculated employing Fresnel's formula as 69%. According to this fact, the exclusion of surface reflection seems to be the very effective device. Etching of the surface by several reagents does not show good results, and coating of the thin layer with proper vitreous substances is expected to be a useful method.

6) F. Treadwell and W. Hall, *Analytical Chemistry*, II, Chapman and Hall, p 83 (1937)

7) H. C. Hafner, *J. Am. Cer. Soc.*, **41**, 315 (1958)

8) H. C. Hafner, *ibid.*, **41**, 371 (1958)

9) A. Winter, *ibid.*, **41**, 464 (1958)

Apart from the good transparency in the infrared region, arsenic trisulfide glass offers interesting subjects of the transformation in solid. Sulfur and selenium are easily transformed in the state of elemental glasses^{10, 11}).

Arsenic trisulfide on heating turns from deep yellow to black at about 170°C, and on cooling it changes into red.

There is little literature on the chromatic thermosensitivity of various substances, and much works are remained in the field of the subjects of transition in solid.

The authors have great pleasure in expressing their sincere thanks to the late Professor. R. Kiyama and Professor W. Jono for their advices and encouragements throughout the course of this investigation. They are also indebted to the Department of Education for the Grant to the Scientific Production Research.

*The Laboratory of Physical Chemistry,
Kyoto University*

10) C. Briske, *Disc. Faraday Soc.*, **23**, 196 (1957)

11) N. E. Brown, *J. Metals*, **7**, 379 (1955)