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Structure, thermal stability and electrical transport in coloured thallous tungstates

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Different coloured thallous tungstates were prepared by solid state reaction between thallous carbonate and tungsten trioxide at higher temperatures. The structure and thermal stability of different thallous tungstates were determined by powder X-ray diffraction and thermogravimetric analysis, respectively. The electrical conductivity (σ) and thermoelectric power (S) of pressed solid pellets of Tl_2WO_4 are reported in the temperature range 295 to 950 K. It is concluded that these materials have large numbers of oxygen ion vacancies and conduction occurs due to the electrons left by oxygen ions while escaping the solid. These electrons are trapped in the valence band and form centres analogous to a helium atom and electrical conductivity results when they enter the conduction band. The values of donor ionization energies have also been evaluated.

1. Introduction

Mixed metal oxides show interesting chemical and physical properties, some of which have been exploited in technical applications. We have examined the structural, thermal stability, catalytic, magnetic and electrical transport properties of such compounds over the last few years [1–8]. The change in colour of thallous tungstate on thermal treatment as well as when exposed to radiation as reported by Rastogi *et al.* [9] attracted our attention towards this compound, and we decided to investigate its physico-chemical properties to achieve a basic understanding. These coloured tungstates can be stabilized. This paper reports the preparation, structure, thermal stability and electrical transport studies of some coloured thallous tungstates.

2. Material preparation and experimental technique

White and coloured thallous tungstates are generally prepared by repeated firing of stoichiometric pelletized mixture of Tl_2CO_3 and WO_3. White thallous tungstate is obtained by firing around 550° C for 5 h. Yellow thallous tungstate is obtained by firing white thallous tungstate around 810° C for 2.5 h and slowly cooling the melt to room temperature Heating white thallous tungstate to around 810° C for 65 min and quenching on a water-soaked cloth yields bluish-green thallous tungstate. Violet thallous tungstate is obtained by heating white thallous tungstate to around 810° C for 2.5 h and quenching on a water-soaked cloth. Exposure of any these coloured compounds to ultraviolet radiation gives brown thallous tungstate.

The structures of all the compounds have been obtained by analysing the X-ray diffraction patterns taken using Cu$K\alpha$ radiation. Thermal stability measurements (TG, DTA) were carried out using a thermogravimetric analyser and a differential thermogravimetric analyser. The electrical conductivity and thermoelectric power measurements were performed on pressed pellets using sample holder instruments and the procedure described elsewhere [8, 10].

3. Results

Electrical conductivity, σ, and thermoelectric power, S, studies have been performed on pressed circular pellets because preparation of single crystals is difficult. 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 is generally achieved by preparing pellets at a very high pressure and

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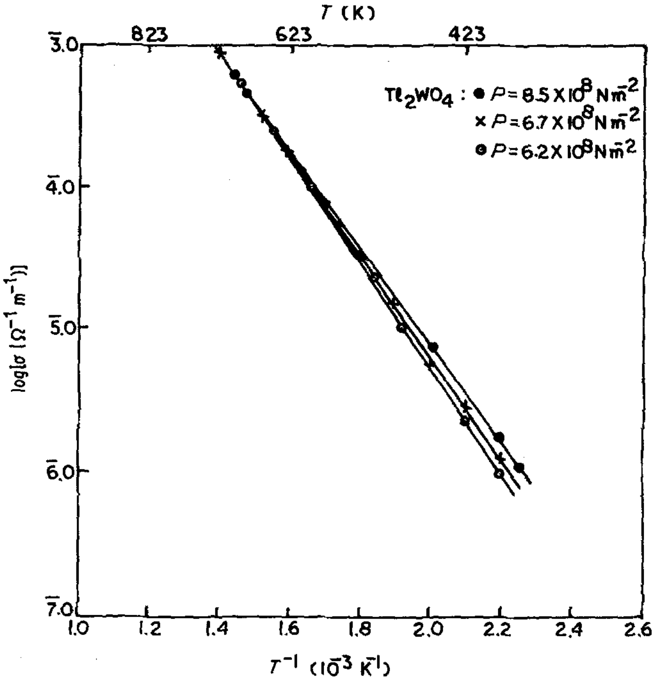

Figure 1 Variation of logarithmic conductivity, σ, with inverse of absolute temperature, T, at various pelletizing pressures, P.

sintering them for a sufficiently long time at an appropriate temperature. It is suggested [11] that a highly pressed pellet acquires a uniform density if its thickness to width ratio is less than 2 (or approximately if t^2/a is less than 0.4 in the case of circular pellets, where t is the thickness and a the cross-sectional area). The pellets used in conductivity and Seebeck coefficient measurements were obtained at a pressure greater than $8 \times 10^8\ \mathrm{N\,m^{-2}}$ and had ratios of 0.03. This ensures a uniform pellet density, d_p, which generally lies between 78 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

$$f = 1 - d_\mathrm{p}/d_\mathrm{x} \tag{1}$$

is generally about 0.22.

