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On the structure and transformation of the orange form of Sb_2S_3 layers

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X-ray diffraction study showed that the orange modification of antimony trisulphide can neither be considered as amorphous material nor does it change into the black modification upon grinding. Thin vacuum-deposited layers, prepared by conventional thermal evaporation of the bulk material in 5×10^{-6} torr on an amorphous substrate at room temperature, were crystalline. The behaviour of the electrical conductivity with temperature in the range 25 to 190° C indicated transition points at 80, 108, 135 and 175° C.

1. Introduction

Antimony trisulphide is a typical binary compound which exists naturally in a black crystalline form known as stibnite. Its crystal structure belongs to the orthorhombic system [1, 2] with a space group D_{2h}^{16}. It consists of ribbon-like $(Sb_4S_6)_n$ polymers linked together by intermolecular attraction between antimony and sulphur atoms. The bonds within the ribbons are different in length owing to the two different types of coordination exhibited by both antimony and sulphur.

Artificially, black and orange forms were prepared using purified Analar reagents [3–5]. The artificial black form has the same crystal structure as the natural one. The orange form was earlier looked upon as amorphous [4, 5]. Chemical and thermogravimetric analysis (TGA) showed that the orange form contains excess sulphur [6].

The principal semiconducting parameters of Sb_2S_3 crystals determined by different authors disagree strongly. Thus, the room-temperature conductivity was reported to range from 10^{-6} [7] to $10^{-10}\ \Omega^{-1}\ cm^{-1}$ [8]. The reported values of the band gap, determined from optical measurements, are 1.55 [9], 1.64 [10] and 0.9 eV [11]; the temperature dependence of the electrical conductivity yielded 0.5 to 0.6 [9], 0.96 and 1.5 eV [8] and 0.35 to 0.4 eV below room temperature and 0.9 to 1.0 eV above room temperature for crystals with various degrees of deviation from the stoichiometric composition [12]. Sometimes, a kink was observed in the $\ln \sigma$ against $1/T$ curve at 180 to 200° C, above which the activation energy was found to be 1.5 eV. In a narrow range of temperatures values between 0.9 and 1.5 eV, sometimes 1.2 eV, were obtained [12].

In the present work we present structural studies concerning the orange modification of antimony trisulphide. The behaviour of the electrical conductivity of thin vacuum-deposited films with temperature in the range from 25 to 190° C is also considered.

2. Experimental techniques

Orange antimony trisulphide (about 45% Sb and 55% S), supplied by BDH Laboratory Chemicals, Poole, England, was used as a starting material. The effect of grinding the bulk material for periods ranging from 2 to 20 h, using a grinding machine (Fritsch Pulverisette, Idar-Oberstein, Germany) comprising an agate mortar and an automatic timer, was studied by X-ray diffraction. A Diano XRD-8000 with Cu*Kα* radiation, a nickel filter, 15 mA and 35 kV was employed for structural investigation.

Thin films were prepared from the bulk material by a conventional thermal evaporation technique using molybdenum boats. The normal working pressure during evaporation was of the order of 5×10^{-6} torr. Deposition was made on thoroughly cleaned and carefully selected glass microscope slides. Thick films of gold or aluminium electrodes were pre-deposited to serve as ohmic contacts. The thickness of the film was measured by multiple-beam interferometry [13]. A two-point probe technique was employed for determining the conductivity. The conduction current was measured by means of a high impedance electrometer (Keithley, Cleveland, Ohio, USA, Type 610C). Measurements were made in air in the temperature range 25 to 190° C.

