

The Infrared Spectra of some Modifications of Arsenic Trioxide and Antimony Trioxide

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The infrared spectra of cubic and monoclinic arsenic trioxide and cubic and orthorhombic antimony trioxide have been compared with the spectra of the vitreous modifications. The latter show best agreement with the spectra of the cubic modifications.

The structures of the crystalline modifications of the trioxides of arsenic and antimony are quite well known. The cubic forms are built up of As_4O_6 and Sb_4O_6 molecules¹, whereas the monoclinic arsenic trioxide² and the orthorhombic antimony trioxide³ have chain or layer structures. The existence of other crystalline modifications has been suggested².

The structures of the vitreous form are, however, a matter of controversy. Shulman and Shumb⁴ inferred from the devitrification of arsenic trioxide glass that it is rather closely related to the cubic form. A comparison of the densities (cubic⁵ 3.87, monoclinic⁶ 4.14, glass⁷ 3.70) seems to strengthen this inference.

As Zachariassen's theory of glass structures⁸ seems to be incompatible with the existence of As_4O_6 molecules, Bötticher, Plieth, Reuber-Kürbs and Stranski⁹ were led by this and other evidence¹⁰ to carry out an X-ray investigation of the vitreous phase. Their conclusion, the similarity of the vitreous and the monoclinic modifications, seems in the light of later investigations¹¹ on the errors involved in this kind of determinations rather uncertain.

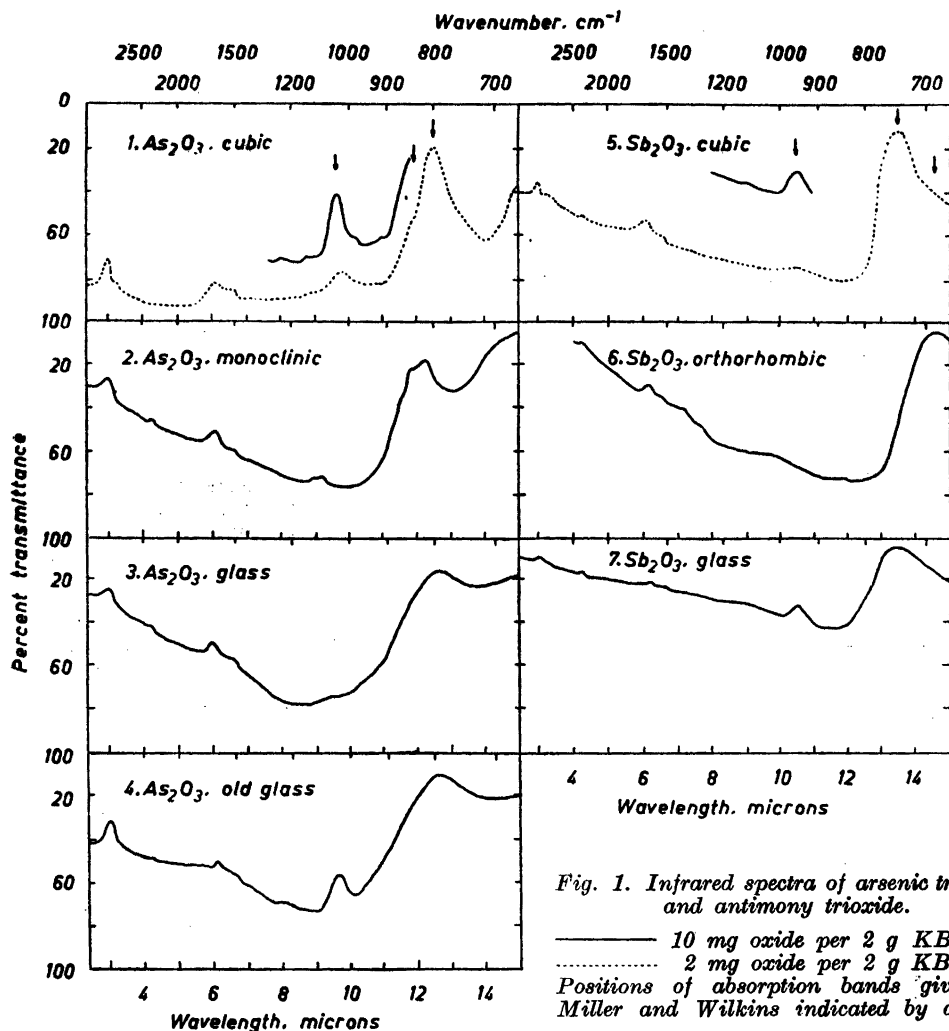
In order to compare the structures of the above trioxides, their infrared spectra have been obtained in the sodium chloride region.

