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Electrical transport in new Tl_2OCl_2 and Tl_4Cl_6

N. B. SINGH, NAMWAR SINGH, B. N. TIWARI, P. N. OJHA
Department of Chemistry, Gorakhpur University, Gorakhpur, 273001, UP, India

Electrical conductivity, σ, Seebeck coefficient, S, measurements on the pressed solid pellets of both Tl_2OCl_2 and Tl_4Cl_6 have been carried out in the temperature range 300 to 580 K. Both log σ and S against T^{-1} plots have two linear regions with a break at temperature T_B and T'_B for both solids. T'_B has been found to few degrees less than T_B, which has been shown due to the experimental condition employed in the measurement of σ and S. These solids are electronic conductors with relatively high conductivity. The conduction above T_B, results due to thermal excitation of electrons from valence to conduction band. The energy band gap for Tl_2OCl_2 and Tl_4Cl_6 have been found to be 1.38 and 1.68 eV, respectively. Below T_B, the hopping of electrons from Tl^{+1} to Tl^{+3} becomes the dominant conduction mechanism. The estimated values of mobility in this range for both the solids are of the order of 10^{-6} m^2 V^{-1} sec^{-1}.

1. Introduction

The investigation on the solid-state chemistry of oxyhalides of thallium have been the subject of one of the most current research activities and a number of publications [1, 2] have been published during the past decade. Among the physical properties of solid materials which have been used as a heterogeneous catalyst in a variety of chemical industries, the electrical conductivity and thermoelectric power are of great fundamental importance [3]. The electric properties of catalysts are of basic importance in the determination of the relationship between electronic structures and catalytic properties of semiconductors. We have recently reported the syntheses of Tl_2OCl_2 and Tl_4Cl_6 [4] by room temperature solid-state reaction between solid thallous carbonate and chlorine gas. The two compounds have been reported for the first time. The products were characterized by chemical analyses and powder X-ray diffraction techniques. This paper describes the electrical conductivity, σ, and thermoelectric power, S, of pressed solid pellets of Tl_2OCl_2 and Tl_4Cl_6 at different temperatures.

2. Material preparation and experimental procedure

Tl_2OCl_2 and Tl_4Cl_6 were polycrystalline materials obtained by solid-state reaction between thallous carbonate, Tl_2CO_3 (of 99.9% purity, from BDH, England), and chlorine gas (dry, prepared in laboratory from MnO_2 and HCl) at room temperature. The details of preparation are described in our earlier publication [4]. The compounds were characterized by X-ray diffraction analysis using Cu$K\alpha$ radiation ($\lambda = 0.15405$ nm).

The compounds were pelletized, at a pressure greater than 6×10^8 N m^{-2} of circular cross-sectional area, $a \sim 0.95$ cm^2 and thickness, $t \sim 0.30$ cm (used in the conductivity measurements) and $t \sim 0.80$ cm (used in the Seebeck coefficient measurements). The pellets were then sintered in air for about 20 h at about 500 K. Sample holder used for σ and S measurements are described elsewhere [5, 6]. Samples were mounted between the rigid electrodes of the sample holder after coating with silver. The electrical conductivity, σ, measurement was carried out at applied a.c. signal frequencies of 10^2, 10^3 and 10^4 Hz using a systronic LCR bridge (Type 921) in the temperature range 300 to 580 K. The experimental values of σ were obtained within 2% accuracy. The Seebeck coefficient, S, measurement was also done in the same temperature range. However, the experimental values of S were obtained in general, to within ± 5% error. After the establishment of a constant thermal environment, a temperature difference, ΔT, of 10 or 15° C was applied and correspondingly

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TABLE I

Compound	t^2/a	P $(10^{-8}$ N m$^{-2})$	d_P $(10^{-3}$ kg m$^{-3})$	d_x $(10^{-3}$ kg m$^{-3})$	Per cent of theoretical density	Pore fraction
Tl_2OCl_2	0.042	8.75	3.59	4.872	79.85	0.27
Tl_4Cl_6	0.037	9.18	4.02	5.725	70.16	0.30

a thermal e.m.f., ΔE, developed across the sample, was measured with a Keithley digital multimeter (type 171 internal impedence 10^{10} Ω). The Seebeck coefficient, S, is the ratio of ΔE and ΔT. The convention of sign for the Seebeck coefficient was hot end as positive and cold end as negative.