3. Results and discussion

3.1. Structure of the orange Sb_2S_3

Fig. 1 shows X-ray diffraction patterns, recorded at the same experimental conditions, for the powdered orange modification of antimony trisulphide from different manufacturers compared to that of the black modification. Prominent reflecting planes occurred at 2θ values corresponding to d spacings of 0.4031, 0.3842, 0.3541, 0.3473, 0.3427, 0.3308 and 0.3192 nm and a broad peak comprising the planes 0.3126 and 0.310 nm. The observed difference in the intensity and sharpness of the reflecting planes of the orange specimens could be attributed to the difference in grain size. This is evident from Fig. 2, which shows the effect of grinding on the structure of the orange form of Sb_2S_3. During grinding the crystallite size is reduced, hence the resolving power of the crystallites is gradually diminished. Diffuse reflections result due to the scattering of X-rays by extremely small crystallites.

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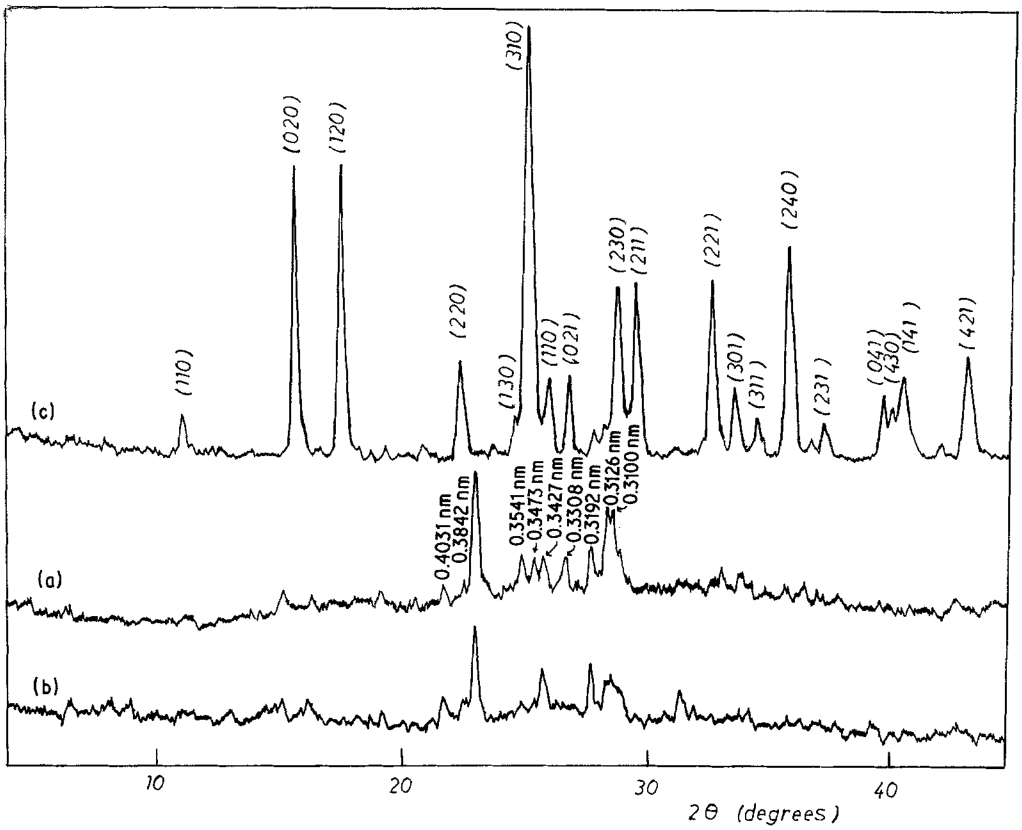

Figure 1 X-ray powder diffraction pattern of the orange Sb_2S_3 supplied from (a) May and Baker Ltd, Dagenham, England and (b) BDH Laboratory Chemicals, Poole, England, compared with (c) that of the black form.

Although grinding was continued for 20 h, no change of colour was observable, in contradiction to de Bacho [14] and to Hanafi and Ismail [6] who mentioned that the orange form changes into the black form upon grinding for 10 h in a porcelain mortar. Furthermore, X-ray diffraction analysis of glassy samples of Sb_2S_3, prepared by quenching the melt at a rate of 250 K sec^{-1}, indicated that grinding and polishing did not result in surface devitrification [15].

