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The electrical properties of Fe_2WO_6

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Fe_2WO_6 was found to be a p-type semiconductor with an energy gap of 1.68 eV. The drift mobility (μ_d) and mean free path (L) of the charge carriers have been calculated by combining the electrical conductivity and thermoelectric power data. It is proposed, from the magnitude of L and μ_d and the temperature dependence of μ_d, that the charge carriers in Fe_2WO_6 are small polarons and that the charge transport process occurs by a hopping mechanism below 800 K. Above 800 K the results are explained using a narrow d-band model. The dielectric constant as a function of temperature exhibits two stages of increase: (i) a slow rise at lower temperature which is attributed mainly to an increase in ionic polarization and (ii) a fast rise at higher temperature which is ascribed to space charge polarization.

1. Introduction

The present work on electrical transport properties of Fe_2WO_6 is a part of an extensive investigation of the electrical transport properties of 3d-transition metal tungstates [1, 2]. The crystal structure of Fe_2WO_6 is of the type tri-α-PbO_2 [3]. Its crystallographic space group is $Pbcn$ (D_{2h}^{14}) [4], and the cell parameters are $a = 4.576 \pm 0.002$ Å, $b = 16.766 \pm 0.005$ Å and $c = 4.967 \pm 0.002$ Å [3], with four formula units per lattice point. Fe_2WO_6 has a canted structure with moments forming an angle of 23.5° to the c-axis [5]. The magnetic space group is $Pn'c2'$ [5], and the structure consists of zig-zag chains of FeO_6 or WO_6 octahedra sharing edges parallel to the c-axis. The bond lengths are: W–O = 1.98 Å and Fe–O = 2.05 Å [3]. The present paper reports a study (on powder samples) of the a.c. and d.c. electrical conductivities ($\sigma_{a.c.}$ and $\sigma_{d.c.}$), thermoelectrical power (θ) and static dielectric constant (ϵ') in the temperature range 300 to 1200 K of Fe_2WO_6.

2. Experimental details

2.1. Sample preparation

The starting materials, Fe_2O_3 (of purity 99.99%, from M/S Koch Light Industries, London) and WO_3 (of purity 99.9% from M/S Merck, Germany) were fired separately at 500° C for 24 h before mixing. The polycrystalline compound of Fe_2WO_6 was prepared by the same method as that employed by Senegas and Galy [3]. The equimolar mixture of prefired Fe_2O_3 and WO_3 was mixed thoroughly and formed into pellets. The pellets were fired at 900° C for 48 h in a tightly covered platinum crucible. The furnace was then cooled slowly to room temperature. The pellets were ground, reformed into pellets and fired again at the same temperature. The process of grinding and firing was repeated until a good product was obtained.

2.2. Experimental procedure

The pellet on which the final measurements were carried out was made at a pressure of $8 \times 10^6\,g\,cm^{-2}$. The pellet had a diameter of 13.00 mm and a thickness of 4.80 mm and was annealed and cleaned. Both the surfaces of the pellet which were in contact with platinum electrodes were painted with silver paint to ensure good electrical contact.

The d.c. electrical conductivity and thermo e.m.f. values were measured by a digital multimeter (PM 2522/90, Philips, India) with an accuracy better than ± 0.025%. A.c. electrical conductivity and the dielectric constant were measured using a Ruttonsaw Universal, LCR Bridge model 901-I (India) which operates at an internal frequency of 1 kHz with an accuracy of ± 1.25% of the reading ± 0.25% at full range scale. The details of the apparatus and procedure have been described in a previous publication [1]. A two-electrode method

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was employed for all the measurements. The thermoelectric power was measured by applying a temperature difference of ~ 20° C across the pellet. The ambient temperature was taken to be the mean of the temperature at both ends. The temperatures were measured using chromel–alumel thermocouples attached to the platinum electrodes.

3. Results and discussion

The variation of $\log_{10}\sigma$ against $1/T$ is shown in Fig. 1 for the temperature range 300 to 1200 K. It yields two straight lines in accordance with the well known relation

$$\log_{10}\sigma = \log_{10}\sigma_0 - \frac{E_a}{kT}. \qquad (1)$$

A break in the $\log_{10}\sigma$–$1/T$ plot is noted around 650 K. The respective activation energies are 0.33 and 0.84 eV below and above the temperature (T_B) at which the break occurs. The activation energy E_a below T_B is too low to be an activation energy of intrinsic conduction. It must therefore be associated with some sort of impurities. These impurities are most probably due to point defects (vacancies and interstitials), which are often present in the oxides of transition metals [6]. The impurity levels lie within the forbidden energy gap. The activation energy above 800 K is 0.84 eV which represents the activation energy of intrinsic conduction. It agrees with the reported value of intrinsic activation energy 0.70 eV for Fe_2O_3 obtained by other workers [7–9]. Thus it can be concluded that the break which occurs around 650 K, is due to a change in conduction mechanism i.e. transition from extrinsic to intrinsic conduction.

