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THE ENANTIOTROPIC PHASE TRANSITION OF ANTIMONY(III) OXIDE

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SUMMARY

Pure cubic senarmontite and pure orthorhombic valentite were characterised by XRD and infrared absorption spectroscopy, these techniques were also used to characterise heat treated samples. Senarmontite was shown to be the stable low temperature polymorph and valentite the stable high temperature form. The application of classical thermodynamics indicated the transition temperature to be 923K. Valentite was shown to exist below 923K but heat treatment below this temperature caused the metastable valentite to revert to senarmontite. DTA of antimony(III) oxide gave a single sharp endothermic peak at 913K, independent of the crystal modification, thus indicating that melting and phase transition were inseparable thermal events.

INTRODUCTION

Antimony(III) oxide is known to exist in two enantiotropic modifications; a cubic form, senarmontite, and an orthorhombic form, valentite. The cubic form is reported to be dimeric (Sb_4O_6) in which the antimony atoms lie at the corners of a regular tetrahedron with the six oxygen atoms lying on the edges, as in P_4O_6 (ref.1). The orthorhombic form is reported to be polymeric, consisting of chains of -O-Sb-O-Sb- joined together by a bridging oxygen atom between each antimony atom in the chain (ref.2).

The cubic form was reported to be stable below 843K and above this temperature the orthorhombic form was reported to be stable (refs.1 and 2). One reference (ref.4) quoted the cubic form as the stable high temperature modification and the orthorhombic form as being the low temperature form. Furthermore, when antimony(III) oxide was prepared by an aqueous precipitation method the resulting material was found to consist mainly of the orthorhombic form (ref.3).

In view of the apparent conflict which exists in the literature the following thermoanalytical study of the enantiotropic phase transition between cubic and orthorhombic antimony(III) oxide was made.

EXPERIMENTAL METHODS

Materials

Antimony(III) oxide was obtained from Aldrich Chemical Company and BDH

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Pure senarmontite was prepared by the thermal decomposition of antimony(III) oxalate in an oxidising atmosphere of pure dry oxygen at 573K for 33 hours (ref.5). Under these conditions, complete decarboxylation without the formation of carbon and without the oxidation of the senarmontite to αSb_2O_4 (ref.6) was achieved.

Techniques

DTA was carried out in a dynamic argon atmosphere, using the Du Pont R90 Thermal Analyzer in conjunction with the 910 Differential Scanning Calorimeter. A heating rate of $5K\ min^{-1}$ was used throughout. The heat treatment of samples was carried out in a dynamic argon atmosphere to prevent oxidation.

XRD was performed using a Philips PW1700 X-ray powder diffraction system.

Infrared absorption spectra were run on KBr discs of the samples using the Perkin-Elmer 598 Infrared Spectrophotometer in conjunction with the 3600 Data Station.

RESULTS AND DISCUSSION

Characterisation of materials

XRD indicated that the Aldrich material was the pure orthorhombic valentite form of Sb_2O_3 whilst that obtained from BDH was a mixture of mainly cubic senarmontite with some valentite also present as a minor component. The sample of antimony(III) oxide prepared by the thermal decomposition of antimony(III) oxalate at 573K was shown by XRD to be pure senarmontite.

The infrared absorption spectrum of the Aldrich material, valentite, is shown in Fig.1A, together with that of pure senarmontite (see Fig.1B), prepared by thermal decomposition of antimony(III) oxalate. The two spectra were characteristically different and contained no common absorption bands. It was therefore possible to distinguish between the two modifications on the basis of infrared absorption spectra alone, a fact not apparent from the literature (ref.7). This observation was made relevant, particularly when the infrared absorption spectrum of the BDH antimony(III) oxide was recorded (see Fig.2A). In this spectrum, absorption bands attributable to both senarmontite and valentite were present, with those of valentite contributing to a minor extent, as was also indicated by the XRD analysis of the BDH material.

