

Electrical properties of the $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$ system

O G PALANNA, A L SHASHI MOHAN and A B BISWAS

Solid State Laboratory, Department of Chemistry, Indian Institute of Technology, Bombay 400 076

MS received 29 April 1978

Abstract. The electrical transport properties of single phase compositions in the system $(\text{Fe}_2\text{O}_3)_x(\text{V}_2\text{O}_5)_{1-x}$, where $0 < x < 0.25$, have been investigated and discussed. The compounds have been found to exhibit thermally activated hopping conduction, where the charge carriers are electrons localised at V^{4+} ($3d^1$) centres. The Fe^{3+} ions appear to occupy interstitial as well as substitutional positions in the V_2O_5 lattice.

Keywords. Stoichiometry; interstitial state; sintering; quasi-amorphous; electro-neutrality.

1. Introduction

Pure and stoichiometric V_2O_5 is expected to be an electrical insulator. In general, however, the oxide exhibits n -type conduction due to non-stoichiometry (oxygen vacancies) and/or presence of impurities, and the charge transport occurs by means of thermally activated hopping of electrons on equivalent V^{5+} and V^{4+} sites (Ioffe and Patrino 1970; Perlstein 1977).

Impurities can be incorporated both substitutionally and interstitially into the V_2O_5 lattice. For example, Mo^{6+} and W^{6+} enter normal lattice positions whereas ions such as Li^+ , Na^+ , Cu^+ , and Ag^+ occupy interstitial sites. Ferric ions, on the other hand, have been shown to go into both the type of sites (Jansen and Sperlich 1973; Abdullaev 1969; Burzo and Stanescu 1976). Depending on the mode of incorporation of these foreign ions, the electrical properties of V_2O_5 may be expected to change differently.

The phase behaviour of the system $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$ was reported by Kurina and Ediseeva (1973) and Idem (1973), who found single phase solid solutions to be formed up to 10 mole % Fe_2O_3 . But recently, Burzo and Stanescu (1976) observed the domain of monophasic compositions to be restricted to about 4 mole % Fe_2O_3 only. Also, the latter authors estimated the ratio of Fe^{3+} (substitutional) to Fe^{3+} (interstitial) to be nearly 1 as against a value of 3/2 reported by Jansen and Sperlich (1973).

In a programme of investigations on mixed oxides containing V_2O_5 , we have also examined the system $(\text{Fe}_2\text{O}_3)_x(\text{V}_2\text{O}_5)_{1-x}$ where $0 \leq x \leq 0.25$. The data, which appear in essence to agree with main conclusions in the above literature, have revealed some new information as described in the following.

2. Experimental

2.1. Materials preparation

The compounds were synthesized by *solid state* reactions in air between AR quality Fe_2O_3 and V_2O_5 . The preparative techniques involved, viz. milling desired proportions of the two oxides in an agate mortar over distilled benzene, pre firing at 800°K for 24 hr, remixing, pelletizing under 10 tons psi, and finally sintering at 1000°K for about 3–4 days. Here it may be relevant to mention the main difference between our procedure and that of Burzo and Stanescu (1976). In the present case, the reactions were performed in the solid state whereas they *melted* the reactants at 1070K to obtain the products.

2.2. X-ray characterization

The materials, prepared as above, were characterized by x-ray powder diffraction using copper -K_α radiation ($\lambda = 1.5418\text{ \AA}$) in a Philips (PW 1010/1051) instrument. The identifications were made by comparing the observed d values and relative intensities (I/I_0) of the diffraction peaks with those reported in the ASTM powder data file.

2.3. DC electrical conductivity and Seebeck coefficient measurements

The d.c. electrical conductivity (σ) and Seebeck coefficient (α) were determined in the temperature range $300\text{--}1000\text{K}$ by the two probe and integral methods respectively.

The sample, in the form of sintered pellet of 15 mm diameter and 2–3 mm thickness, was held firmly, between two spring-loaded Pt disk electrodes. These were placed at the centre of a tubular furnace whose temperature could be maintained within $\pm 3^\circ$ of the desired value by means of a Phillips 'Plastomatic' controller. Two calibrated chromel-alumel thermocouples, placed in contact with the two ends of the pellet, were used to measure the sample temperature. Both heating and cooling cycles were taken. Thermal hysteresis effects, if any, were negligible.