3. Results and discussion

The studies have been performed on pressed circular pellets because it is difficult to prepare single crystals and melt solid polycrystalline materials due to their decomposition. In the pelletized material it is highly desirable to reduce the grain boundaries as much as possible and to obtain a uniform pellet density. This aspect is generally achieved by preparing pellets at very high pressure and sintering them for a sufficiently long time at an appropriate temperature. It is suggested [7] that a highly pressed pellet acquired a uniform density if its thickness-to-width ratio is less than two (or approximately if t^2/a is less than four in the case of circular pellets, where t is the thickness and a is the cross-sectional area). The pellets used in conductivity and Seebeck coefficient measurements were obtained at a pressure above 8×10^8 N m^{-2} and had t^2/a ratios of approximately 0.02 and 0.08, respectively (see Table I). This ensures a uniform pellet density, d_p, which generally lies between 70 and 80% of the theoretical value of crystal density, d_x, of the corresponding material. A fractional change in the density or pore fraction, f, given as

$$f = 1 - d_\mathrm{p}/d_\mathrm{x} \qquad (1)$$

is generally about 0.30 (see Table I).

The presence of grain boundaries greatly affects the transport behaviour of the material. Russel [8] has shown that in such cases the bulk value of the electrical conductivity, σ, can be given by the relation

$$\sigma = \sigma_\mathrm{p}\left(1 + \frac{f}{1 + f^{2/3}}\right) \qquad (2)$$

where σ_P is the experimental value of pellet conductivity and f is given by Equation 1. In order to verify the applicability of Equation 2, the electrical conductivity of samples of Tl_2OCl_2 and Tl_4Cl_6, prepared at different pelletizing pressures, has been measured. The log σ against T^{-1} plot obtained from them in the temperature range 450 to 540 K, as shown in Fig. 1, reveal that the dependence of conductivity on pelletizing pressure, P, is more pronounced below 480 K and a pore fraction correction, introduced as in Equation 2, does not appear to be very effective. However, above, 480 K, the lines of log σ against T^{-1} plots corresponding to σ values at different P values are in good agreement. The conductivity values as obtained from these plots at 450 K are given in Table II. The activation energy, E_a, also shows a significant decrease with increasing P for these cases (see Table II). The larger activation energies seen at lower pressures appear, presumably, to be

TABLE II

Compound	P $(10^{-8}$ N m$^{-2})$	Per cent of theoretical density acquired	Conductivity at 450 K (ohm^{-1} m^{-1})	E_a (eV)
Tl_2OCl_2	4.5	78.25	139.0	–
	6.0	78.90	199.8	–
	8.7	79.12	140.7	0.68
	9.2	79.32	142.1	0.67
	9.5	79.47	144.2	0.66
Tl_4Cl_6	4.6	69.75	–	–
	6.0	69.90	35.04×10^{-5}	0.80
	8.4	69.93	35.82×10^{-5}	0.79
	8.9	69.98	35.93×10^{-5}	0.78
	9.1	70.14	46.17×10^{-5}	0.78