McDevitt and Baum (ref.7) discussed the concept of polymorphism and the use of infrared absorption spectroscopy in characterising polymorphs. With respect to the anatase and rutile forms of TiO_2, they concluded that the technique left much to be desired, due to the poor definition and minor spectral differences between the polymorphs. These same problems were also

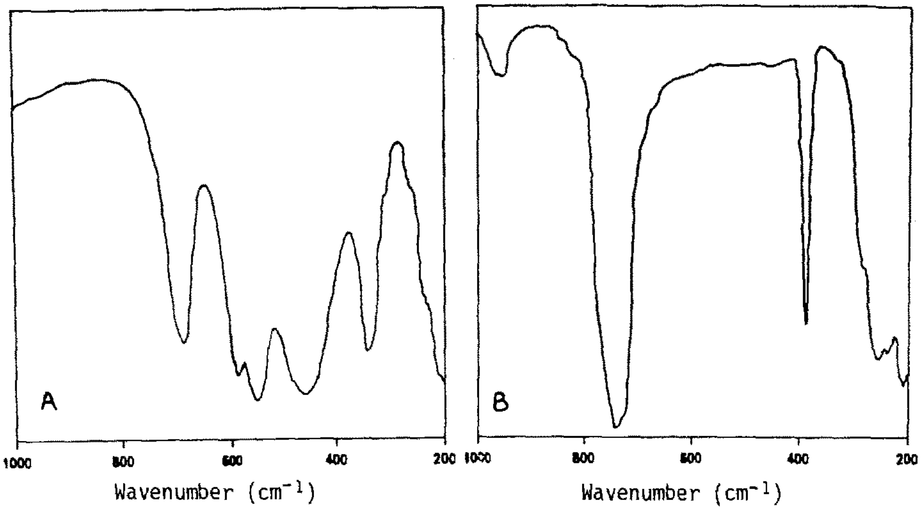

Fig.1 Infrared absorption spectra: A. Pure valentite, ex-Aldrich Chemical Company; B. Pure senarmontite.

apparent when the α-Fe_2O_3/γ-Fe_2O_3 system was studied (ref.8). Although the antimony(III) oxide system has been reported to be one in which the infrared absorption spectra of the alternative crystal modifications were well defined (ref.7), published data, reputedly to be that of cubic senarmontite, actually represented a mixture of the two polymorphs.

DTA of all three antimony(III) oxide materials studied was characterised by a single, sharp, endothermic peak at 913K, independent of the crystal modification and attributable to the melting of the sample. At a heating rate of 20K min^{-1}, this peak occurred at 928K, the reported value for the melting point of valentite (ref.3). There was no evidence of the melting of senarmontite, reported as occurring at 821K (ref.1), or no separate thermal event that could be attributed to the enantiotropic transition between senarmontite and valentite.

The effect of heat treatment on polymorphic stability

Using previously published standard thermodynamic data relating to the formation of senarmontite and valentite (ref.3), the following standard thermodynamic function changes were calculated:

$$\text{cubic (senarmontite)} \xrightarrow{\Delta} \text{orthorhombic (valentite)}$$

$$\Delta H_{298K} = 12.0 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta S_{298K} = 13 \text{ J mol}^{-1}$$

$$\Delta G_{298K} = 8.1 \times 10^3 \text{ J mol}^{-1}$$

Whilst ΔG was positive at 298K, it would tend to zero with increasing temperature, eventually becoming negative. Since the thermodynamic criterion for spontaneous change is ΔG ⩽ 0, then the temperature, T, at which ΔG = 0, would correspond to the temperature at which the enantiotropic phase transition would occur. Assuming ΔH and ΔS to be approximately independent of temperature and using the expression ΔG = ΔH - TΔS, the temperature 923K was calculated as corresponding to the transition temperature below which senarmontite would be stable and above which valentite would predominate. This calculated transition temperature was just below that of the reported melting point of valentite (928K). Since the observed melting point in this study was found to lie between 913K and 928K, depending on heating rate, it would appear that the single, sharp, endothermic DTA peak represented inseparable thermal events accompanying phase transition and melting.

