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Electrical conduction in narrow band trivalent transition metal tungstates

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The measurements of electrical conductivity (σ) and Seebeck coefficient (S) of trivalent transition metal tungstates $M_2(WO_4)_3$ with M = Cr, Fe and Ni have been reported in the temperature range of 450 to 1250 K. The results have been explained on the basis of a schematic energy band diagram appropriate for these solids. The estimated value of the energy band gap is slightly more than 3 eV.

1. Introduction

The compounds of 3d transition elements have been extensively studied and many useful materials both from theoretical and application point of view have been obtained. Trivalent tungstates have been an exception in this regard. The first attempt to form such compounds was done by Nassau *et al.* [1]. They have reported that unlike rare-earth elements all 3d elements do not form such trivalent compounds. Besides this early information, very little data [2–5] are available on these compounds. This lack of study prompted us to prepare and investigate magnetic and electrical properties of these compounds. We have been able to prepare and investigate three trivalent tungstates namely chromium, iron and nickel. The electrical transport properties of these compounds are reported in this paper.

2. Experimental procedure

The starting materials for the preparation of chromium, iron and nickel tungstates were their respective sesquioxides Cr_2O_3, Fe_2O_3 and Ni_2O_3 (obtained from Rare-Earth Research Chemicals India, with stated purity of 99.99%) and WO_3 (from Bonds India, with stated purity of 99.99%). All these compounds were dried around 500 K before use. The stoichiometric amount of starting materials were thoroughly mixed, made into pellets and fired around 700 K for chromium, 800 K for iorn and 600 K for nickel tungstates in a platinum crucible in air for 24 h. The reaction product was reground, again made into pellets and fired around 800 K for more than 24 h. This process has been found sufficient for the formation of single phase compounds as evident from X-ray diffraction (XRD) patterns and their analyses.

The measurements of electrical conductivity (σ) and Seebeck coefficient (S) have been done on pressed pellets. The details of pellet formation, electrode making and techniques of σ and S measurements were the same as described in earlier publications [6, 7] of our group.

3. Results and discussion

Electrodes play an important role in the measurement of σ and S. The stringent criteria [8] is to have ohmic contact in both measurements. We have used platinum foil (thickness $\simeq 0.02$ mm), pressed mechanically on the pellet faces as electrodes. The ohmic contact was confirmed by linear current density (J) against applied d.c. electric field plot (not given in this paper) at constant temperature. The current density has also been measured as a function of time keeping temperature and applied d.c. electric field constant. J values have been found almost independent of time indicating that electrical current in these solids is completely electronic.

The air pores and grain boundaries, which have a significant effect on the values of σ and S, cannot be avoided in pellets but they can be significantly reduced in highly pressed pellets of uniform density. The pellets used in our measurements were made using fine and uniform grain powders at pressures exceeding $8 \times 10^8\,\mathrm{Nm^{-2}}$ and sintered around 700 K for two days in air. It has been observed that pellets of different dimensions yield almost the same values of σ and S. Further, σ has also been found independent of a.c. frequency (0 to 10^5 Hz). The independence of σ from dimensions, pelletizing pressure and signal frequency indicates that measured values of σ represent the bulk value of the material and grain boundary effects are considerably reduced. The σ values have been further corrected for air pores using relations given in our earlier publication [9].

The σ and S measurements on a few of the pellets of each material have been carried out in air over a temperature range of 450 to 1250 K. The values of σ and S and their variation with temperature do not differ considerably from sample to sample. The average of σ and S over a few pellets have been taken as their representative value. Fig. 1 (a, b and c) shows the plots of log σ and S against inverse of temperature, T^{-1} for chromium, iron and nickel tungstates. These plots show linear regions in some temperature intervals for each material and can be represented by relations

$$\sigma = \sigma_0 \exp(-W/2kT) \qquad (1)$$

$$S = \eta/eT + H \qquad (2)$$

where σ_0, W, η and H are constants. The evaluated

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TABLE I Summarized results of σ and S measurements