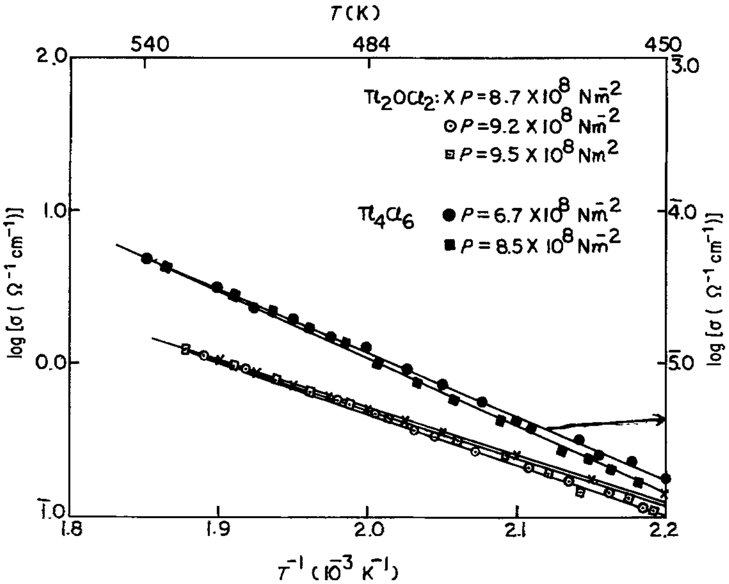

Figure 1 Variation of logarithmic conductivity, σ, with the reciprocal of absolute temperature, T, at various pelletizing pressures, P.

due to larger intercrystalline barriers at the grain boundaries. The dependence of S on P is difficult to determine because of the relatively large (± 5%) error in the experimental values of the former. In this case, no correction for pore fraction has been suggested.

The electric current density, J, was found to be independent of time for both Tl_2OCl_2 and Tl_4Cl_6. However, its variation with applied electric field, E, is linear, in accordance with Ohm's law, only for low fields, $E \leqslant 25\ V\ cm^{-1}$ (see Fig. 2). At higher fields, $E > 25\ V\ cm^{-1}$, the ohmic current is replaced by a space charge limited current and J varies steeply with E. Furthermore, the curve, particularly of Tl_2OCl_2, do not necessarily pass through the origin which leaves some doubt as to assigning the contact as true ohmic. E, however, was maintained below $25\ V\ cm^{-1}$ where the condition of ohmic contact prevailed.

The a.c. conductivity, σ_{ac}, of both Tl_2OCl_2 and Tl_4Cl_6 pellets at a constant temperature between 300 and 580 K was found to be independent of the applied signal frequency (of 10^2 to 10^4 Hz). These observations show that grain boundary effects are insignificant and that σ_{ac} reflects the bulk value of conductivity between 10^2 to 10^4 Hz. The d.c. conductivity, σ_{dc}, at any given temperature was found to be a little higher than the value of σ_{ac} at the same temperature. This supports the view that the lack of

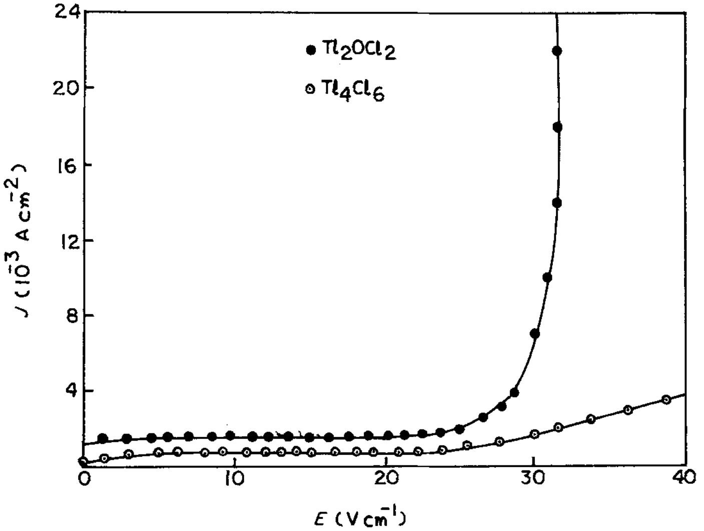

Figure 2 Variation of electric current density, J, with applied electric field, E.

additional resistance in practice is due to the absence of grain boundaries; even if they are present their contribution to the resistance is not very effective, presumably due to the highly conductive nature of Tl_2OCl_2 and easy passage of the charge carriers from one grain to another. Besides, the σ value for both Tl_2OCl_2 and Tl_4Cl_6 at a particular temperature, or its variation with temperature, do not differ considerably for samples of different thicknesses. The electrode materials (silver paint, silver foil, platinum foil, etc.) were found to have an insignificant effect on the conductivity. However, platinum foil electrodes have been preferred for our measurements. The conductivity was also found to be independent of the shelf-life of the pellet.