Fig. 3 shows the X-ray diffraction pattern obtained from the surface of a disc of finely powdered orange antimony trisulphide compressed under 40 ton cm^{-2} (40.6 tonne cm^{-2}). Two prominent reflecting planes appear at 2θ values corresponding to d spacings of 0.4587 and 0.2641 nm indicating that compression leads to preferred orientations.

The above results indicate that the orange modification of antimony trisulphide can neither be considered as amorphous material, in contradiction to previous authors [4–6, 16], nor does it change into the black modification.

3.2. Structure of thin vacuum-deposited layers

Fig. 4 shows a typical X-ray diffraction pattern of a vacuum-deposited layer of Sb_2S_3 prepared from the

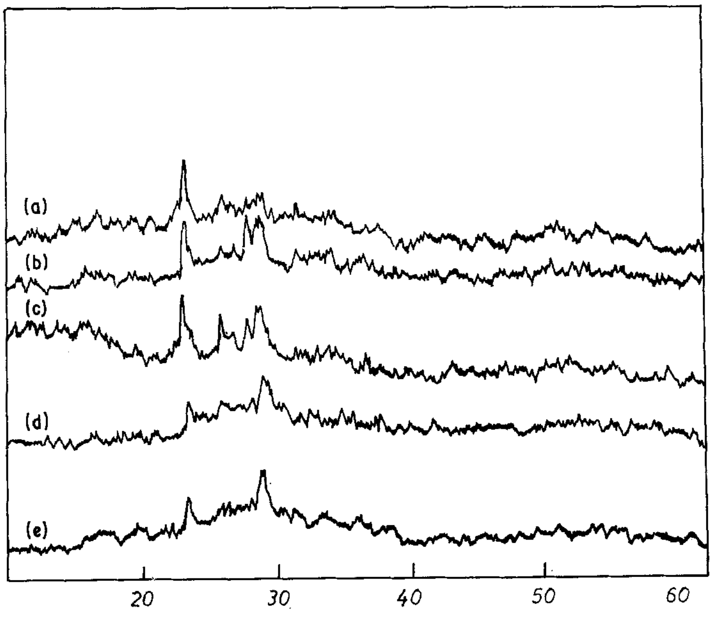

Figure 2 X-ray powder diffraction patterns of orange Sb_2S_3 after different periods of grinding: (a) 0 h, (b) 1 h, (c) 4 h, (d) 7 h, (e) 20 h.