The presence of grain boundaries greatly affects the transport behaviour of the material. Russel [12] has shown that in such cases the bulk value of the electrical conductivity, σ, can be given by the relation

$$\sigma = \sigma_\mathrm{p}\left[1 + \frac{f}{1 + f^{2/3}}\right] \tag{2}$$

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 yellow Tl_2WO_4, prepared at different pelletizing pressures, was measured. The plot of log σ against T^{-1} obtained in the temperature range 445 to 800 K as shown in Fig. 1, reveals that the dependence of conductivity on pelletizing pressure, P, is more pronounced below 525 K and a pore fraction correction, introduced as in Equation 2, does not appear to be very effective. However, above 525 K, the plots of log σ against T^{-1} corresponding to σ values at different values of P are in good agreement. The dependence of S and P is difficult to determine because of the relatively large (± 5%) error in the experimental values of S. In this case, no correction for pore fraction has been suggested.

The electric current density, J, was found to be independent of time for all coloured Tl_2WO_4. However, its variation with applied electric field, E, is linear, in accordance with Ohm's law, only in low fields $E \leqslant 30 \times 10^{-2}\ \mathrm{V\,m^{-1}}$ (see Fig. 2). In higher fields, $E \geqslant 30 \times 10^{-2}\ \mathrm{V\,m^{-1}}$, the ohmic current is replaced by a space charge limited current and J varies slowly with E. Furthermore, the curves, particularly of white and bluish-green Tl_2WO_4, do not necessarily pass through the origin which leaves some doubt in assigning the contact as being true ohmic. However, E was maintained below $30 \times 10^{-2}\ \mathrm{V\,m^{-1}}$ where the condition of ohmic contact prevailed.

The a.c. conductivity, $\sigma_{\mathrm{a.c.}}$, of all sample

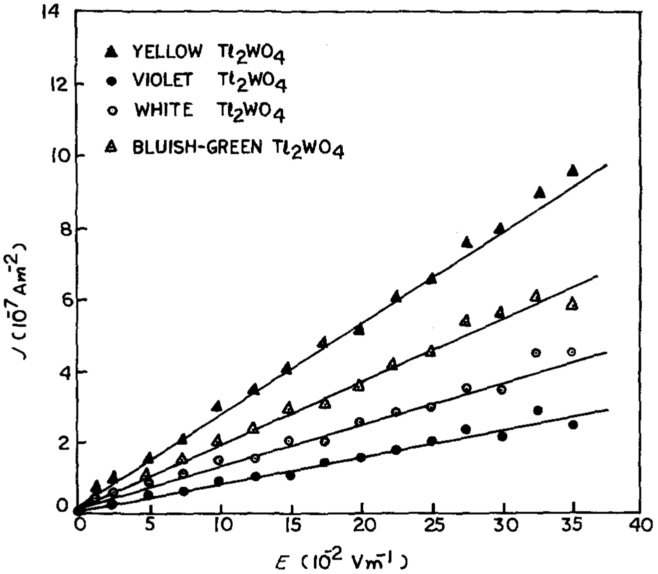

Figure 2 Variation of electric current density, J, with applied field, E.

pellets at a constant temperature between 295 and 850 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 $\sigma_{\text{a.c.}}$ reflects the bulk value of conductivity between 10^2 and 10^4 Hz. The d.c. conductivity, $\sigma_{\text{d.c.}}$, at any given temperature was found to be little higher than the value of $\sigma_{\text{a.c.}}$ at the same temperature. This supports the view that the lack of 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_2WO_4 and easy passage of the charge carriers from one grain to another. The values of σ for all samples (different coloured tungstates) at a particular temperature, or their variation with temperature, do not differ considerably for different sample 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 were preferred for our measurements. 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 the heating and cooling cycles, but after a few heating and cooling cycles of 20 to 24 hours, 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, are presented as log σ against T^{-1} plots (Fig. 3) in the temperature range studied for all tungstates of thallium. The experimental points are in accordance with Equation 2. It is seen from this figure that plots of log σ against T^{-1} are linear in all cases with a break in the slope at a specific temperature (T_{B}) which may be termed the break temperature.