σ measurement				S measurement			
Temperature range (K)	W (eV)	σ_0 (Ω^{-1} m^{-1})	T_B (K)	Temperature range (K)	η (eV)	H (mV K^{-1})	Charge carrier*
(a) $Cr_2(WO_4)_3$							
450–560	0.52	5.86×10^{-5}	580	450–600	0.05	0.10	*e*
600–800	1.50	7.08×10^{1}	–	630–715	0.75	−1.05	*e*
800–950	Nonlinear		950	715–950	peak at 860 K		–
950–1250	3.20	2.47×10^{5}	–	950–1110	0.064	0.04	*e*
(b) $Fe_2(WO_4)_3$							
450–700	0.60	6.14×10^{1}	700	450–700	0.28	−0.84	h
700–885	Nonlinear		885	700–885	Minima at 770 K		–
885–1100	1.68	6.31×10^{4}	–	885–1055	0.22	−0.44	h
(c) $Ni_2(WO_4)_3$							
450–685	0.84	1.13×10^{-1}	685	–	–	–	*e*
685–1030	Nonlinear		1030	685–1085	peak at 990 and 1020 K		–
1030–1235	1.66	4.59×10^{-2}	–	–		–	h

**e* – electron, h – hole

values of these constants for different materials in different linear regions are given in Table I. Both log σ and S plots also have nonlinear regions for each material as mentioned in Table I. In the case of chromium-tungstate the S variation with T^{-1} shows a sharp peak around 860 K. To accommodate this high peak in the plot (Fig. 1a) a different scale has been used. Similarly there exists a deep drop in S against T^{-1} plot around 770 K for iron tungstate. In the case of nickel tungstate the variation of S with T^{-1} (Fig. 1c) is found to be very irregular. Measurement of S for this material could be made only for the temperature interval of 685 to 1175 K. The nature of the majority charge carrier has been obtained on the basis of the sign of S and is also given in Table I.

From the study of time dependence of d.c. electrical

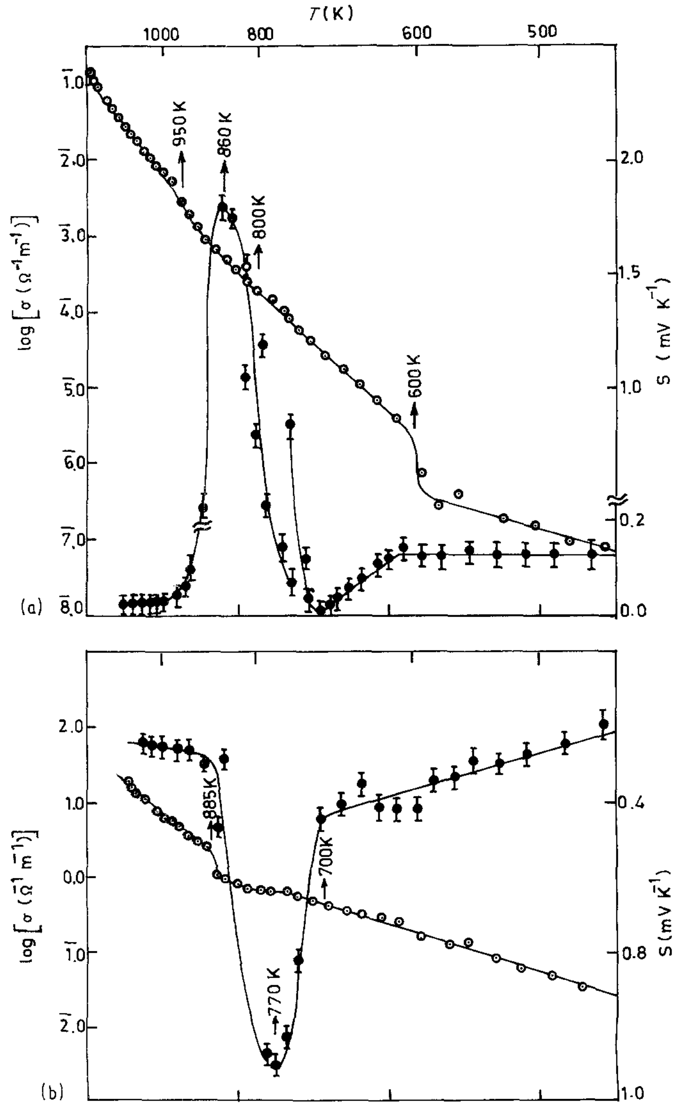

Figure 1 Plots of log σ and S against inverse of temperature for (a) chromium, (b) iron and (c) nickel tungstates, (○) σ, (●) S.