The study of the electrical conductivity and the Seebeck coefficient as a function of temperature is the main feature of the present work. The electrical conductivity was found to depend upon the thermal history of the sample. The value of electrical conductivity depends, initially, on heating and cooling cycles, but after a few (twenty to twenty four) hours heating and cooling cycles, they become repeatable in successive cycles. These repeatable values have been taken as the bulk value of the parameters for the solids. The results of electrical conductivity measurements in the first heating cycle at an a.c. signal frequency of 10^3 Hz, have been presented as log σ against T^{-1} plots (Figs. 3 and 4) in the studied temperature range for Tl_2OCl_2 and Tl_4Cl_6, respectively. The experimental points are in accordance with Equation 2. It is seen from these figures that the log σ against T^{-1} plots are linear in both these cases with a break in the slope at a specific temperature (T_B), which may be termed the break temperature. These plots can be expressed by general relation

$$\sigma = \sigma_0(T)\exp\left(-\frac{E_a}{kT}\right) \tag{3}$$

where $\sigma_0(T)$ and E_a are, respectively, a constant and the activation energy for conduction. The evaluated values of these constants together with the value of T_B are given in Table III.

The Seebeck coefficients, S, at a particular temperature for both Tl_2OCl_2 and Tl_4Cl_6, are essentially independent of thermal history and shelf-life of the pellet, and are reproducible to within ± 5%. The S against T^{-1} plots are given in the Fig. 5. The sign of S is negative in both cases in the entire temperature range indicating that the charge carriers are electrons. The S against T^{-1} plot has also two regions with a break temperature (T'_B). In these regions S can be expressed by the relation

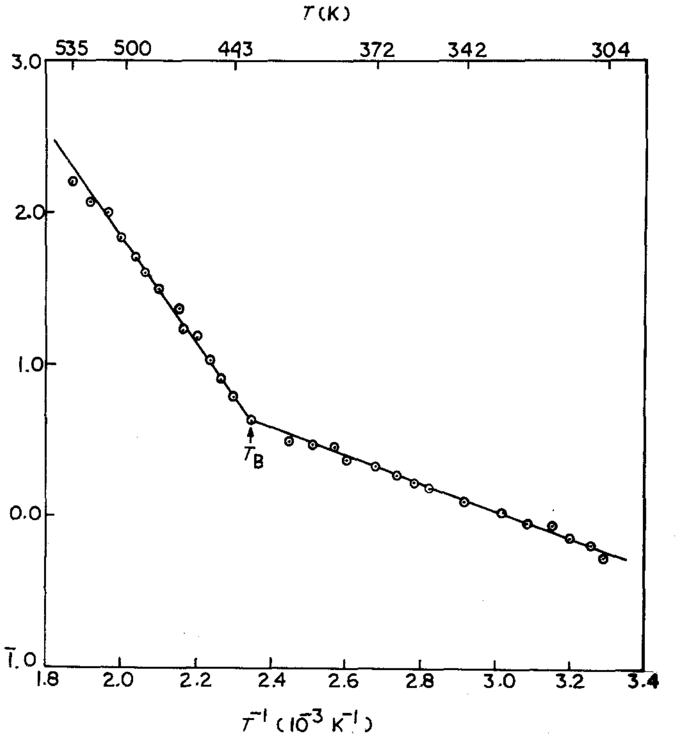

Figure 3 Variation of log$[\sigma(\Omega^{-1}\,m^{-1})]$ against T^{-1} $(10^{-3}\,K^{-1})$ in the temperature range 300 to 540 K of pressed solid pellets of Tl_2OCl_2.

