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Note

SOME STUDIES ON THALLIUM OXALATES. XII. ELECTRICAL PROPERTIES OF THALLIUM(I) OXALATE

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In our earlier communication, thermal decomposition studies by TG and optical, X-ray diffraction and infrared absorption properties of thallium(1) oxalate were reported [1]. The electrical properties are discussed in this article.

Electrical conductivity by its nature, is more sensitive than gravimetry to the sub-microscopic changes in the solid state. Therefore, conductivity has the added potential of providing a more detailed preview of the solid-state processes occurring below the decomposition temperature. However, in the region of active decomposition, conductivity data may be less reliable in view of the fact that measurements are susceptible to composite or masking effects arising from the products.

EXPERIMENTAL

Preparation of the compound and details of the method for measurement of electrical conductivity are already reported [1].

For the Seebeck coefficient measurements, the sample pellet was pressed between two platinum discs fixed at the ends of two ceramic blocks; one of the blocks was spring loaded to obtain good pressure contacts. The ceramic blocks were clamped together using three steel rods by a nut-bolt arrangement as shown in Fig. 1. This sample holder was placed in the constant temperature zone of a furnace which was maintained at the desired temperature. In order to impose the necessary temperature gradient, an auxiliary heater (Nichrome wire of 28 swg) was wound over the top ceramic block. The temperature of the ends of the sample were measured using chromel–alumel thermocouples placed in such a way as to touch the sample ends.

The auxiliary heater was put on and a ΔT of 8–10°C was maintained and the thermoelectric voltage was measured.

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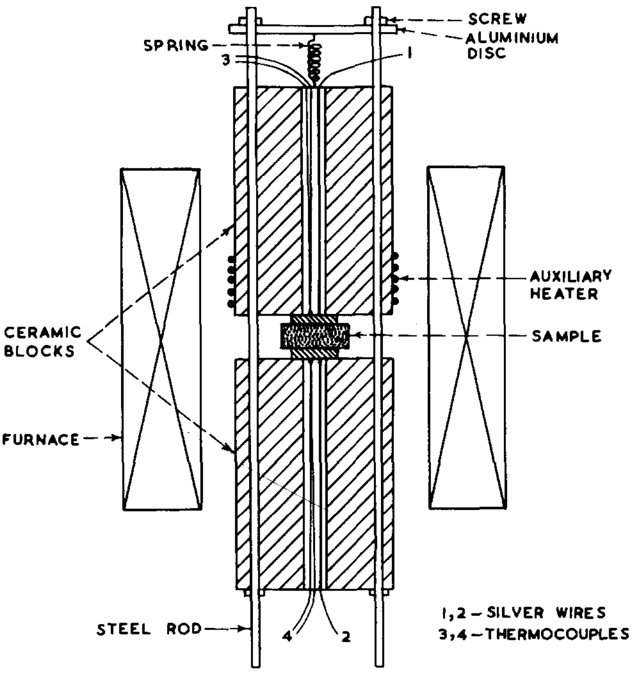

Fig. 1. Sample holder for Seebeck coefficient measurements.

RESULTS AND DISCUSSION

A plot of the logarithm of the resistivity vs. $1/T$ for thallium(I) oxalate is shown in Fig. 2. From the curve it is evident that at low temperature the compound behaves as an insulator and as the temperature is increased it behaves as a semiconductor; the conductivity increases exponentially with increase in temperature. This may be due to the fact that at room temperature the thermal energy, kT, being of the order of 0.025 eV only, is not sufficient to promote the electrons from the valence band to the conduction band in this case. But this promotion is likely to occur at elevated temperatures giving rise to the high conductivity observed. The slope of the curve markedly changes beyond 200°C suggesting that the phenomenon is more complicated in this region. It may be a case where the ionization of some defect is taking place around that temperature. Since the deviations from stoichiometry are too small to determine analytically, the Seebeck (thermoelectric) coefficient measurements were carried out to characterise the type of semiconduction.

The plot of Seebeck coefficient (α) vs. T is shown in Fig. 3. From the figure it is clear that the α value is negative and increases with increase in temperature. On cooling, the same trend is observed with some hysteresis. The negative value of α shows that the charge carriers are negative and probably the electrons in this case.