The ohmic nature of the electrical contacts was confirmed by the linearity observed in the I-V plots. For α measurements, a temperature gradient of $\sim 10\text{K}$ was established between the two ends of the sample, by winding an auxiliary heater near one of the ends.

2.4. ESR and IR spectra

The electron spin resonance (esr) spectra were recorded in a Varian (V4502) x-band instrument operating at 8.82 GHz, with DPPH as the g marker.

The infrared (IR) absorption spectra were recorded in a Perkin Elmer (Model 237 B) spectrometer using Nujol mull.

3. Results

The x-ray powder data of the solid solutions were comparable with those of V_2O_5 , up to about 25 mole % Fe_2O_3 . That is, the compounds were monophasic in this

compositional range, and become biphasic, containing a V_2O_5 -type phase and the vanadate, FeVO_4 , beyond 25 mole % of Fe_2O_3 . A representative of these data is reproduced in table 1. The present results are thus in contrast with the report of Kurina and Ediseeva (1973) and Burzo and Stanescu (1976) who found solubility limits of 10 and 4 mole % Fe_2O_3 respectively. However, it is difficult to comment on the discrepancy at this stage as the preparative conditions and methods of characterization used by the above workers are not clearly described.

Table 1. X-ray data for the $(\text{Fe}_2\text{O}_3)_x(\text{V}_2\text{O}_5)_{1-x}$ systems ($x=0.25$).

$d \text{ \AA}$	I/I_0
5.75 (5.76)	20 (40)
4.38 (4.38)	100 (100)
4.08 (4.09)	45 (35)
3.40 (3.40)	30 (90)
2.88 (2.88)	40 (65)
2.76 (2.76)	10 (33)
2.60 (2.61)	20 (40)
2.20 (2.19)	20 (18)
2.15 (2.15)	10 (12)
1.92 (1.91)	10 (25)
1.89 (1.90)	10 (18)
1.86 (1.86)	5 (16)

Note: Values in parentheses refer to pure V_2O_5 .

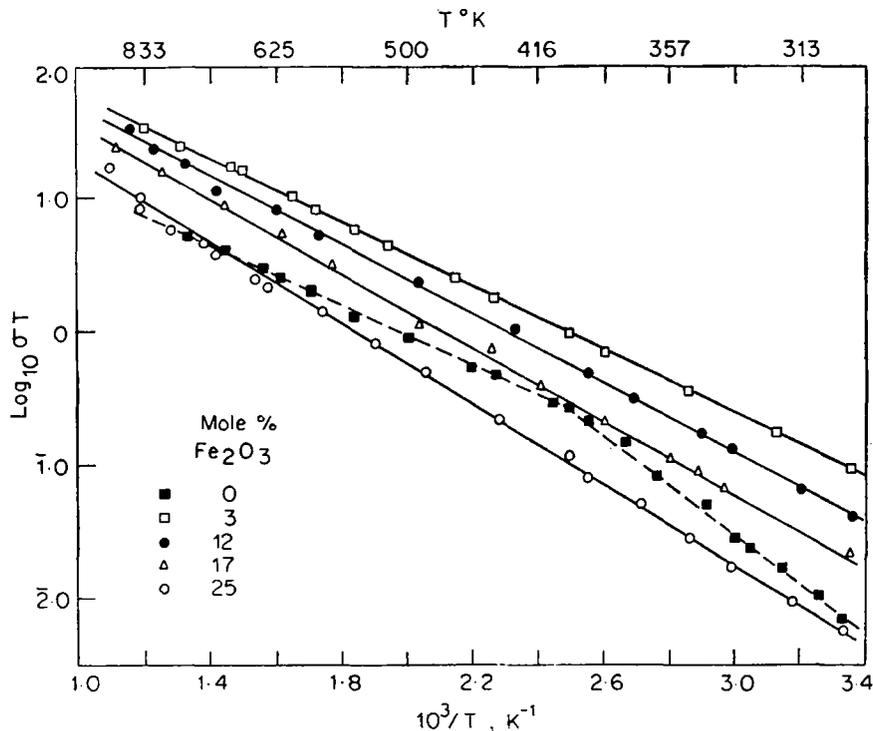


Figure 1. $\text{Log}(\sigma T)$ vs $1/T$ for $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$ system.