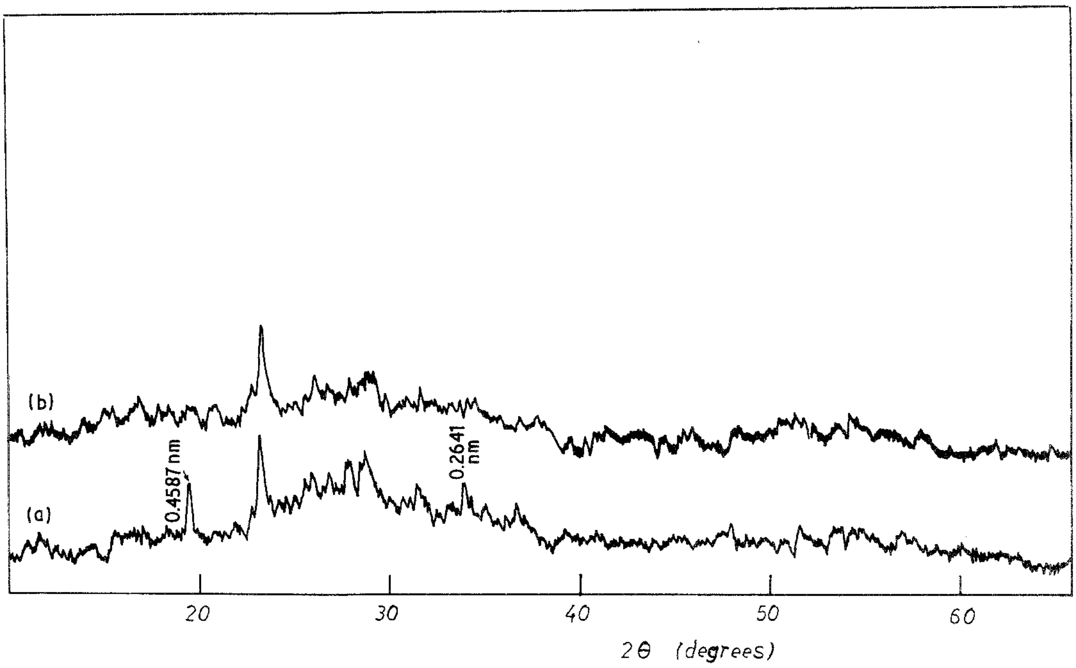

Figure 3 X-ray diffraction pattern from (a) the surface of a disc of fine powdered orange Sb_2S_3 compressed under 40 ton cm^{-2} (40.6 tonne cm^{-2}) compared with (b) the powder pattern.

orange form, compared with the powder pattern. Two prominent reflecting planes are observable at 2θ values corresponding to d spacings of 0.6384 and 0.3192 nm. The plane 0.6384 nm is double the plane 0.3192 nm which is exhibited in the powder pattern. Moreover, the plane 0.6384 nm does not correspond to sulphur. Hence, the diffraction pattern indicates that the vacuum-deposited layers are crystalline in nature, a result which contradicts that of Patel and George [16] that vacuum-deposited films from the orange form of Sb_2S_3 were amorphous in nature.

3.3. Behaviour of the electrical conductivity with temperature

The typical temperature dependence of the electrical conductivity of thin vacuum-deposited layers is shown in Fig. 5. The behaviour can be divided into three characteristic regions. The first one extends from room temperature up to 60° C, showing a decrease in conductivity probably corresponding to the desorption of surface states and the removal during heating of the non-stoichiometric atoms. The second region ranges from 60 up to 135° C, showing rapid fluctuations in conductivity in the temperature range 60 to 80° C involving a continuous transition to another state. During the study of switching in Sb_2S_3 films, it was found that destruction of the ordered structure occurred beyond the temperature range of the first phase transition at about 80° C [17]. Above 80° C a stable semiconducting behaviour of the conductivity