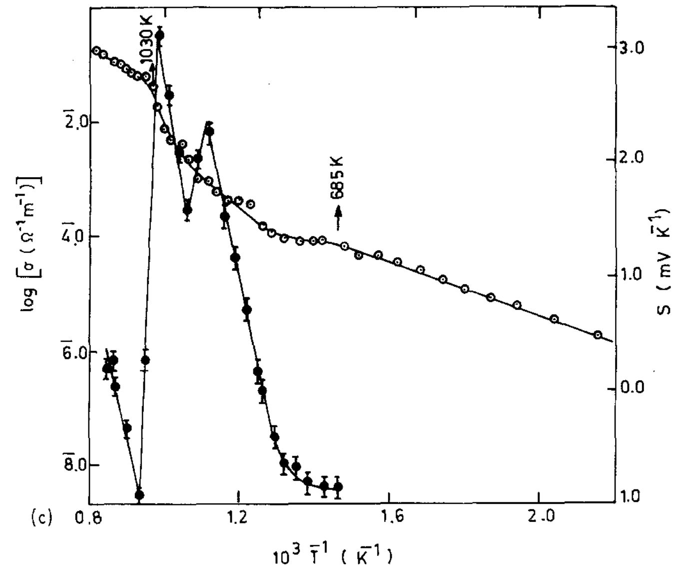

Figure 1 Continued.

conductivity, we have concluded that all the three studied tungstates are essentially electronic conductors. Hence we can attempt to explain electrical conduction in them using a simple energy band model. The relevant electron energy bands which may be important in these solids are O^{2-} : 2p, M^{3+} : 3d, M^{3+} : 4s and W^{6+} : 6d in order of increasing energy. Probably the W^{6+} : 6d band will not come into the picture of electrical conduction. Out of the remaining three bands, M^{3+} : 3d band (which might split into e_g and t_{2g} by the crystal field) is partially filled and should support metallic conduction. Thus according to band theory predictions, all these tungstates should be metallic. But none of them are so. It can, therefore, be concluded that the 3d band is narrow and is unable to support metallic conduction. Hence 3d electrons either do not take part in electrical conduction, or if they do so, it is through a low mobility small polaron (localized electrons in 3d bands behave as a small polaron). On the basis of the above discussion, we can draw a schematic energy band diagram of trivalent transition metal tungstates as given in Fig. 2. This energy band diagram can be used to explain the genesis of charge carriers and conduction processes in these solids.

Looking at the summarized results of σ and S given in Table I we find that the activation energy (E_a = W/2) in the lowest temperature region, starting from 450 K is small (0.26 eV for chromium, 0.30 eV for iron and 0.42 eV for nickel). Such a low value of E_a cannot be associated with any of the conduction processes which one can visualize on the basis of the energy band diagram given in Fig. 2. The source of charge carriers seems to be a defect. The deficiency of oxygen

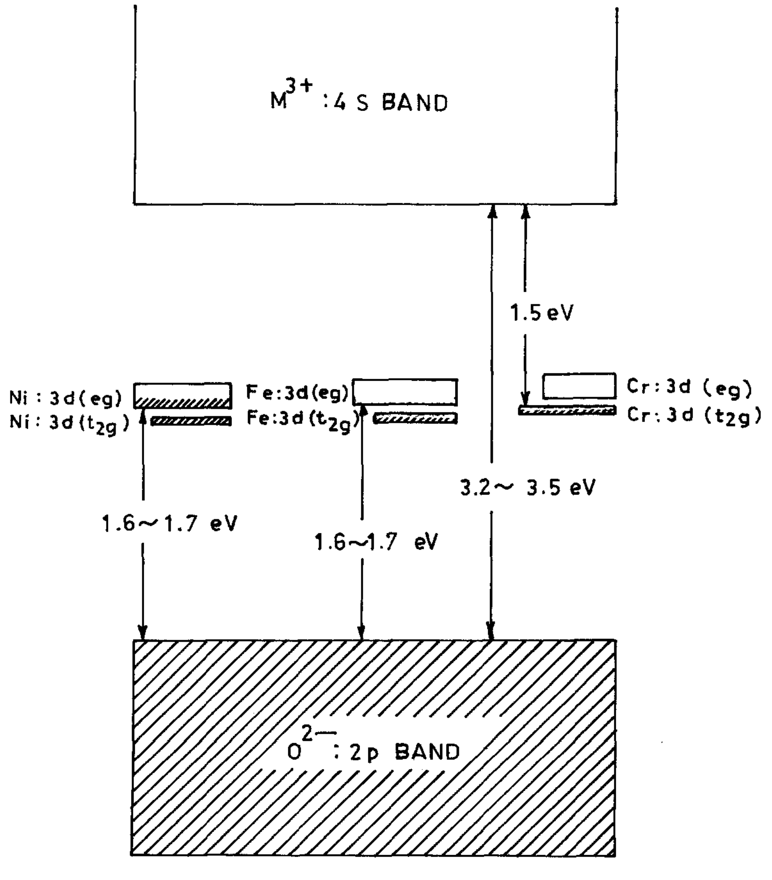

Figure 2 Schematic energy band diagram of transition metal tungstates.

