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Effect of SO_2 Impurity on the Optical Transmission of As_2S_3 Glass

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Abstract—To assess the effect of sulfur dioxide impurity on the optical properties and absorption spectrum of glassy arsenic sulfide, we have prepared As_2S_3 glass samples containing 0.01 to 0.12 wt % SO_2 and have measured their transmission spectra in the range 500–5000 cm^{-1}. The extinction coefficient of sulfur dioxide in glassy arsenic sulfide, evaluated from the intensity of the 1158-cm^{-1} absorption band, is 10.0 ± 0.7 cm^{-1}/wt %.

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INTRODUCTION

The optical transmission of arsenic–sulfur glasses is sensitive to carbon impurities (COS, CS_2, CO_2), hydrogen-containing species (dissolved H_2O and H_2S; OH and SH groups), and combined oxygen (As_2O_3 and SO_2). The effects of H_2S, COS, CS_2, and CO_2 concentrations on the strength of the corresponding IR absorptions were quantified by Devyatykh et al. [1] and Borisevich [2].

Data on the effect of SO_2 impurities on the transmission spectrum of arsenic sulfide glasses are still limited. Tsuchihashi and Kawamoto [3] attributed the absorption bands at 1320–1330 and 1140–1170 cm^{-1} to SO_2 impurity. Based on earlier results [4], one might expect the spectra of arsenic sulfide glasses containing SO_2 to show a number of bands in addition to those above (Table 1).

The objective of this work was to prepare As_2S_3 glass samples containing known levels of sulfur dioxide, to measure their transmission spectra, and to establish a quantitative relationship between the sulfur dioxide content and the strength of the corresponding absorption bands.

EXPERIMENTAL

As_2S_3 glass samples were prepared by reacting arsenic tetrasulfide and sulfur, both purified by vacuum distillation. Glass batches were melted and homogenized in a rocking furnace at 800°C for 7 h, followed by furnace-cooling. The resultant glass ingot was 25 mm in diameter and 170 mm in length. IR transmission measurements (IFS-113V spectrometer) showed that the absorption coefficients of the SH and OH groups in the as-prepared glass were 1.2×10^{-2} and 2.5×10^{-3} cm^{-1}, respectively. The calculated SH content was 2.1×10^{-4} at %.

Sulfur dioxide was prepared by oxidizing extrapure-grade sulfur in flowing oxygen and was then purified by fractional distillation.

The procedure for introducing SO_2 into glassy arsenic sulfide was similar to that used in determining the extinction coefficients of CO_2, COS, and CS_2 [1].

Table 1. Vibrational frequencies of the SO_2 molecule [4]

Frequency, cm^{-1}	Characterization technique	Assignment
519 (524.5)	IR (gas), Raman (liquid)	ν_2
606	IR (gas)	$\nu_1 - \nu_2$
1151.2	IR (gas), Raman (gas)	ν_1
1361 (1336)	IR (gas), Raman (liquid)	ν_3
1871	IR (gas)	$\nu_2 + \nu_3$
2305	IR (gas)	$2\nu_1$
2499	IR (gas)	$\nu_1 + \nu_3$

Note: ν_1 is the symmetric stretching mode, ν_2 is the bending mode, and ν_3 is the antisymmetric stretching mode.

After rinsing in high-purity carbon tetrachloride, a glass sample (12–14 g) was placed in a quartz ampule, which was then connected to a leak-in system of known volume (Fig. 1). The volume of the system and ampule was measured relative to a calibrated volume. After pumping down the ampule containing glassy arsenic sulfide to a residual pressure of 6.5×10^{-4} Pa, sulfur dioxide was admitted in an amount sufficient for producing initial pressure p_0 in the system. Next, the ampule was disconnected from the system by sealing off tube *2*, and sulfur dioxide was removed from the leak-in system. The ampule was heated under static conditions for 4 h at 650°C and then furnace-cooled. In this way, we obtained glassy arsenic trisulfide in the form of a plate 5 mm in thickness, containing sulfur dioxide. Next, SO_2 was again introduced into the leak-in system, to pressure p_0, the partition was broken, and the residual pressure was measured after SO_2 dissolution. The difference between the initial and residual pressures was due to the SO_2 dissolution in arsenic sulfide. From this value, we calculated the amount of dissolved sulfur dioxide and its concentration in the sample using the Clapeyron equation. The sulfur dioxide content of the samples thus prepared was 1.3×10^{-2} to 12.4×10^{-2} wt % (Table 2).