The Seebeck coefficient, S, at a particular temperature for all different coloured tungstates of thallium, is essentially independent of thermal history and shelf-life of the pellet, and is reproducible to within ± 5%. Plots of S against T^{-1} are given in Fig. 4. The sign of S is negative in all cases over the entire temperature range indicating that the charge carriers are electrons. The plot also has two regions for different coloured thallous tungstates, with a break temperature, T'_{B}.

4. Discussion

Table I shows the structural parameters of different coloured thallous tungstates. The unit cell is hexagonal consisting of two molecules in all cases with a slight difference in their lattice parameters. The lattice parameters and the variation in intensities of the respective diffraction lines indicate that there is a greater identity

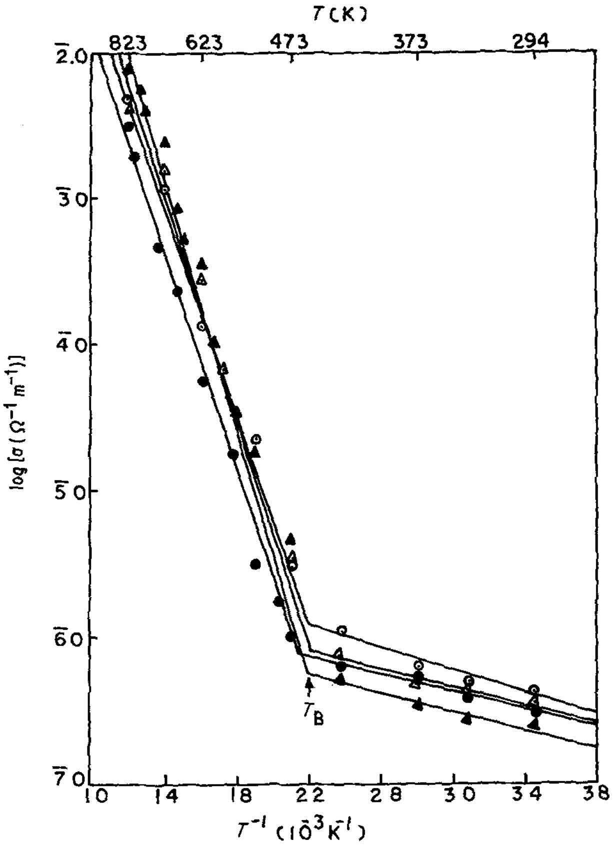

Figure 3 Variation of log σ (Ω^{-1} m^{-1}) with inverse of absolute temperature for coloured thallous tungstates: ●, white, ◎, yellow; △, bluish-green; ▲, violet.

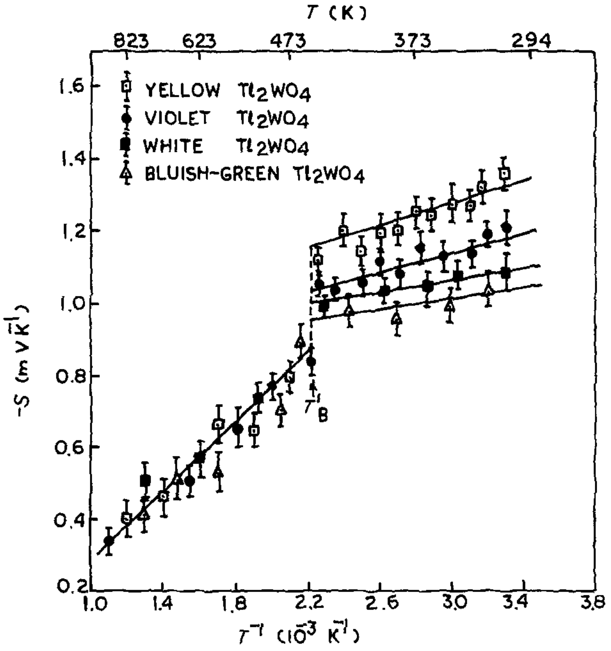

Figure 4 Variation of thermoelectric power, *S* (m V K^{-1}) with inverse of absolute temperature for thallous tungstates.