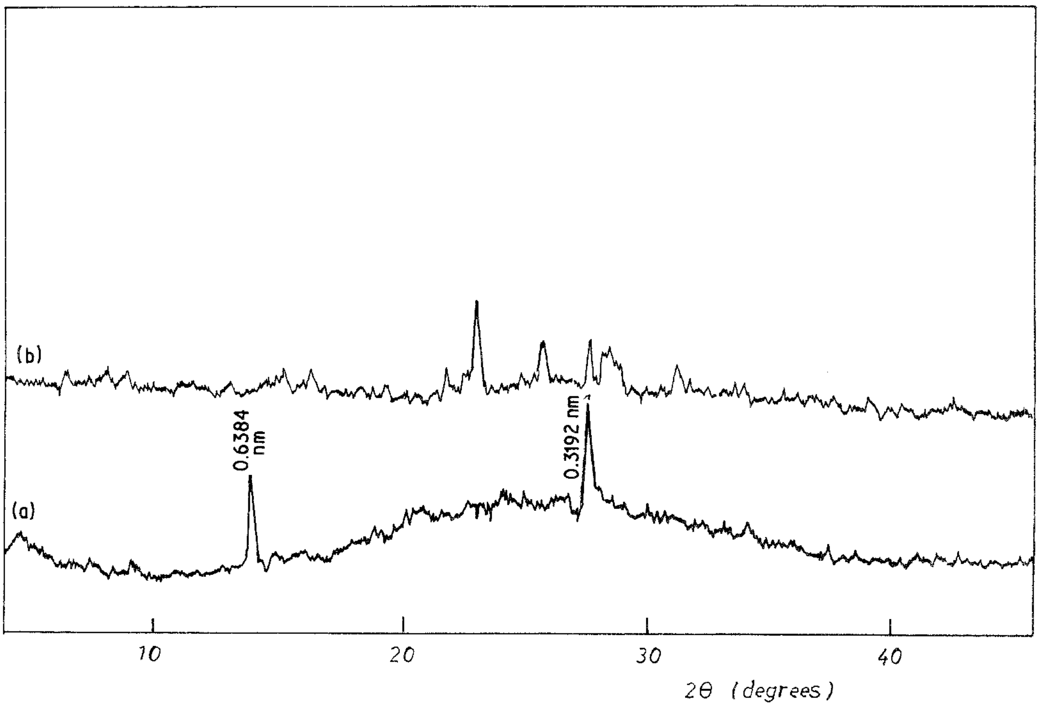

Figure 4 X-ray diffraction pattern of (a) a vacuum-deposited layer (500 nm thick), prepared by a conventional thermal evaporation technique from the bulk material, compared with (b) the powder pattern.

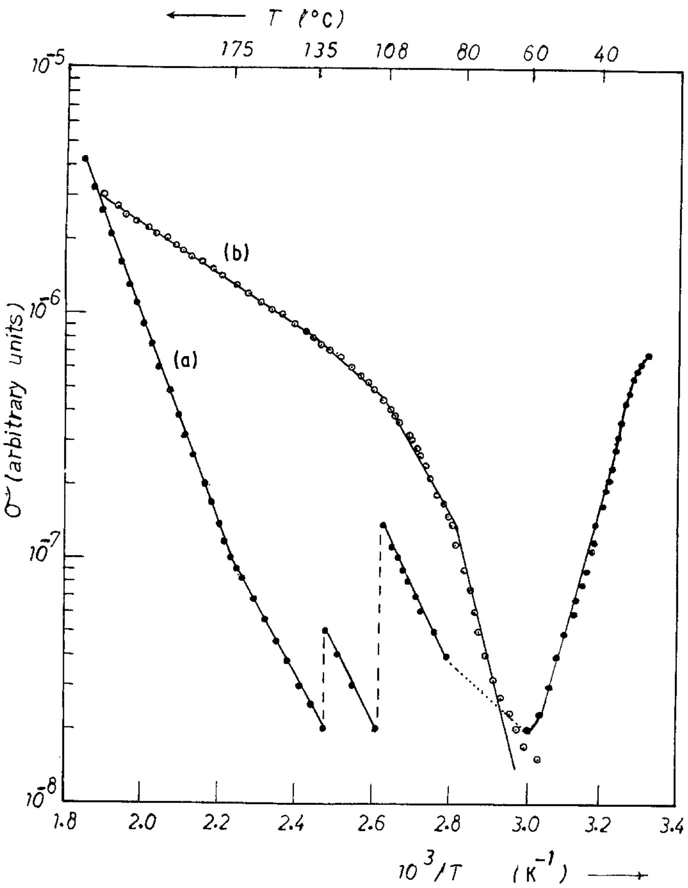

Figure 5 The temperature dependence of the electrical conductivity of a vacuum-deposited layer (500 nm thick) of orange Sb_2S_3: (a) on heating and (b) on cooling.

with temperature occurs in the ranges 80 to 108° C and 108 to 135° C, having an activation energy 0.56 eV and sudden falls in conductivity beyond 108 and 135° C, respectively.

