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THE TEMPERATURE DEPENDENCE OF MAGNETIC SUSCEPTIBILITY AND THERMOGRAVIMETRY OF ANTIMONY TRIOXIDE AND ANTIMONY TRISULPHIDE SPECIMENS IN RELATION TO THEIR METHOD OF PREPARATION

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ABSTRACT

Several samples of pure antimony trioxide and pure antimony trisulphide of various origins were investigated for the temperature dependence of their magnetic susceptibility for the first time. Numerous measurements have been carried out, comprising X-ray diffraction patterns, pycnometric density, thermogravimetric analysis and the temperature dependence of magnetic susceptibility. Results indicate that both antimony trioxide and antimony trisulphide specimens are diamagnetic. The origin or method of preparation of each material investigated had a consistent effect on the values of diamagnetic susceptibility obtained. This could be attributed to the degree of purity, grain size and crystal structure of the materials of various origins investigated.

INTRODUCTION

The interest in the present investigation is due to the useful application of the material investigated in radar, transistor and diode industries.

The diamagnetic susceptibility of antimony trioxide and that of antimony trisulphide were given by Prasad et al. [1] as 0.190×10^{-6} and 0.255×10^{-6} c.g.s., respectively.

In view of the scarcity of reliable susceptibility data and the lack of information regarding their temperature dependence; the present measurements were performed at both room and elevated temperatures using antimony trioxide and antimony trisulphide specimens of various origins. This was a continuation of earlier physical measurements.

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EXPERIMENTAL

A. Sample preparation

Antimony trioxide: Sb_2O_3 (BDH) and heat treated Sb_2O_3 (12 h at 590 °C) were used.

Antimony trisulphide: orange Sb_2S_3 (prepared by the wet process) and grey-black Sb_2S_3 (prepared by heating the orange form at 280 °C for 8 h) were investigated.

B. X-ray diffraction measurements

X-ray diffraction measurements were undertaken using Cu $K\alpha$ radiation and nickel filter at room temperature.

C. True density measurements

True density measurements were carried out using pycnometry at room temperature.

D. Thermogravimetric analysis

TGA measurements were performed using an automatic thermobalance in air in the temperature range from 20 °C to 500 °C.

E. The temperature dependence of magnetic susceptibility measurements

The Gouy method was applied [2]. The electromagnet used was capable of producing a field strength of 12000 gauss for a current of 10 A in the coil at a gap width of 20 mm. This was quite sufficient for a non-inductive tubular heating oven, the temperature of which could be measured by means of a copper constantan thermocouple. A Mettler balance was used which had a damping system and could read accurately to 10^{-5} g. A silica specimen tube 20 cm long with a uniform inner diameter of 6 mm was used throughout. Four sets of readings were taken corresponding to the field current which indicated the absence of any ferromagnetic impurities in the specimens. The mass susceptibility was calculated from the following equation:

$$\chi_s = 0.72 \times 10^{-6} \frac{W/\mathrm{d}W}{\mathrm{d}S/S} + 0.29 \times 10^{-6} \left(\frac{1}{\sigma} - \frac{W}{\mathrm{d}W} \frac{\mathrm{d}S}{S} \frac{1}{d} \right)$$

where $\mathrm{d}S$ is the net force resulting from the material, $\mathrm{d}W$ is the net force resulting from the reference material (water) and σ is the true density. Corrections for porosity were made using Krishnan's equation [3]. Measurements were undertaken on samples having comparable average grain size, at room and elevated temperatures up to 280 °C.

RESULTS AND DISCUSSION

Table 1 shows values of the measured true density (g cm^{-3}) for the various materials investigated with those given by earlier investigators.

TABLE 1

True densities (g cm^{-3}) for the various antimony trioxide and antimony trisulphide specimens

Antimony trioxide specimens			Antimony trisulphide specimens		
Supplied (BDH)	Prepared	Previous results	Orange	Grey-black (280 °C 8 h)	Grey-black (previous results)
5.61	5.78	5.79 [4]	4.68	4.69	4.64 [5]

Results obtained from the room temperature X-ray diffraction patterns indicated that: (1) BDH antimony trioxide contained a mixture of orthorhombic and cubic crystalline phases; (2) the freshly prepared antimony trioxide (heat treated at 590 °C for 12 h) was found to possess only the orthorhombic crystal form; (3) the orange antimony trisulphide is the amorphous phase having no crystalline modification; (4) grey-black antimony trisulphide was found to possess only the orthorhombic crystal phase.

For antimony trioxide (Table 1) the lower density obtained for the sample supplied could be attributed to the structure difference between the specimens (as confirmed by X-ray analysis) and/or the degree of purity. The structure difference indicates that the prepared specimens possess a purely orthorhombic crystal form and hence has a higher degree of packing (higher density) than the supplied specimens. The supplied specimens were found to possess a cubic (30%) rather than the orthorhombic (70%) crystal form as proved from X-ray investigation.

