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SEMICONDUCTION IN MERCURY(1) CARBONATE

K. TENNAKONE^{a,b}, A. H. JAYATISSA^b, S. PUNCHIHEWA^a, R. TANTRIGODA^c AND W. A. C. PERERA^a

a) Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka.

b) Department of Physics, University of Rubuna, Matara, Sri Lanka.

c) Open University of Sri Lanka, Nawala, Sri Lanka.

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> Abstract : The temperature variation of the conductivity and diffuse reflectance spectra of mercury(I) carbonate was determined. It is found that the material behaves as a semiconductor of band ca. 2.3 eV. Differential thermal analysis indicated that the decomposition temperature of mercury(I) carbonate is ca. 265°C. The polycrystalline nature of the material was established by X-ray diffractometry.

1. Introduction

The study of electrical transport properties of materials continues to be a fruitful area of research. New semiconductors, superconductors, fast ion conductors and catalysts with potential practical applications are results of such investigations [1-4]. In this note we report our observations on semiconducting properties of mercury(I) carbonate.

2. Experimental

Mercury(I) carbonate was prepared by the gradual addition of carbon dioxide saturated 0.02 mol dm⁻³ sodium bicarbonate to a 0.1 mol dm⁻³ solution of the mercury(I) nitrate kept vigourously stirred. [Mercury(I) nitrate free from mercury(II) nitrate was first prepared by boiling acidified (HNO₃) mercury(I) nitrate avoiding the entry of atmospheric oxygen]. The saturation of sodium bicarbonate solution with carbon dioxide prevents contamination of the product with basic mercury(I) carbonate resulting from hydrolysis. The yellow precipitate of Hg₂CO₃ was washed with ice cold water followed by alcohol and diethyl ether and dried in vaccum at 70[°]C. The X-ray diffraction spectrum was obtained with Shimadzu XD-7A, X-ray Diffractometer. Shimadzu DT-40 Thermal Analyser was used to determine the decomposition temperature. The diffuse reflectance spectrum of the powder was obtained from a Shimadzu UV-3000 spectrophotometer provided with an integrating sphere. To carry out the conductivity measurements, the powder was compacted between gold plated copper rods in a pyrex glass tube (pressure Ca. 10⁶ pa, diameter of the tube ca. 0.6 cm) and the ends of the tube were sealed with epoxy resin. The tube

was immersed in a thermostatted oil bath and temperature variation $(23^{\circ} - 180^{\circ}C)$ of the a.c. conductivity at 80 H_z was measured with a conductivity meter (Philips PW 9527). A d.c four probe measurement was carried out at selected temperatures $(30^{\circ}C, 100^{\circ}C)$.

3. Results and Discussion

Figure 1 shows the characteristic X-ray diffraction spectrum which shows that the material is crystalline. The decomposition temperature determined by differential thermal analysis is ca. 265°C (Figure 2). The products of decomposition were identified to be mercury(I) oxide and carbon dioxide if heated in an inert atmosphere, and mercury(II) oxide and carbon dioxide if heated in air. Figure 3 shows the temperature variation of the conductivity (plot of in σ vs T⁻¹). The thermal activation energy from both methods are comparable and is found to be ca. 0.72 eV. The diffuse reflectance spectrum presented in Figure 4 shows clear evidence for a band edge and the band gap derived from the spectrum is ca. 2.5 eV. Room temperature (30°C) conductivities obtained by a.c and four probe d.c were $\sigma_{a,c} = ca. 11.3 \times 10^{-4}$ S, $\sigma_{d.c} = ca$, 5.3 x 10⁻⁴ S. A similar disparity is seen in the values of conductivity at 100^oC ($\sigma_{a.c} = 6.2 \times 10^{-3}$ S, $\sigma_{d.c} = 4.1 \times 10^{-3}$ S). The higher value for the d.c conductivity can be understood as resulting from the grain boundary insulation. We have not succeeded in determining the carrier mobilities; thermoelectric tests indicate that the material is n-type. The crystal structure of Hg₂CO₃ has not been reported in the literature to our knowledge. Although, the gel and diffusion methods were attempted, we were not able to produce single crystals of Hg₂CO₃.

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