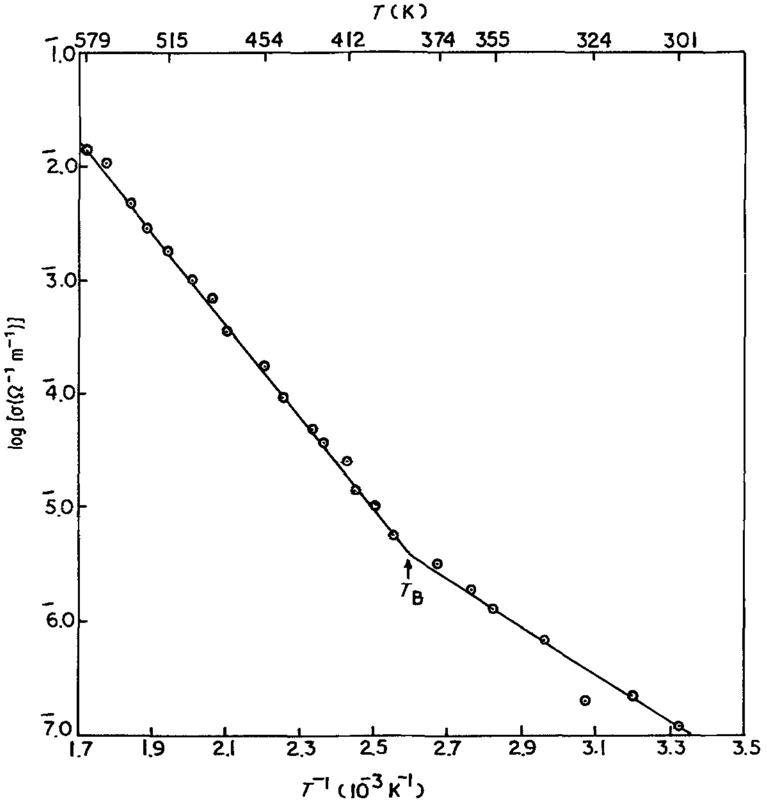

Figure 4 Variation of log $[\sigma(\Omega^{-1}K^{-1})]$ against T^{-1} (10^{-3} K^{-1}) in the temperature range 300 to 580 K of pressed solid pellets of Tl_4Cl_6.

$$S = -\frac{Q}{eT} + H \qquad (4)$$

where Q and H both are temperature independent constants and e is the electronic charge. The values of Q and H in the two regions for both these solids are given in Table IV, along with the values of T'_B. It is seen from Tables III and IV that there exists a small difference between T_B and T'_B. This small difference appears due to the difference in the experimental conditions used in the σ and S measurements. In the σ measurement the whole of the sample was kept at a constant temperature and this temperature, recorded here, reflects the true thermal state of the sample, where as in the case of the S measurement it was subjected to a thermal gradient and the mean temperature recorded here does not reflect the true thermal state of the sample. Obviously, if something is happening in the sample at a particular temperature, it will be closely reflected in σ at the same temperature, however in the S measurement it may appear at the mean temperature a few degrees below or above the actual temperatures. Thus a few degrees difference observed in the break temperatures is not very significant and they essentially reflect to some happening in the sample. The second important point which we observe from this table is that E and Q values are not equal for any region for both samples, and σ_0 values are very high for high temperature ($T > T_B$) regions for both these samples. The thermoelectric power(s) was found to be negative throughout the studied temperature range for both these samples. Therefore as per convention of the semiconductor theory [9], the dominant charge carrier in conduction should be a negatively charged carrier. It is found that d.c. electrical conductivity at a particular temperature, both above and below T_B, is independent of time for both the solids. Thus ionic conductivity in both these solids seems to be negligible and total conductivity may be attri-