The glass was withdrawn from the ampule, and several plane-parallel samples 2–3 mm thick were prepared for IR measurements. A control sample was prepared by the same procedure but without introducing sulfur dioxide.

Transmission spectra were recorded in the range 500–5000 cm^{-1} with an IFS-113V Fourier transform IR spectrometer.

The homogeneity of the SO_2 distribution was checked by measuring the spectra of samples cut from the upper and lower portions of the ingot. The spectra showed no variations in absorption with position in the ingot.

RESULTS AND DISCUSSION

Figure 2 shows the IR absorption spectra of arsenic sulfide glasses doped with sulfur dioxide in comparison with the spectrum of the control sample. The effect of sulfur dioxide on the absorption spectra of the glass is clearly seen in the range 800–1400 cm^{-1}. The introduction of sulfur dioxide into the glass gives rise to an absorption peaked at 1158 cm^{-1} (Fig. 2), which becomes stronger with increasing sulfur dioxide content. In addition, the spectra of the SO_2-doped samples show absorption bands centered at 985, 1053, and 1270 cm^{-1}. The bands at 1053 and 1270 cm^{-1} are due to As–O vibrations [5, 6]. Since the absorption bands in the range 800–1400 cm^{-1} have a complex structure, the spectrum in this range was deconvoluted into elementary components as described by Bychkova et al. [7]. As an example, Fig. 3 shows the spectrum of the sample containing 0.11 wt % SO_2 and the deconvolution results.

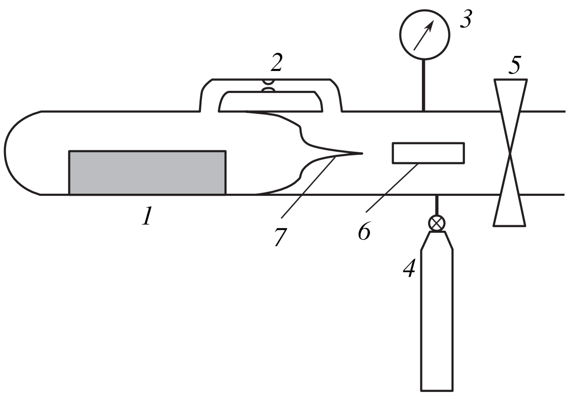

Fig. 1. Schematic of the apparatus for introducing sulfur dioxide into glassy arsenic sulfide: (*1*) ampule containing a glass sample, (*2*) tube for sealing off under vacuum; (*3*) manometer; (*4*) cylinder containing SO_2; (*5*) outlet valve; (*6*) striker, (*7*) partition.

At sulfur dioxide contents within 0.12 wt % and sample lengths no greater than 30 mm, the absorptions at 1361, 1871, 2305, and 2499 cm^{-1}, due to the fundamental and mixed frequencies of SO_2 (Table 1), were missing.

The spectrum of the control sample (2 mm in thickness) shows no bands due to H_2O or OH groups (Fig. 2). As seen in Fig. 2, the spectra of the SO_2-doped samples contain absorption bands arising from H_2O (1588 and 3590 cm^{-1}), CO_2 (2324 cm^{-1}), and OH and SH groups (3450 and 2487 cm^{-1}, respectively). Note that the intensities of the absorption bands due to H_2O, CO_2, and OH groups do not correlate with the SO_2 con-

Table 2. Sulfur dioxide content of glassy arsenic sulfide

Sample no.	Sample weight, g (±0.001)	Δp, Pa (±260)	V, cm^3 (±0.4)	wt % $SO_2 \times 10^2$ (±0.5)
1	14.106	650	103.2	1.3
2	14.953	1560	95.0	2.7
3	12.556	1950	106.9	4.4
4	12.185	2990	91.0	6.1
5	13.987	3120	102.0	6.2
6	12.470	5460	94.0	11.2
7	13.719	6370	98.0	12.4

