Studies on Arsenic Trisulfide Glass

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The arsenic trisulfide glass has been studied as one of the new optical materials, because it can transmit infrared rays very well and has marked resistance to water and acid, and is more easily manufactured than single crystals[1-5].

The author once studied some different methods of preparation for technical arsenic trisulfide glass, and found the transmission value to be about 70% between 2 and 12 μ for 1 mm. thickness[6]. This figure is the maximum of the transmission value of this glass and the rather low transparency in this case results from the surface reflection and high refractive index[7]. If this glass can be properly coated on the surface, it will be more suitable for optical purposes, for this process must assist in reducing the reflection at the surface and raising the poor resistance to alkali.

Apart from the question of optical materials, the arsenic trisulfide glass is the interesting experimental glass composed of one component which melts at low temperature (about 300°C). Since the publication of the theory by Zachariasen[8] and the introduction of the X-ray analysis by Warren[9], glassy substances are explained as homogeneous polymers which characterize the amorphous substances consisting of network formers and modifiers, but some writers have insisted that glass is composed of a microheterogeneous system by microcrystalline structure[10]. These different views are closely related to the process of the transition of solids[11]. What process of transition occurs in glassy substances? The solution of this problem is very interesting and necessary in investigating the structure of glass. The various physical properties have frequently been studied on this point. The color of arsenic trisulfide has been found to be remarkably sensitive to changes in temperature. When it is heated yellow arsenic trisulfide is transformed to red and then to black. At 100°C, red aesenic trisulfide and at 170°C black substances can be obtained[12,13].

The author studied the thermal expansion values of red arsenic trisulfide glass

1) R. Frerichs, *Phys. Rev.*, **78**, 643 (1950).
2) W. A. Fraser, *J. Opt. Soc. Am.*, **43**, 322 (1953).
3) W. A. Fraser, ibid., **43**, 823 (1953).
4) R. Frerichs, ibid., **43**, 1153 (1953).
5) M. H. Bloch, *J. Research Natl. Bur. Standards*, **59**, 2774 (1957).
6) Presented before the Annual Conference on the Artificial Minerals, Nagoya, October, 1958. This result was published in *the Review of Physical Chemistry of Japan*, **29**, 22 (1959).
7) 2.43 at 5μ.
8) W. H. Zachariasen, *J. Am. Chem. Soc.*, **54**, 3841 (1932).
9) B. E. Warren et al., *J. Am. Ceram. Soc.*, **21**, 49 (1935).
10) For example, K. S. Evstropyev, "The Structure of Glass", Consultants Bureau, Inc., New York (1958), p. 9.
11) F. C. Kracer, "Phase Transformations in Solids", John Wiley & Sons, Inc., New York (1951), p. 257.
12) H. Winter, *Z. anorg. u. allgem. Chem.*, **34**, 228 (1904).
13) E. W. Blank, *J. Chem. Educ.*, **20**, 171 (1943).

at transition temperatures by the quenching method and investigated the process of the transition.

Experimental

The preparation of techincal arsenic trisulfide, the casting and the polishing of the glass were done by the same methods as mentioned in the previous report (Ref. 6).

Terylene film was used to coat the surface of the glass, because it can form the transparent, thin and filmy state easily at fairly low temperature and has a proper refractive index to remove the surface loss peculiar to the arsenic trisulfide glass. Terylene was dissolved in *o*-chlorophenol and this dilute solution was dropped on the glass which was horizontally rotated by an electric motor. Such treated glass was dried at 80°C in an air bath. The chemical durability of the glass to alkali was measured by spectroscopic method; that is, some pieces of glass were experimentally dipped in aqueous solution of sodium hydroxide for a limited time. After such etching they were washed and dried and measured on the falling of the transmittance at 2 μ wavelength.

The thermal expansion was measured by the ordinary optical lever method. Throughout the measuring, the samples were heated in succession at the constant rate of 2°C a minute. Before heating they were annealed at the constant temperature (187°C) for three days and allowed to cool very slowly to room temperature about 60 hr. in the electric annealing oven. They were then reheated for several hours at various temperatures ranging from 153 to 180°C and were quenched in the air.

The heating was made always in an mobile oil bath to prevent arsenic trisulfide from oxidizing.