TABLE III Values of σ_0, E_a, T_B, E_g and c for Tl_2OCl_2 and Tl_4Cl_6

Parameters	Tl_2OCl_2	Tl_4Cl_6
$E_a(T > T_B)$ (eV)	0.69	0.82
σ_0 $(T > T_B)$ $(\Omega^{-1}$ $m^{-1})$	57.54×10^7	15.14×10^4
T_B(K)	425	383
$E_a(T < T_B)$ (eV)	0.19	0.42
E_g(eV)	1.38	1.64
μ_e/μ_h	1.30	1.34

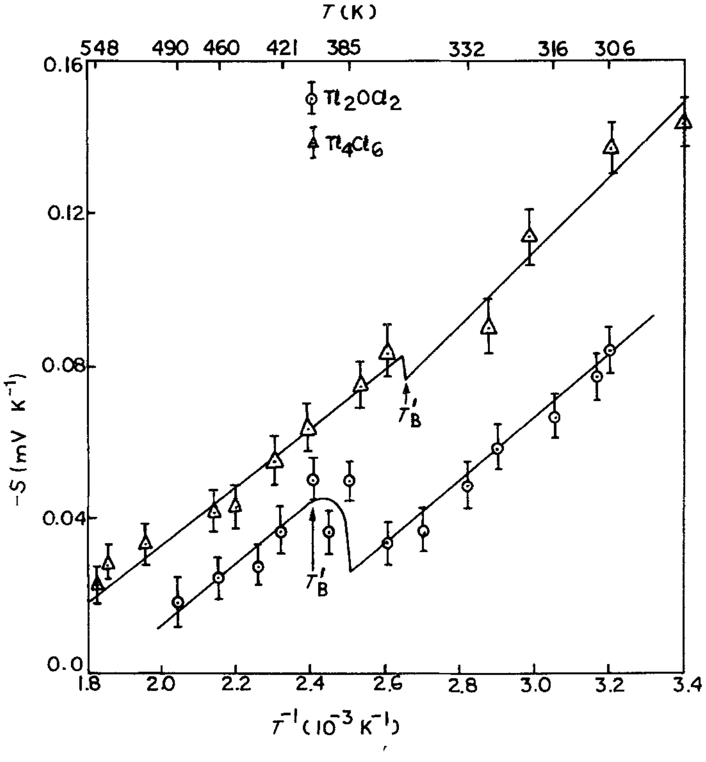

Figure 5 Variation of thermoelectric power, S (mV K^{-1}) against T^{-1} of pressed solid pellets of Tl_2OCl_2 and Tl_4Cl_6.

buted to be due to electrons. The conductivity of Tl_2OCl_2 in the whole temperature range and that of Tl_4Cl_6 in the high temperature range are high. Such high conductivity can result only when number of charge carriers taking part in conduction, as well as their mobilities, are high. This indicates that the band theory of conduction with a small energy gap is applicable in the present systems. The electrical conductivity throughout the temperature range increases exponentially with temperature, thus the nature of σ is not metallic and it is not resulting as a consequence of a free charge carrier in a partially filled band. The two regions, apparent in the log σ against T^{-1} plots, seem to be the result of two different mechanisms. It is customary to employ the energy band theory for explaining electrical conduction in electronic semiconductors. The high value of the constant σ_0, in the higher temperature range, which we may call intrinsic, also speaks of band conduction. Thus the conduction in the intrinsic range of these solids seems to be due to a band mechanism, with an equal number of holes and electrons thermally generated in the valence and conduction bands, respectively. The latter are more mobile and thus dominate the electrical conduction. The activation energy in such a case becomes equal to $E_g/2$, where E_g is the energy band gap of the solid. Thus the energy band gap (E_g) of Tl_2OCl_2 and Tl_4Cl_6 are equal to 1.38 and 1.64 eV, respectively. The thermoelectric power in such a case, does not yield a slope equal to $E_g/2$. Instead the expression for S becomes [9]

$$S = \frac{E_g}{2}\left(\frac{c-1}{c+1}\right)\frac{1}{eT} + \frac{2(c-1)}{(c+1)}\frac{k}{e} + \frac{3}{4}\frac{k}{e}\log\left(\frac{m_e}{m_h}\right) \tag{5}$$

where $c = \mu_e/\mu_h$, μ_e and μ_h being the mobilities of an electron and a hole in the conduction and