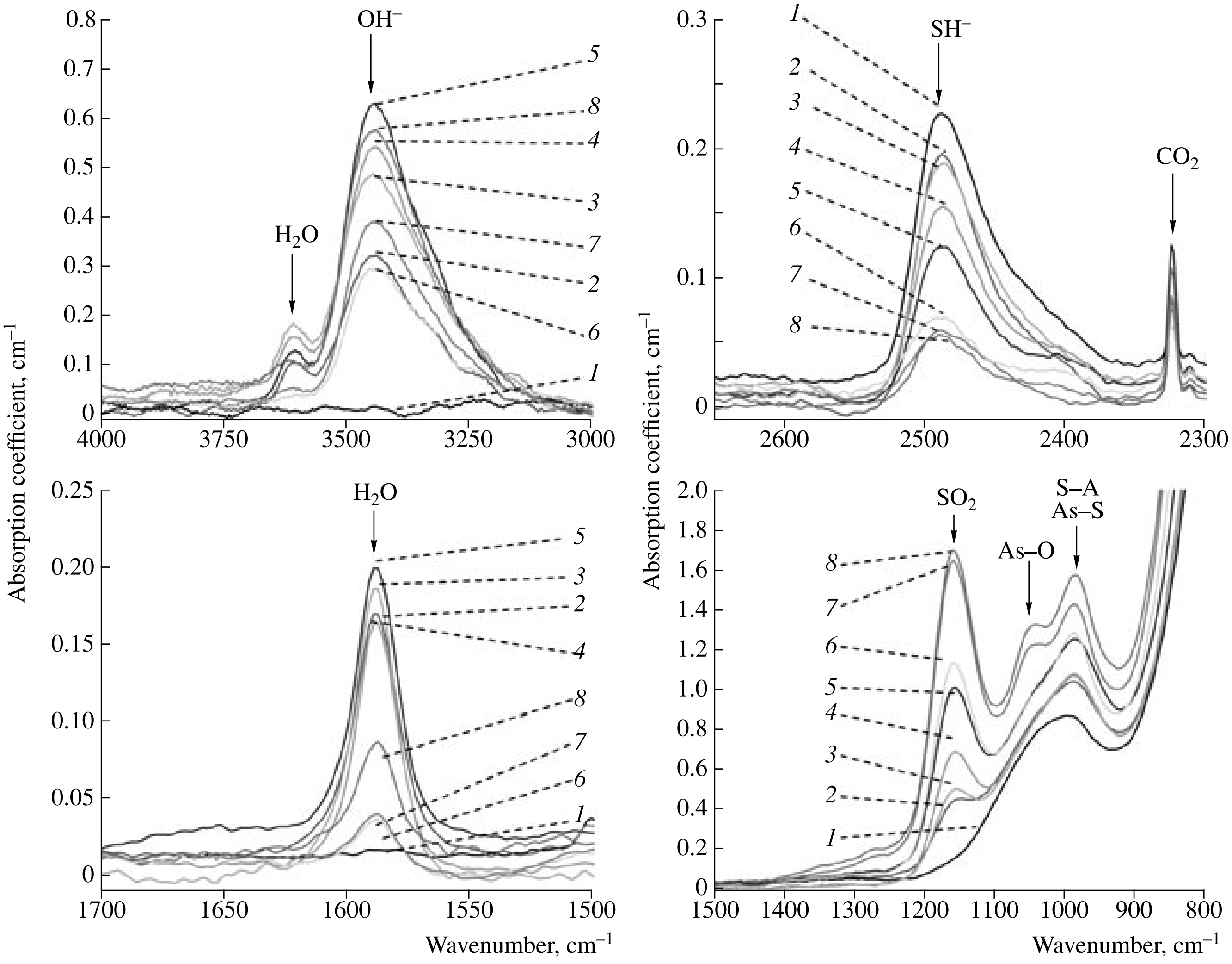

Fig. 2. IR absorption spectra (in different ranges) of arsenic sulfide glasses containing (*2*) 0.013, (*3*) 0.027, (*4*) 0.044, (*5*) 0.061, (*6*) 0.062, (*7*) 0.112, and (*8*) 0.124 wt % SO_2; (*1*) control sample.