EXPERIMENTAL

The spectra were obtained on a Perkin-Elmer 21 recording spectrometer in the interval of 2 to 15 microns. The samples were prepared by the potassium bromide technique with 2 or 10 milligrams of oxide in 2 grams discs of about one inch diameter. A pressure of 20 tons was applied for 15 minutes.

The trioxide modifications were prepared from Merck *pro analysi* reagents after recrystallisation. The identities were ascertained by means of the X-ray diffraction patterns.

The samples were as follows



Arsenic trioxide: 1) cubic, 2) monoclinic⁴, 3) glass, freshly prepared by quenching melted oxide, 4) glass, stored over P_2O_5 for a month after grinding with potassium bromide.

Antimony trioxide: 5) cubic, 6) orthorhombic¹³, 7) glass, two days old, prepared by pouring melted oxide into water.

The resulting spectra are shown in Fig. 1.

RESULTS AND DISCUSSION

A number of recurrent absorption bands between 2 and 6.5 microns are caused by water and other impurities. Infrared spectra of arsenic and antimony trioxides of unknown purity have been obtained by Miller and Wilkins¹³.

They agree well with our spectra of the cubic forms. These are quite similar in appearance with the bands displaced towards lower wavenumbers in the case of antimony trioxide, as would be expected.

In the spectrum of monoclinic arsenic trioxide the principal band is found at higher wavenumbers than for the cubic form. The corresponding band of orthorhombic antimony trioxide, however, is displaced towards lower wavenumbers. This seems to indicate a structural difference between the modifications of lower symmetry.

For both the vitreous modifications, the principal band is found at the same position as for the cubic modifications. The bands are of less peak intensity and quite broad. Old arsenic trioxide glass and antimony trioxide glass have a secondary band at the same position as found for the cubic modifications. It therefore seems that these samples are partially transformed to the cubic forms. By comparison of all spectra, the vitreous modifications seem to be closer related to the cubic forms than to those of lower symmetry.

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REFERENCES

1. Bozorth, R. M. *J. Am. Chem. Soc.* **45** (1923) 1621.
2. Becker, K., Plieth, K. and Stranski, I. N. *Z. anorg. allgem. Chem.* **266** (1951) 293.
3. Buerger, M. J. and Hendricks, S. B. *Z. Krist.* **98** (1938) 1.
4. Schulman, J. H. and Schumb, W. C. *J. Am. Chem. Soc.* **65** (1943) 878.
5. Straumanis, M. *Z. Physik* **126** (1949) 49.
6. Groth, P. *Poggendorfs Ann. Physik* **137** (1869) 414.
7. Kordes, E. *Z. physik. Chem.* **B43** (1939) 177.
8. Zachariasen, W. H. *J. Am. Chem. Soc.* **54** (1932) 3841.
9. Bötticher, H., Plieth, K., Reuber-Kürbs, E. and Stranski, I. N. *Z. anorg. allgem. Chem.* **266** (1951) 302.
10. Kürbs, E., Plieth, K. and Stranski, I. N. *Z. anorg. allgem. Chem.* **258** (1949) 238.
11. Borgen, O., Grjøtheim, K. and Krogh-Moe, J. *Kgl. Norske Videnskab. Selskabs Forh.* **27** (1954) No. 17.
12. Debray, H. *Compt. rend.* **58** (1864) 1209.
13. Miller, F. A. and Wilkins, C. H. *Anal. Chem.* **24** (1952) 1253.

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