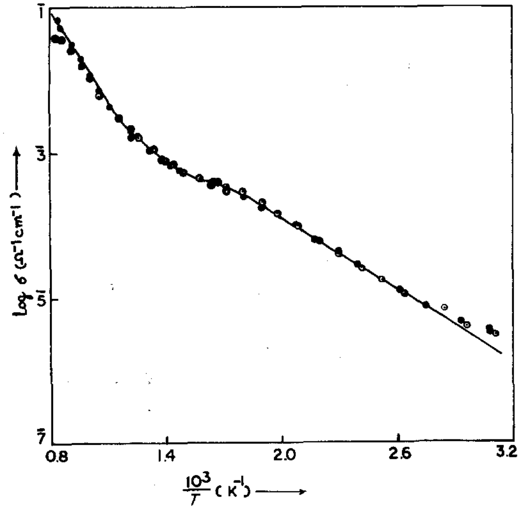

Figure 1 Variation of a.c. and d.c. electrical conductivities ($\sigma_{a.c.}$ and $\sigma_{d.c.}$) with temperature for Fe_2WO_6. ⊙ indicates d.c. conductivity and ● indicates a.c. conductivity.

Fig. 2 shows the variation of θ with $1/T$ in the temperature range 350 to 1250 K. θ is independent of temperature from 350 to 900 K but above 900 K, it decreases with T. Therefore the carrier concentration is constant up to 900 K. Since θ is positive over the entire range of temperature studied, the compound must be p-type, i.e. charge carriers are holes. The drift mobility $\mu_d^{(sp)}$ can be estimated from the conductivity data and thermoelectric power measurements [2], to be 4.7×10^{-4} cm^2 V sec. ($T = 400$ K and $m_h^* = 10$ m). The mean free path, L, calculated from the expression

$$L = \frac{3\mu}{4e}(2\pi mkT)^{\frac{1}{2}} \qquad (2)$$

is 0.0012 Å. The independency of θ of T, the lower value of activation energy (0.33 eV) and the much smaller value of mobility and mean free path (0.0012 Å, which is much smaller than the interatomic distance and an essential condition for the formation of a small polaron), suggest that small polaron conduction dominates for this compound in the temperature range 350 to 900 K. This agrees with the localized electron model of Goodenough [10] for 3d-transition metal compounds having very narrow d-bands. The small polaron can conduct in two ways [9]: either according to the band model or to the hopping model. At such a high temperature, the small polaron band model cannot be applied [9] and must be ruled out; thus the hopping conduction model must be considered. The variation of σ with temperature due to this mechanism is given by the following expression [11],

$$\sigma T^{1/2} = A(T)\exp\left(-\frac{W_H}{kT}\right), \qquad (3)$$

where W_H is the small polaron hopping energy and A is a constant. Fig. 3 shows the variation of $\log(\sigma T^{1/2})$ with $1/T$. The plot is a straight line in the temperature range 300 to 750 K and the hopping energy can be calculated to be 0.33 eV. Hence the conduction is consistent with thermally activated small polaron hopping and the activation

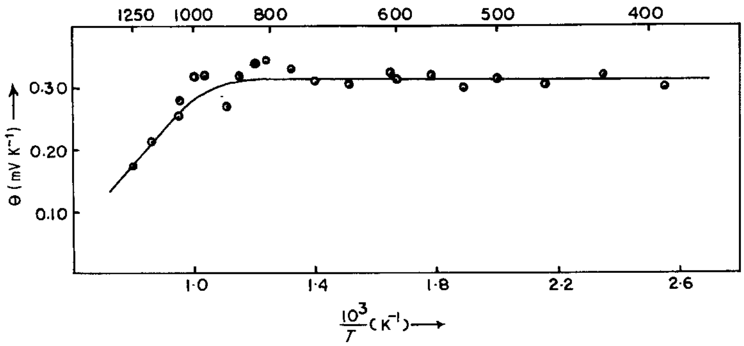

Figure 2 Variation of thermoelectric power (θ) as a function of temperature for Fe_2WO_6.

energy is then entirely due to the thermally increased mobility which increases according to the following relation [12],

$$\mu_d^{(sp)} \alpha \mu_0 T^{-3/2} \exp(-E_m/kT) \qquad (4)$$

where E_m is the activation energy for mobility.