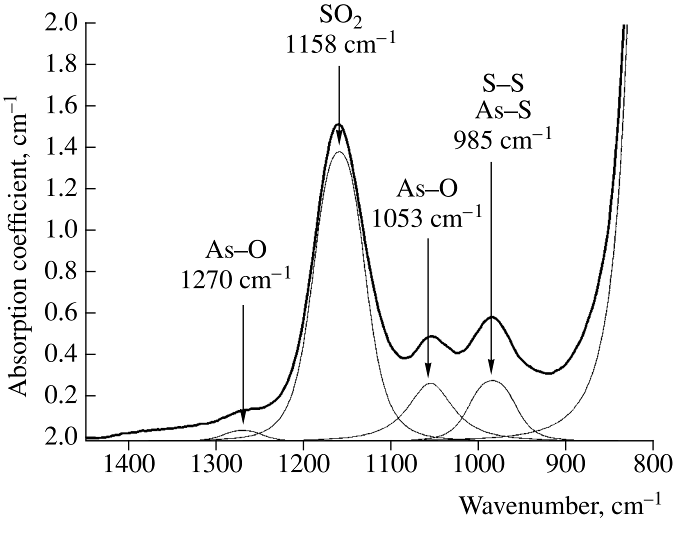

Fig. 3. IR absorption spectrum of the As_2S_3 sample containing 0.11 wt % SO_2 and deconvolution results.

tent of the glass. The content of SH groups decreases with increasing SO_2 concentration in the glass (Fig. 4), by virtue of the reaction

$$SO_2 + 2H_2S \longleftrightarrow 2H_2O + 3S. \qquad (1)$$

The reduction in the sulfur dioxide content of the glass via reaction (1), evaluated from the intensity of the absorption band at 2487 cm^{-1}, is insignificant (from 5.6×10^{-4} to 1.5×10^{-4} wt %, i.e., less than 1% relative) compared to its initial content (1.3×10^{-2} to 12.4×10^{-2} wt %).

The presence of bands due to oxygen–arsenic vibrations attests to chemical reaction between the sulfur dioxide and glass. The overall reaction scheme

$$2As_2S_3 + 3SO_2 \longleftrightarrow 2As_2O_3 + 9S \qquad (2)$$

accounts for the formation of As–O and S–S bonds in the glass. One possibility is the incorporation of SO_2 molecules into the glass network through the breaking of As–As bonds and formation of >As–O–S–O–As< linkages. As seen in Fig. 5, the intensity of the As–O and S–S bands increases with SO_2 content. According to Shiryaev et al. [6], the extinction coefficient for the 1050-cm^{-1} absorption band, arising from oxygen impurities in glassy As_2Se_3, is 27 ± 12 cm^{-1}/wt %. Using this value, we find that the fraction of oxygen involved in As–O bonds in the As_2S_3 glass is no greater than 19% of its amount introduced into the glass in the form of SO_2. On the whole, reactions (1) and (2) in As_2S_3 glass doped with sulfur dioxide to above 6.2×10^{-2} wt % consume no more than 10% of the dissolved SO_2.

Figure 6 shows the composition dependence of the absorption coefficient for the 1158-cm^{-1} band (due to sulfur dioxide) in glassy arsenic sulfide. Using the Bouguer–Lambert–Beer law,

$$I = I_0 e^{-\varepsilon C l},$$

where I and I_0 are the intensities of the transmitted and incident radiation, respectively, ε is the extinction coefficient, l is the optical path, and C is the concentration of the absorbing impurity, the extinction coefficient of sulfur dioxide at concentrations from 1.3×10^{-2} to 6.2×10^{-2} wt % was determined to be 10.0 ± 0.7 cm^{-1}/wt %. In the spectral range 1100–1200 cm^{-1}, the intrinsic optical losses in As_2S_3 glass are 0.01–0.21 cm^{-1} [8]. It follows, therefore, from the above extinction coefficient that the presence of 0.009 wt % SO_2 gives rise to optical losses comparable to intrinsic losses.