In the case of antimony trisulphide, the low density obtained for the orange form (Table 1) may be due to the presence of excess sulphur as proved by chemical and thermogravimetric analyses of the materials investigated, and/or to the existence of larger amounts of holes incorporated in the orange form. The present state of affairs bears resemblance to the case of amorphous selenium which possesses lower density and a larger number of holes as compared with its crystalline modification [6,7]. This is also similar to results with germanium whose amorphous form possesses a larger number of holes than the crystalline form. Thus, results for the magnetic susceptibility of the test samples (Table 2) indicated good agreement with those of earlier authors [1,8]. The value obtained for the supplied specimens was found to deviate from that of the prepared one by a paramagnetic value of 0.025×10^{-6} c.g.s. This deviation is correlated to the presence of traces of paramagnetic impurities [9] and/or their structure difference and the accompanying degree of packing from that of the prepared specimen. This was proved by chemical, spectral and X-ray analyses as resulting from a paramagnetic contribution term which is responsible for lowering the diamagnetic value obtained for the present specimens. Comparison of magnetic susceptibility values for orange and for grey-black antimony trisulphide

TABLE 2

Values of the diamagnetic susceptibility obtained at room temperature for antimony trioxide and antimony trisulphide specimens together with previous results

Antimony trioxide specimens			Antimony trisulphide specimens		
Supplied	Prepared	Previous result	Orange	Grey-black	Previous result
0.17×10^{-6}	0.195×10^{-6}	0.190×10^{-6} [1]	0.315×10^{-6}	0.352×10^{-6}	0.255×10^{-6} [1]

samples reveals a difference of -0.09×10^{-6} c.g.s. This is apparently due to the amorphous nature of the orange form as confirmed by X-ray diffraction results. This explanation is in good agreement with similar findings of previous authors [10,11] who suggest it was due to the effect of degree of crystallinity of the test specimens.

TGA results for antimony trioxide revealed that both specimens suffered no weight change up to about 500 °C. However, thermogravimetric analysis of antimony trisulphide indicated that both the orange and the grey-black forms showed no weight change up to 290 °C. The magnetic susceptibility of these specimens in the above stable temperature zone was measured (see Figs. 1 and 2). It can easily be seen that the susceptibility of each compound showed a temperature independent character over the range of temperature studied. This could be explained on the basis that the two compounds investigated may be considered as either free from impurities or that their impurity contents are too law to influence the diamagnetic character. This

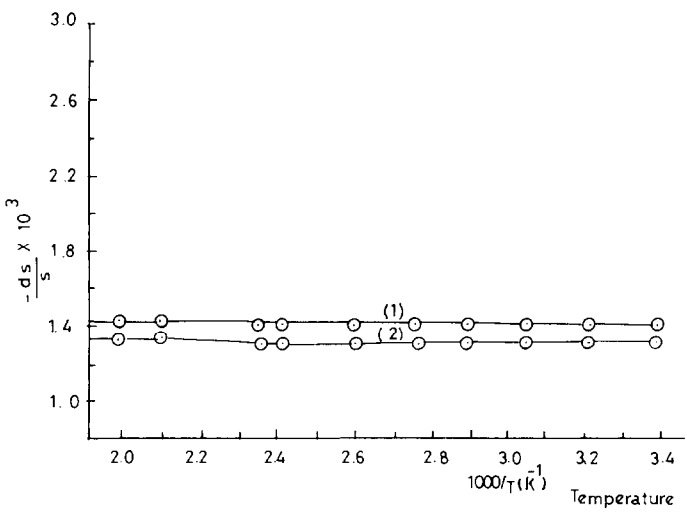

Fig. 1. The temperature dependence of the magnetic susceptibility of antimony trioxide specimens: (1), freshly prepared; (2), supplied.

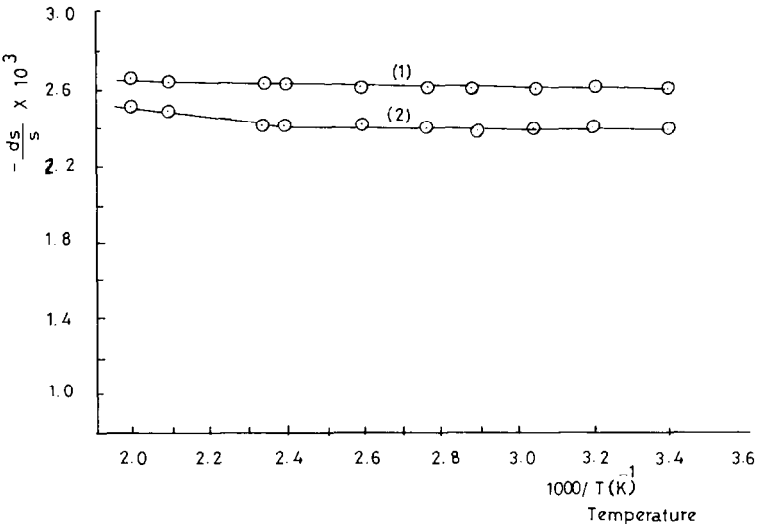

Fig. 2. The temperature dependence of magnetic susceptibility of antimony trisulphide specimens: (1), grey-black form; (2), orange form.

was in accordance with the X-ray data indicating that the test materials possess the smallest amount of impurities and lattice strains. Comparing the data given in Fig. 1 with those of Fig. 2 indicates that antimony trioxide specimens have higher values of magnetic susceptibility values that for antimony trisulphide specimens. This could plausibly be correlated to a higher electronegativity difference and hence bond strength for the former.

Accordingly, the results obtained were in conformity and the dependence of mass magnetic susceptibility on the origin and method of preparation for both antimony trioxide specimens and antimony trisulphide specimens were evaluated, explained and correlated with their phase constitution for the first time.

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