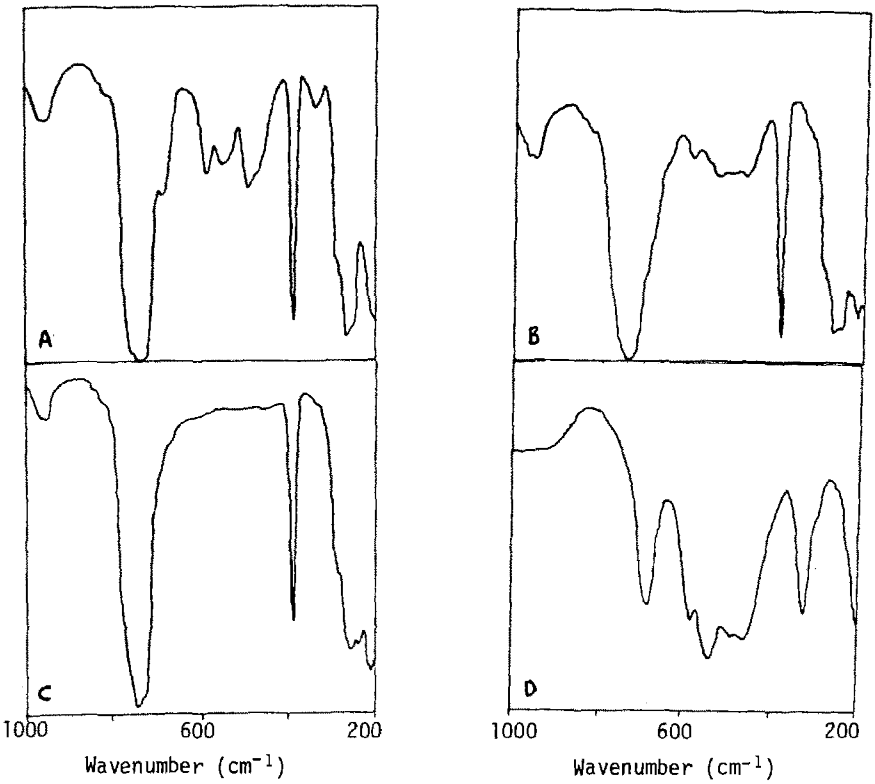

Fig.2 Infrared absorption spectra.
The effect of heat upon antimony(III) oxide, ex-BDH Chemical Company.

A. Prior to heat treatment; B. Heated at 883K for 33 hours;
C. Heated at 903K for 33 hours; D. Heated to 933K.

In order to confirm the above thermodynamic predictions and also to clarify the conflicting evidence existing in the literature, the effect of heat treatment on the characterised antimony(III) oxide materials, reported here, was carried out. A sample of the BDH material, which consisted of senarmontite and valentite, was heated to a temperature just above that of the recorded DTA peak at 928K. This temperature (933K) was also above that predicted by the thermodynamic considerations as being the temperature for the senarmontite to valentite enantiotropic phase transition. The material was allowed to cool to ambient temperature, whereupon the recorded infrared absorption spectrum showed the material to be pure valentite (Fig.2D). This observation indicated that the senarmontite component of the sample had transformed to the valentite high temperature modification, which had then remained stable during the cooling process.

Fig.3 The effect of heat upon valentite. A. Prior to heat treatment; B. Heated at 903K for 33 hours.

A sample of BDH antimony(III) oxide, when heated to 883K and held at this temperature for 33 hours before it was allowed to cool, revealed that the amount of the valentite component, originally present, had decreased (Fig.2B). Heating the BDH antimony(III) oxide to 903K and maintaining this temperature for 33 hours, resulted in the complete disappearance of infrared absorption bands characteristic of the valentite component of the material (Fig.2C).

It would appear that valentite, although present at temperatures below 923K, was metastable and that heating it above 873K provided the activation energy necessary for it to transform to the thermodynamically preferred senarmontite. This observation was confirmed by heating a sample of the Aldrich antimony(III) oxide (pure valentite) to 903K and maintaining this temperature for 33 hours, whereupon the recorded infrared absorption spectrum of the resulting cooled material corresponded to pure senarmontite (Fig.3B). When the Aldrich material was heated above 928K and allowed to cool, the resulting material corresponded to metastable, pure valentite as expected.

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