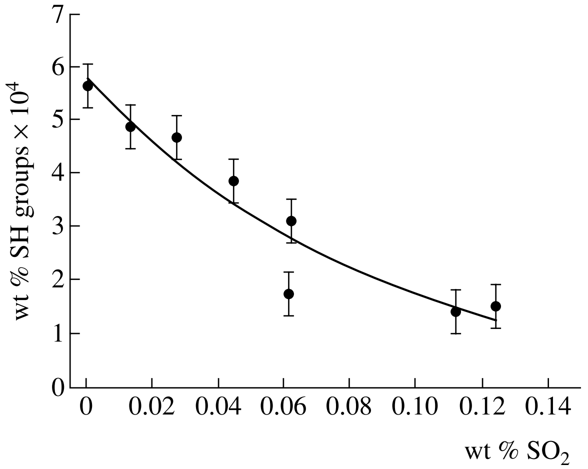

Fig. 4. Content of SH groups as a function of SO_2 concentration in the glass.

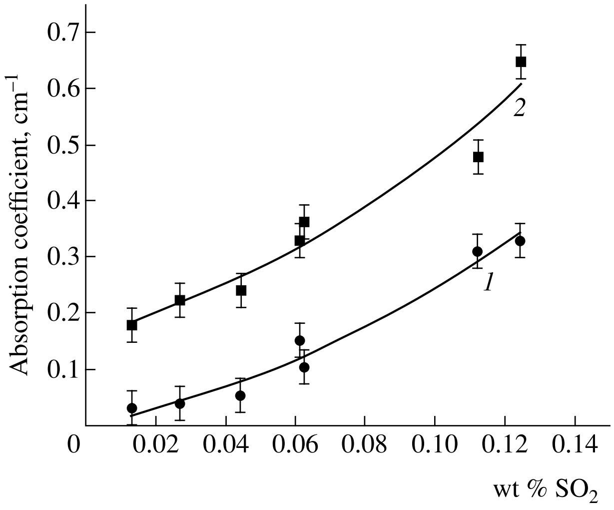

Fig. 5. Absorption coefficient at (*1*) 1053 (As–O) and (*2*) 985 cm^{-1} (S–S) as a function of sulfur dioxide content for arsenic sulfide glasses.

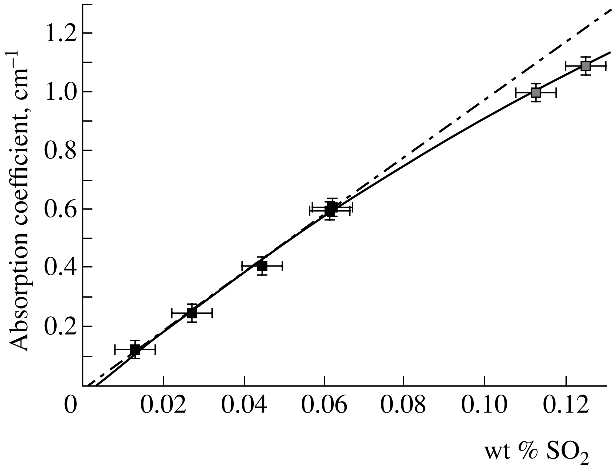

Fig. 6. Absorption coefficient at 1158 cm^{-1} as a function of sulfur dioxide content for arsenic sulfide glasses.

CONCLUSIONS

The presence of sulfur dioxide in As_2S_3 glass leads to significant absorption in the spectral range 900–1300 cm^{-1}. The transmission spectra of SO_2-containing samples show an absorption band at 1158 cm^{-1}, due to SO_2 (ν_1 mode), and bands at 1053 and 1270 cm^{-1}, arising from As–O bonds. The extinction coefficient evaluated from the composition dependence of the intensity of the 1158-cm^{-1} band is 10.0 ± 0.7 cm^{-1}/wt %.

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