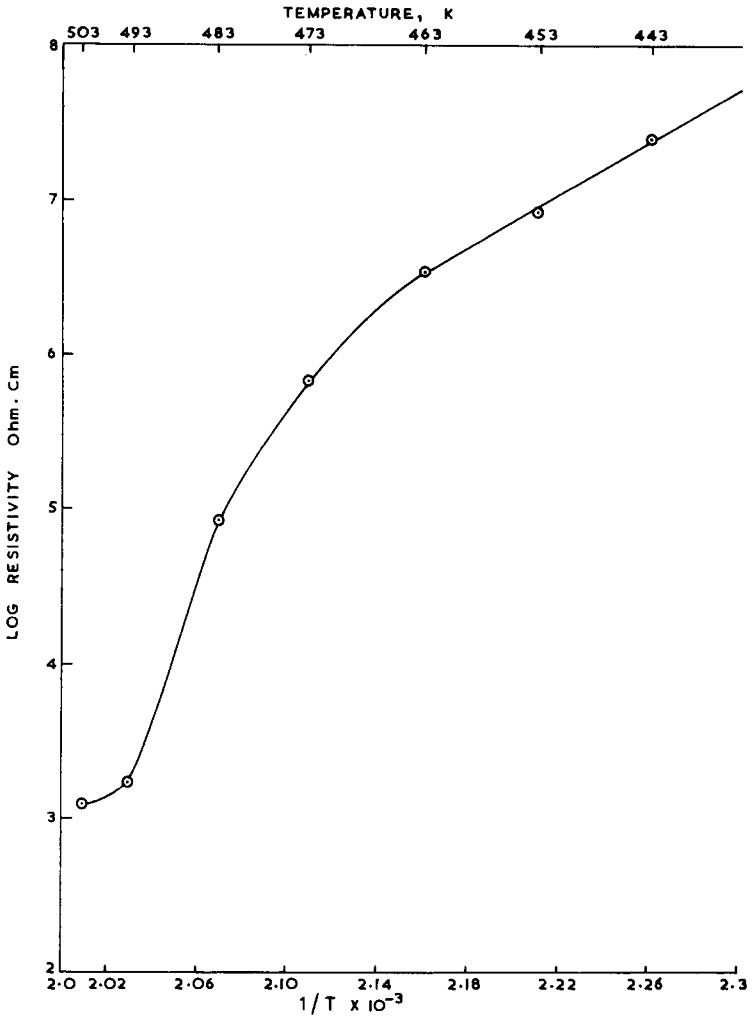

Fig. 2. Log resistivity vs. reciprocal temperature for thallium(I) oxalate.

This behaviour of the sample may be due to the presence of metallic thallium in the matrix formed due to the reduction of minute traces of thallium(I) by oxalate ion (which cannot be determined by normal chemical analysis) forming a non-stoichiometric compound. The thallium metal in the solid becomes ionised around 200°C and the electrons released in the process of ionisation contribute to the large conduction observed. The solid-state reactions occurring at this remperature may be represented as

$$Tl^{I}_{2}C_{2}O_{4} \rightarrow Tl^{I}_{2-x}Tl^{0}_{x}(C_{2}O_{4})_{1-x/2}$$

$$Tl^{0} \rightarrow Tl^{+} + e$$

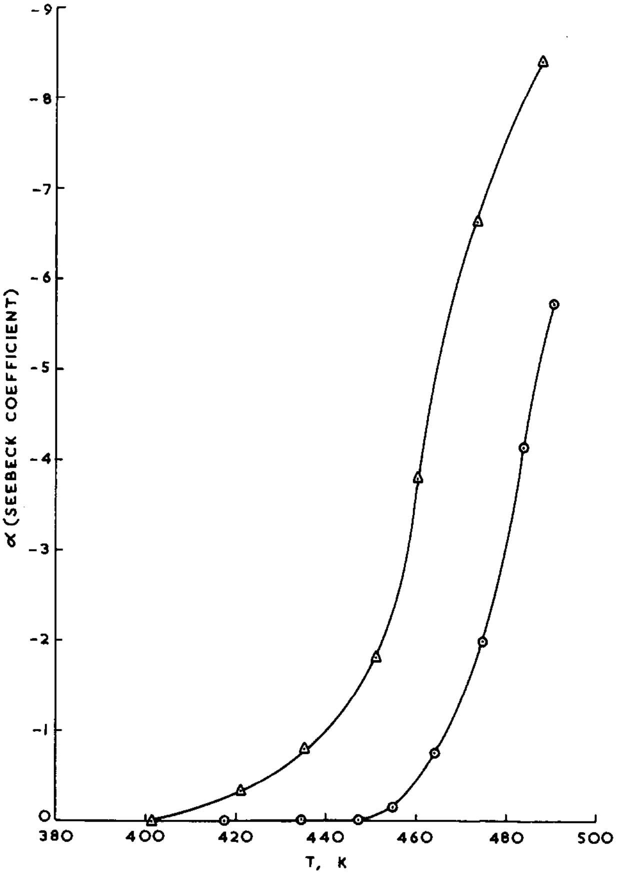

Fig. 3. Seebeck coefficient vs. temperature for thallium(I) oxalate. ⊙, Heating; △, cooling.

Thallous oxalate obtained by the decomposition of other bisoxalato thallate(III) salts [1,2] is also found to behave in a similar manner.

REFERENCES

1 S.R. Sagi, K.V. Ramana and M.S. Prasada Rao, Thermochim. Acta, 31 (1979) 285.
2 K.V. Ramana, Ph.D. Thesis, Andhra University, 1976.