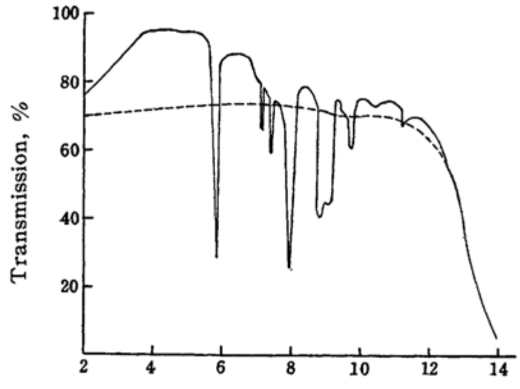

Fig. 1. Effect of coating on the arsenic trisulfide glass of 1 mm. thickness.
——: coated.
----: not coated.

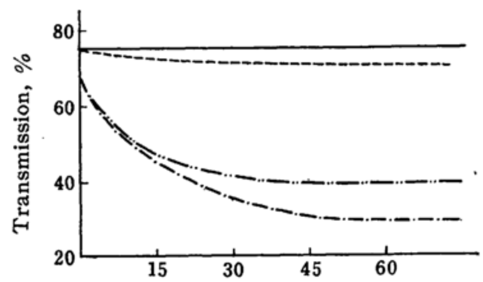

Fig. 2. Transmission after treatment in alkali.
—— and ----: coated glass treated in 0.05 and 0.1 N, respectively.
-··-·· and -·-·: uncoated glass treated in 0.05 and 0.1 N, respectively.

Results and Discussion

Coating of the Surface. — As shown in Fig. 1, the effect of the coating is very remarkable in the range of short wavelengths, while it gradually decreases in the wavelengths which are over 7 μ and many absorption bands of surface film appear. If the film coated on the surface is so thin that interference color can be seen, the efficacy of the treatment in the rays of the short wavelengths is very conspicuous. In that case the transmittance is 75 to 95% between 2 and 5.7 μ. Moreover, even such a thin film markedly increases durability to alkali. As shown in Fig. 2, when dipped in 0.05 N alkaline solution, the coated glass is hardly affected at all. After 15 hr. etching the transmittance decreases by about only 4%.

In the case of 0.1 N, the coated glass is affected in some degree, but even after dipping for 30 min. the transmittance decreases by only 1~2%. All these decreases of the transmission were observed to be caused by etching pits which grew up from mechanical scratches on the film. These results mean that terylene film has sufficient protecting action against alkaline etching in such concentrations. As these results show, such coated arsenic trisulfide glass is of good use as optical material of the cell in the infrared between 2 and 5.7 μ and as seen in Fig. 1, the uncoated glass can be utilized as basic glass to study infrared absorption of various substances. Besides the terylene film, by proper coating of other materials the arsenic trisulfide glass seems to be the more valuable optical material.

Thermal Expansion. — The physical properties of glass are affected remarkably by different thermal histories. The abnormal thermal expansion of borosilicate

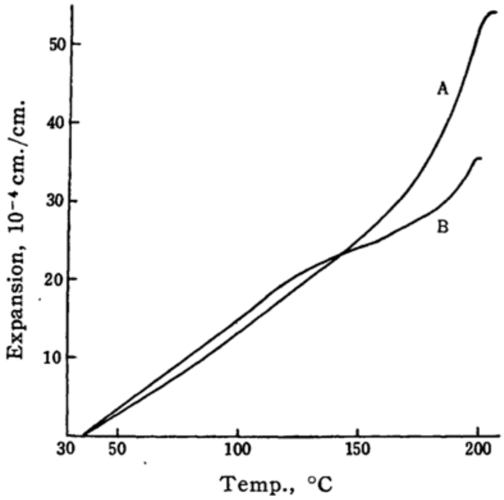

Fig. 3. Thermal expansion.
A: annealed, B: chilled.

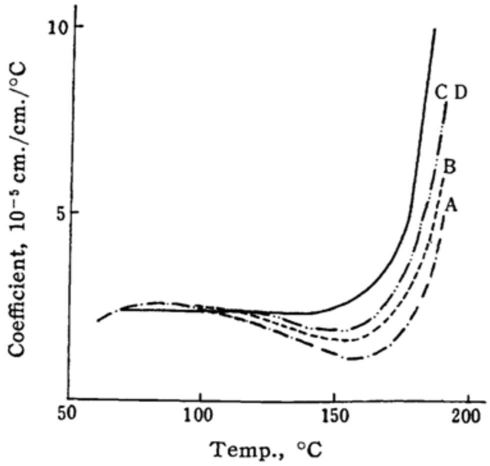

Fig. 4. Different coefficients among annealed and chilled glass.
——: annealed glass.
A, B, C and D are quenched at 180, 174, 164, and 153°C, respectively.

glass is one of the well-known examples of these sorts. As shown in Fig. 3, the annealed arsenic trisulfide glass shows transformation point at 170°C. The meaning of the transformation point in glass is not always the same in crystallography, but it is an undoubted fact that the structure of glass may change to a certain extent near the point. On the other hand, the precipitated arsenic trisulfide is said to have transformation points near 100 and 170°C[12-14]. However, in the case of the glassy state, the transformation appeared only at 170°C. Accordingly in order to study the common transformation point of these different solid states, the various coefficients of expansion were measured by the quenching method. A, B, C and D shown in Fig. 4. represent respectively the quenched specimens at 180, 174, 164 and 153°C. In Fig. 4, both A and B indicate larger values of the coefficients than in annealed glass below 100°C, but C and D almost the same values as annealed glass; that is, the quenching effect does not appear in the case of C and D.