TABLE I Crystal data for different coloured thallous tungstates

Form of Tl_2WO_4	Crystal cell dimensions		X-ray density ($g\ m^{-1}$)	z^*	Reference
	a nm	c nm			
White	0.6296	0.8296	7.80	2	[9]
	0.6289	0.8301	7.81	2	Present study
Yellow	0.6296	0.8126	7.80	2	[14]
	0.6294	0.8126	7.81	2	Present study
Bluish-green	0.6326	0.8126	7.73	2	[14]
	0.6325	0.8126	7.74	2	Present study
Violet	0.6326	0.8126	7.73	2	[14]
	0.6326	0.8125	7.74	2	Present study

z^* = number of molecules per unit cell.

between white and yellow thallous tungstates in comparison to bluish-green and violet. The slight variation in lattice parameters of bluish-green and violet compared to those of white and yellow appears to be due to lattice distortion. However, DTA studies show a single endothermic peak around 620 ± 10° C for all coloured tungstates indicating their melting points. Thus the melting point is almost the same for all coloured thallous tungstates.

The different forms of thallous tungstates having different colours are non-stoichiometric oxygen compounds [13] having the formula Tl_2WO_{4-w}, where x may have different values for the different coloured species. This is supported by our TGA studies. Thermogravimetry of different thallous tungstates shows a weight loss. However, on cooling after TG, they regain their weight. There may be three reasons for the decrease in weight: (i) weight loss due to vaporization of the compound; (ii) weight loss due to moisture; and (iii) weight loss due to the escape of oxygen atoms from some of the lattice sites. The increase in weight of the sample almost to the original weight on cooling after TG clearly rules out the first possibility. The second possibility has also been discarded in a very simple manner by heating a weighed amount of thallous tungstate at 800° C for 2.5 h and cooling to room temperature in a desiccator and weighing it again. It was observed that the weight of the sample remained unchanged. This should not occur if the moisture had evaporated from the sample on heating. This clearly indicates that the decrease in weight during the TG experiment was due to escape of oxygen from some of the oxide ion lattice sites and the weight gain during the cooling might be due to the uptake of atmospheric oxygen. It follows from the above arguments that the oxygen deficiency is smallest in the white thallous tungstate, followed by yellow, bluish-green and violet thallous tungstates and they can be represented by the general formula, Tl_2WO_{4-x}. This conclusion is supported by other workers [14].

It has already been said that Tl_2WO_4 are usually oxygen deficient. To keep the material neutral, oxygen should leave the sample by conversion of O^{2-} into oxygen atoms. The two electrons of the oxygen will be left in the sample. These two electrons may either be trapped in the oxygen ion vacancy or may be attached to neighbouring cations. In the first case they can be pictured as a solid state anologue of a helium atom [15] and will have two ionization energies: the first, when one of the two electrons is excited to the conduction band, and the second when the other electron leaves to the conduction band. In general, both ionization energies will be very small compared to the ionization energy of helium because of the lack of a central charge and the large value of the dielectric constant of the material compared to vacuum. Again, the first will still be very small compared to the second. Thus, generally, two electrons trapped in the oxygen ion vacancy can be pictured as donor centres, with shallow and deep levels. The depth of these levels seems to depend upn the concentration of oxygen vacancies and this variation in their depths leads to the appearance of the different colours. The electrons will take part in conduction when the trapped electrons are excited to the conduction band. The number of electrons left in the conduction band and taking part in conduction will increase exponentially with temperature. However, once they are in the conduction band their mobility will be large and almost independent of temperature. Obviously the conduction will be band-type with two slopes