The value of hole mobility μ_h as $7\,cm^2$ (V sec)$^{-1}$ has been calculated from the intercept (σ_0) of the $\log_{10}\sigma - 1/T$ plot, and the slope and intercept of the θ against $1/T$ graph [2]. Also the value of the mean free path (L) has been calculated to be 10 Å in the temperature range 900 to 1200 K. These values of μ_h and L suggest that the broad band as well as the narrow band conduction mechanism can be applied (since according to Bosman and Van Daal [9] in a broad band semiconductor $\mu \gtrsim 8\,cm^2$ (V sec)$^{-1}$ and the mean free path $L > a$ [lattice constant]). It seems quite reasonable since in Fe_2WO_6 wide 2p-bands associated with O^{2-} ions, as well as narrow 3d-bands associated with Fe^{3+} ions are present together. Kleiner [13] and Suchet [14] have suggested that the electronic properties of 3d-transition metal sesquioxides having 1, 3, 5, 7 and 9d electrons per cation, can be explained by a normal band model. Fe_2WO_6 has $3d^5$ electrons per cation, hence electrical properties can be explained by the normal band approach in the intrinsic region. The relevant bands for this compound are filled Fe^{3+}: $3d^5$, O^{2-}: 2p and empty Fe^{3+}: $3d^5$, W^{6+}: 5d along with 4s and 4p empty bands which are associated with Fe^{3+} ions. The octahedral crystalline field splits the 3d-band into a lower six-fold degenerate (t_{2g}) sub-band and an upper four-fold (e_g) sub-band [15]. Hence the valence band for this compound is O^{2-}: 2p together with Fe^{3+}: $3d[(t_{2g}\uparrow)^3\ (e_g\uparrow)^2]$ and the conduction bands are $Fe^{3+}[(t_{2g}\downarrow)^3\ (e_g\downarrow)^2]$, W^{6+}: 5d along with the 4s and 4p bands which are associated with Fe^{3+} ion. The estimated value of the band gap is 1.68 eV. It can be seen from Fig. 2 that θ decreases with temperature. This can be explained by an exponential increase and decrease in the number of electrons and holes, respectively. Moreover, it is also due to an exponential increase in the mobility of n-type charge carriers with temperature, thereby compensating rapidly for some of the p-type charge carriers and the resulting decrease in thermoelectric power.

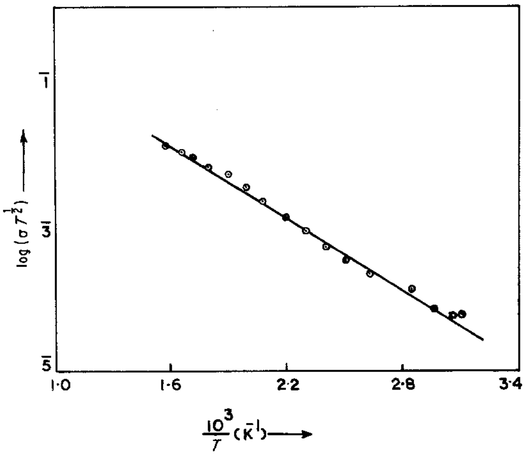

Figure 3 Variation of log ($\sigma T^{1/2}$) against $1/T$ for Fe_2WO_6.

The variation of the static dielectric constant ϵ' with temperature at 1 kHz is shown in Fig. 4 in which, two stages of increase in ϵ' can be observed: (I) a slow increase in ϵ' (300 to 600 K) and (II) a rather fast increase (700 to 1200 K). The increasing rate of ϵ' below 600 K is five times larger than the increasing rate of ϵ' below 600 K. The temperature has a complicated influence on ϵ'. The dielectric constant of such a solid consists of four contributions, namely, ionic, dipolar, electronic and space charge polarization. All four factors will contribute at the low frequency used here. Owing to the ionic nature of the compound

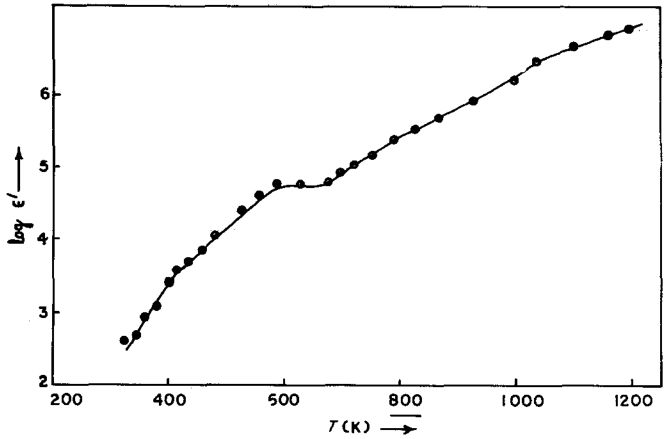

Figure 4 Variation of log ϵ' against T for Fe_2WO_6.

(ionicity 0.6 to 0.7) [16], the increase in ϵ' below 600 K can be attributed mainly to ionic polarization and to some extent space charge polarization. The concentration of impurities and defects also contribute to space charge polarization in such solids around room temperature and cannot be ignored. Above 600 K the fast increase in ϵ' is largely due to space charge polarization and to some extent due to creation and destruction of dipoles, which will take place at higher temperatures [17].

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