In the high temperature range, the higher the quenching temperature becomes, the smaller the coefficient becomes, arriving at the minimum value near 160°C, but no substantial difference can be found among A, B, C and D curves and these results suggest that there is no intrinsic difference among the internal structures of the four specimens; that is, the difference of the coefficients shows the extent of their polymerization, and the higher the quenching temperature becomes, the more insufficient the polymerization becomes. This fact is guessed also from the difference among their exact temperatures at which the graduation of the dilatometer begins to show shrinking.

TABLE I. QUENCHING EFFECT ON THE EXACT TEMPERATURE AT WHICH THE ELONGATION CURVE ON THE DILATOMETER BEGINS TO SHOW SHRINKING

Sample	Temp., °C
A	200
B	200
C	202
D	206
annealed	209

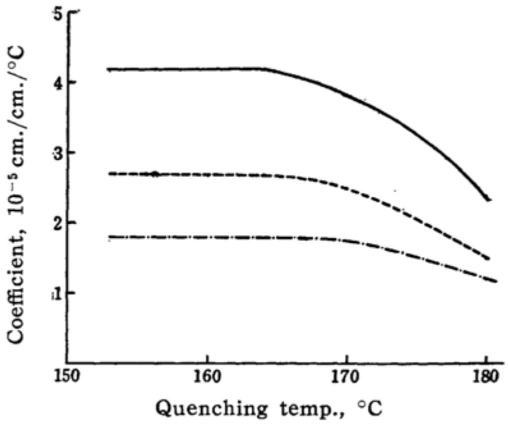

Fig. 5
——, ----, and —·—: measured at 180, 170 and 160°C, respectively.

14) W. A. Jonker, *Z. anorg. u. allgem. Chem.*, **62** 89, (1909).

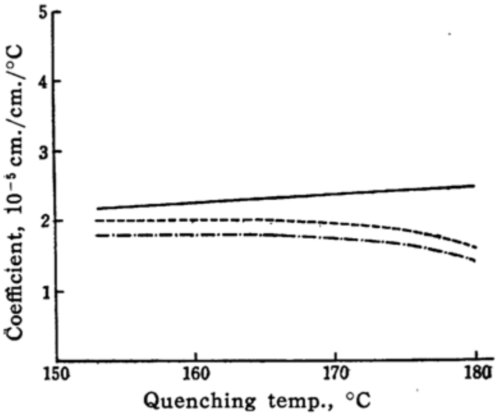

Fig. 6

——, ----, and —·—: measured at 100, 140 and 150°C, respectively.

These results are given in the table. As can been seen, the higher the quenching temperature becomes, the lower the exact temperature becomes; that is, the less sufficient the polymerization becomes.

Figs. 5 and 6 show the interrelation between the quenching temperature and the temperature in measuring of the coefficients. The abscissa means the quenching temperature. The differences among four specimens are notable at 180°C of measuring-temperature and become smaller at low temperature and at 100°C almost disappear. In all specimens the coefficients measured above 160°C, increase as the temperature rises, but this phenomenon appears in reverse below 150°C. Consequently all specimens show the minimum coefficient between 150 and 160°C. However, while the quenching temperature rises, the coefficients decrease in all cases above 100°C.

Summary

Arsenic trisulfide glass shows 70% of transmittance between 2 and 12 μ. This transmittance is somewhat insufficient for the optical cell in the infrared. Moreover, the chemical durability to alkali is very weak. These defects can be removed by proper coating on the surface. For instance, it can be of good use between 2 and 5.7 μ by using terylene film.

In thermal expansion, the transformation point of glassy arsenic trisulfide is nearly 170°C. In order to study what process of transformation occurs in the glass, the quenching method was applied. Some pieces of annealed glass were experimentally quenched at 180, 174, 164 and 153°C. Thermal expansion was measured on these quenched glasses.

Because of their various controls of expansion by temperature, glassy transformation at 170°C has no connection with transformation at the same temperature in arsenic trisulfide.

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