TABLE IV Values of Q, H and other parameters for Tl_2OCl_2 and Tl_4Cl_6

Parameters	Tl_2OCl_2	Tl_4Cl_6
$Q(T > T'_B)$ (eV)	0.09	0.08
$H(T > T'_B)$ (mV K^{-1})	−0.168	−0.126
T'_B(K)	417	377
$Q(T < T'_B)$ (eV)	0.08	0.12
$H(T < T'_B)$ (mV K^{-1})	−0.174	−0.246
E'_a (eV)	0.11	0.30
N_s(per m^3) × 10^{-28}	11.7	6.7
n(per m^3) × 10^{-28}	8.5*	4.8†
$a^2\nu$(m^3 Hz) × 10^7	2.5*	2.5†
μ(m^2 V^{-1} sec^{-1}) × 10^6	3.2*	5.7†

*$T = 372$ K.
†$T = 360$ K.

valence bands, respectively, and m_e and m_h their effective masses in their respective bands. Thus S against T^{-1} yields a slope

$$Q = \frac{E_g}{2}\left(\frac{c-1}{c+1}\right). \qquad (6)$$

Knowing the values of E_g and Q from the σ and S plots, one can obtain the value of c. These values of c are also given in Table III.

The low temperature region ($T < T_B$) may be referred to as the extrinsic region. The activation energy in this range are smaller, (see Table III) compared to the region $T > T_B$, as expected. The external region in normal semiconductors comes because of impurities are defects, which are usually pictured as donor or acceptor centres. However, in such cases the E_a and Q values are expected to be the same. This has not been found to be true experimentally. Further, the values of E_a are relatively large. Thus the conduction can not be assigned to donor-type impurities. The low value of S and its small, temperature dependence, indicates a hopping-type conduction. Looking at the chemical formula of these compounds, we find that in order to compensate the well defined valence state of chlorine and oxygen, thallium has to exist in two valence states. The natural valence state of thallium is Tl^{3+} and Tl^{1+}, which may exchange electrons at a suitable temperature and applied electric field. The sequence of electron exchange may be as follows

$$Tl^{1+} + Tl^{3+} \rightarrow Tl^{2+} + Tl^{2+} \rightarrow Tl^{3+} + Tl^{1+}.$$

In this way almost all the thallium ions will be taking part in electrical conduction. The thermoelectric power (S) and electrical conductivity (σ), resulting from this type of exchange, will be given by the relations [10]

$$S \approx \frac{k}{e}\log_{10}\left[\frac{N_s}{n} - 1\right] \qquad (7)$$

$$\sigma = \frac{ne^2a^2\nu}{kT}\exp(-E_a/kT) \qquad (8)$$

where N_s and n are the number of sites and impurity centres per unit volume, respectively, and a and ν are the jump distance and the jump frequencies, respectively. S in such a case is expected to have a very small temperature dependence. The mobility of the charge carriers (μ) will be given by the expression

$$\mu = \left(\frac{ea^2\nu}{kT}\right)\exp(-E'_a/kT) \qquad (9)$$

where E'_a is the mobility activation energy and is given by the relation

$$E'_a = E_a - Q. \qquad (10)$$

In order to judge the validity of the above supposition, it is essential to estimate the value of μ. This has been done using the following procedure. N_s has been calculated from the composition and density. From the known value of S and N_s, one can obtain n at any temperature from Equation 7. Using this value of n, and the known values of σ and E_a, one can obtain $a^2\nu$. Using this value of $a^2\nu$, it is easy to calculate ν from Equation 9. These evaluated values of μ at one temperature are given in Table IV. The mobilities came out to be of the order of $10^{-6}\,m^2\,V^1\,sec^{-1}$, which is of the right order of magnitude for the hopping success.

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