or a cation can produce such defects. In the case of chromium tungstate the slope of S against T^{-1} plot is very small, suggesting a hopping-type conduction process. The same may be true for nickel tungstate, although the S data is not there to strengthen this hypothesis. In the case of iron tungstate the values of E_a and η are nearly the same, which hints towards deep acceptor type defect centres. The conduction will be through thermally generated holes in oxygen 2p band.

The plot of $\log \sigma$ against T^{-1} in the case of chromium tungstate, in the temperature range 600 to 800 K, is linear. The S against T^{-1} plot is also linear in this temperature range. Further values of E_a and η are nearly the same. It seems that genesis of charge carriers in this range is due to excitation of electrons from the chromium 3d to chromium 4s band. The case is similar to a case discussed by us in an earlier paper [10]. The only difference is that the $4f^n$ band is now replaced by a $3d^n$ band. We can use relations for σ and S given therein for the case *c*. Thus W in σ expression stands for $E_c - E(t_{2g})$. The computed values of N are $5.01 \times 10^{27}/\mathrm{m}^3$ and μ_e at 600, 700 and 800 K are 5.5×10^{-3}, 4.8×10^{-3} and $4.4 \times 10^{-3}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{sec}^{-1}$ respectively. Above 715 K, S starts increasing and shows a peak at 860 K. This discrepancy seems to be due to a structural phase transition. Above the phase transition temperature both $\log \sigma$ and S against T^{-1} plots are linear. The value of S is small. This suggests normal band conduction in two relatively wide bands. These bands will be the oxygen 2p valence band and the chromium 4s conduction band. The expressions for σ and S will be as discussed by us elsewhere [10]. On computation one gets $W = E_g = 3.20\,\mathrm{eV}$, $m_e^*/m_h^* = 0.50$ and values of μ_e and μ_h to be 26.1 and $23.9\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{sec}^{-1}$ respectively. The values of mobilities are quite appropriate for the band conduction.

The values of W in the temperature range 885 to 1100 K for iron tungstate and 1030 to 1235 K for nickel tungstate are nearly the same and pre-exponential constants in both cases are relatively large. S data indicates that holes are the majority charge carriers. However, values of η and W/2 are not the same. It appears that for these materials 3d bands lie almost in the middle of oxygen 2p and iron (or nickel) 4s bands and the genesis of charge carrier is taking place by excitation of electrons from oxygen 2p to iron (or nickel) 3d (e_g-sub band) and excitation of electrons from iron (or nickel) 3d (t_{2g}-sub band) to iron (or nickel) 4s bands. The holes in oxygen 2p and electrons in iron (or nickel) 4s bands will conduct via band mechanism. It is not straightforward to evaluate mobilities of charge carriers in such a situation. However, if it is true, the energy band gap of these solids will be more than 3 eV. The dip appearing in S against T^{-1} plot around 770 K for iron tungstate hints towards structural phase transition in this material.

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References

1. K. NASSAU, R. J. LEVINATION and G. M. LOIACONO, *J. Phys. Chem. Solids*, **26** (1965) 1805.
2. K. NASSAU, J. W. SHIEVER and E. I. KEVE, *J. Solid State Chem.*, **3** (1971) 411.
3. A. W. SLEIGHT and L. H. BRIXNER, *Mater. Res. Bull.*, **8** (1973) 1269.
4. R. R. ZARIKOV, G. M. BARTNESE and A. D. TAYGANOV, *J. Struct. Chem.* (*USA*) **16** (1975) 568.
5. L. N. PLAYSOVA, *J. Struct. Chem.* (*USA*) **17** (1976) 637.
6. H. B. LAL, B. K. VERMA and N. DAR, *Indian J. Cryogenics* **1** (1976) 119.
7. A. K. TRIPATHI and H. B. LAL, *J. Mater. Sci.* **17** (1982) 1595.
8. G. G. ROBERTS, "Transfer and Storage of Energy of Molecules" Vol. 4 (John Wiley and Sons, New York, 1976).
9. K. GAUR and H. B. LAL, *J. Mater. Sci.* **19** (1984) 3326.
10. H. B. LAL and K. GAUR, *J. Mater. Sci.* **23** (1988) 919.

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