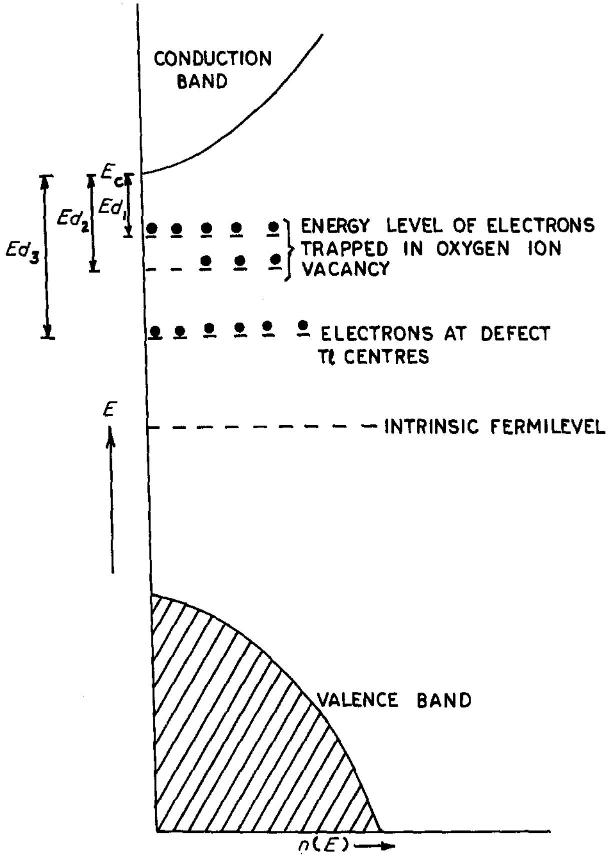

Figure 5 Schematic energy band diagram and defect levels for Tl_2WO_4.

in the plot log σ against T^{-1}. In the second case, when the remaining electrons are attached to neighbouring atoms, we obtain two neighbouring cations with excess electrons (thallium atom in the present case). These electrons will take part in conduction when they hop from thallium to a neighbouring Tl^+ ion. The conduction mechanism will be of the hopping type and mobility will become thermally activated. Thus one slope is expected in the log σ against T^{-1} plot. Furthermore, in the second case, it is obvious that number of defect thallium centres will be constant, being twice the number of vacant oxygen sites. In such a situation thermoelectric power should be independent of temperature. Looking of our experimental results (Fig. 4) we find that the thermoelectric power is strongly temperature dependent. This rules out defect Tl centres being responsible for electrical conduction. Their existence in our sample is not completely ruled out; however, it is not thought that they energetically contribute towards electrical conduction. An electron trapped in an oxygen ion vacancy can be pictured as two electron donor centres. At lower temperatures the first of these electrons is excited to the conduction band. The conductivity in this situation will be given by the expression

$$\sigma = \sigma_0 \exp\left(-\frac{Ed_i}{2kT}\right) \qquad (3)$$

where Ed_i, $i = 1, 2$, is the depth of the first and second electron energy level below the conduction band. This is expected to be small. The first slope of the log σ against T^{-1} plots reflects this mechanism (Fig. 5), the slope is almost the same for all forms of tungstates as expected, and has a value of $Ed_1 \simeq 0.10\,\text{eV}$. The values of σ, however, will be larger for the material having larger oxygen defects, which has not been found to be true. This is not surprising, because as bluish-green and violet samples are made by quenching, we expect the formation of defect thallium centres in this case, which automatically leave fewer electrons trapped in an oxygen ion vacancy.

The thermoelectric power resulting from electrons excited from donor centres will be given by the expression

TABLE II Summarized results of electrical conductivity measurements on different coloured Tl_2WO_4

Parameters	White		Yellow	Bluish-green	Violet
	Obs.	Previous data [9]			
Ed_1 ($T < T_B$) (eV)	0.10	0.05	0.10	0.10	0.10
σ_0 ($T < T_B$) (k Ω^{-1} m^{-1})	0.004	–	0.03	0.004	0.01
Ed_2 ($T > T_B$) (eV)	0.68	0.53	0.69	0.68	0.69
σ_0 ($T > T_B$) (k Ω^{-1} m^{-1})	5459	–	15 250	6457	29 510
T_B (K)	454	454	454	454	454

TABLE III Summarized results of thermoelectric power measurements on different coloured Tl_2WO_4

Parameters	White	Yellow	Bluish-green	Violet
Ed ($T < T'_B$) (eV)	0.10	0.10	0.10	0.10
T'_B (K)	450	450	450	450
Ed ($T > T'_B$) (eV)	0.67	0.67	0.67	0.67

$$S = -\frac{Ed}{2eT} - \frac{2k}{e} + \frac{3}{4}\cdot\frac{k}{e}\log T - \frac{k}{e}\log\left[\left(\frac{Nd}{2}\right)^{1/2}\left(\frac{h^2}{2\pi mkT}\right)^{3/4}\right] \qquad (4)$$

where Ed is the depth of donor level below conduction band, Nd is the number of donor centres per unit volume. The variation of the log term is always much smaller compared to Ed/T variation, hence later and all other terms may be taken to be practically constant. Thus a plot of S against T^{-1} should be a straight line, the slope of which should be the same as that of the log σ against T^{-1} plot. The values of Ed obtained from the slopes of the log σ against T^{-1} and S against T^{-1} plots below and above T_B and T'_B, are given in Tables II and III. The values obtained from these data are nearly the same. This confirms the vaidity of the proposed mechanism for conduction in these solids.

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