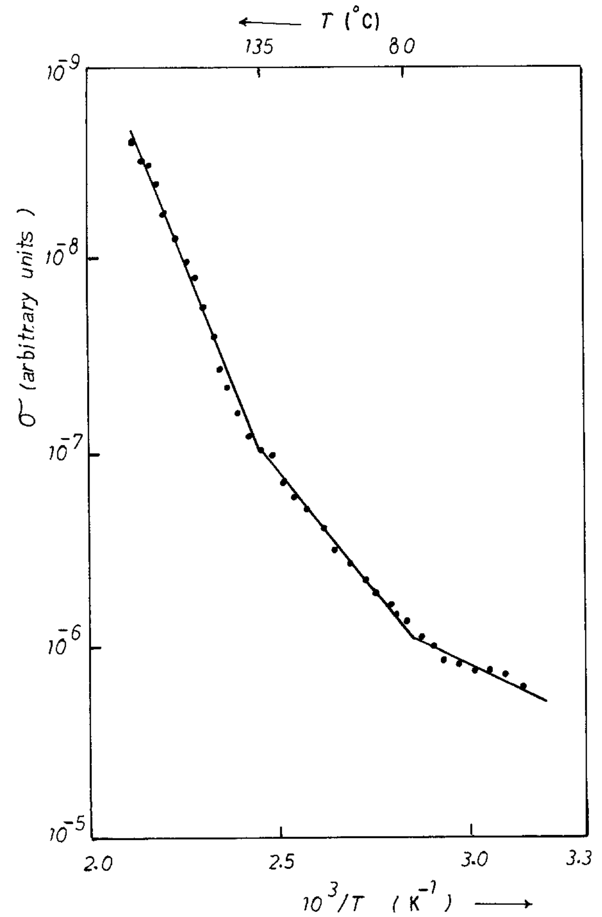

Figure 6 The temperature dependence of the electrical conductivity of a vacuum-deposited film (700 nm thick) of orange Sb_2S_3 preheated at 170° C and left to cool down to 50° C.

A loss in weight was recorded by TGA of orange antimony trisulphide over the temperature range 130 to about 190° C [6, 18]. Morandat and Duval [18] concluded that this loss was due to the elimination of water and excess sulphur, while Hanafi and Ismail [6] attributed it to the oxidation of sulphur. Differential thermal analysis (DTA) of orange antimony trisulphide showed that it undergoes a phase transformation at 140° C [6]. The third region extends above 135° C where the conductivity is stable and increases exponentially with $1/T$, showing a kink at 175° C below which the activation energy is 0.56 eV, similar to the previous region. Above 175° C the activation energy is 0.9 eV, in good agreement with the value of 0.9 to 1.0 eV obtained for Sb_2S_3 crystals with various degrees of deviation from stoichiometric composition obtained by Grigas and Karpus [12], who sometimes found a kink in the ln σ against $(1/T)$ curve at 180 to 200° C. It was reported [3–6] that orange Sb_2S_3 undergoes phase transformation to the black form by heating at 170° C.

On cooling down, the conductivity becomes stable with higher values where kinks are observable at 135, 108 and 80° C corresponding to the temperatures at which sudden decreases or fluctuations in conductivity occurred on heating. No kink was observable at 175° C.

Fig. 6 shows the typical behaviour of the conductivity with temperature for a film preheated at 170° C and then left to cool gradually to 50° C. Kinks appear at 80 and 135° C. The activation energy is 0.55 eV in the range 80 to 135° C and 0.92 eV above 135° C. No kinks are observable at 108 or 175° C. DTA of the orange form of antimony trisulphide preheated at 170° C showed a phase transformation at 140° C [6].

The kink observed in the conductivity behaviour at 175° C was detected only during heating the as-deposited films, but not on cooling down. It was also not detected in the case of films preheated at 170° C and then cooled to 50° C. It is most probable that the transition at 175° C is due to an irreversible process. However, the anomalous behaviour at 80 and 135° C detected in the case of as-deposited and pre-heated films. One could attribute such transitions to reversible processes. Furthermore, the anomalous behaviour at 108° C was detected for as-deposited but not for preheated films. Thus, one may suggest that this is due to an intermediate stage of transition between 80 and 135° C.

Although the above conclusions seem to be most probable, investigations are in progress in our laboratory to determine the exact mechanism and the results will be published later.

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