The lattice parameters of the single phase materials did not vary appreciably, despite the large addition of Fe_2O_3 . This may be due to (1) similarity of the ionic sizes of Fe^{3+} (0.69 Å), V^{4+} (0.73 Å) and V^{5+} (0.68 Å); (2) the fact that the two oxides have readily compatible crystal structures (orthorhombic V_2O_5 and rhombohedral Fe_2O_3) or (3) the disordered (or quasi-amorphous?) nature of the V_2O_5 lattice containing the foreign ions.

The temperature dependence of σ (figure 1) may be expressed as:

$$\sigma = (\sigma_0/T) \cdot \exp(-\Delta G^*/kT)$$

where σ_0 is a constant and ΔG^* the free energy of activation for electrical conduction. The corresponding plot of $\log(\sigma T)$ vs $1/T$ is linear with the value of slope ($=\Delta G^*$)

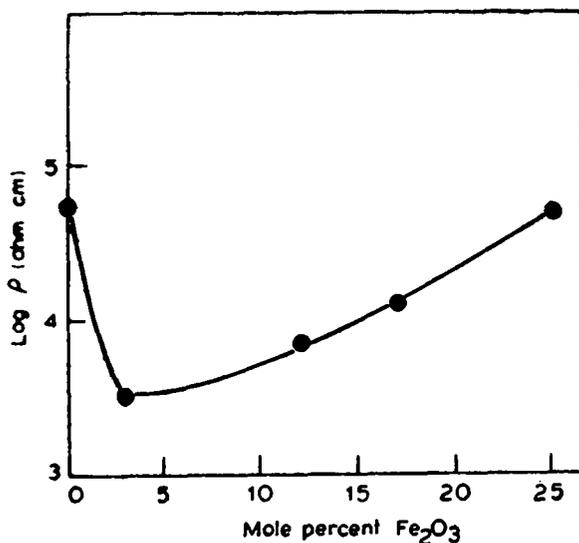


Figure 2. $\text{Log } \rho$ (300K) against mole % Fe_2O_3 .

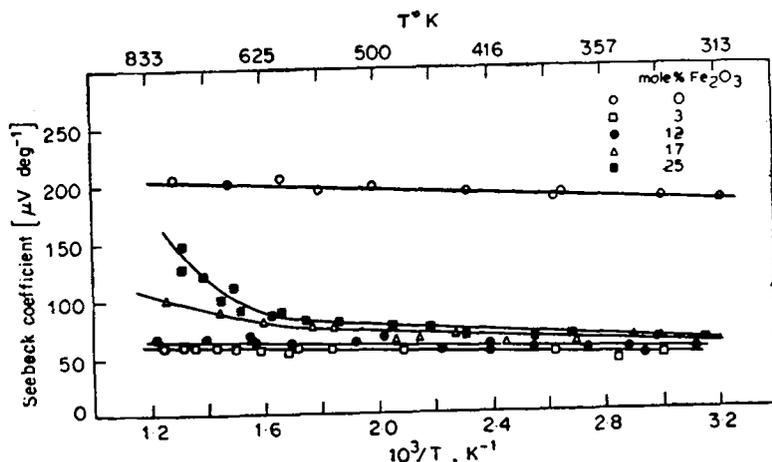


Figure 3. α vs $1/T$ for Fe_2O_3 - V_2O_5 system.

being nearly the same (~ 0.20 eV) in all cases. The compositional variation of resistivity ρ ($=1/\sigma$) is depicted in figure 2, from an inspection of which it may be seen that ρ decreases upto ~ 3 mole % Fe_2O_3 and later increases with additions of Fe_2O_3 .

α is nearly temperature independent (figure 3) and has a negative sign indicating the preponderance of electrons as majority charge carriers. The change of α with Fe_2O_3 content is small but shows the same trend as for ρ .

4. Discussion

4.1. Mechanism of electrical conduction

The electrical data reported above are reminiscent of a hopping type of conduction as in the case of pure V_2O_5 . The current carriers appear to be electrons localised at V^{4+} ($3d^1$) centers. The presence of V^{4+} is evidenced by a signal at $g=1.96$ in the ESR spectra (not shown here.) Conduction, therefore, occurs due to thermally activated jumps of these electrons on equivalent V^{4+} and V^{5+} sites. The activation energy of ~ 0.20 eV observed above comes from mobility μ of the electrons, which is independent of impurity concentration. The compositional dependence of σ (figure 2) must be due to change in n , the density of charge carriers, since $\sigma = ne\mu$.

Before attempting to explain the impurity effects, it must be indicated here that, in general, the parent oxide V_2O_5 is oxygen deficient, with doubly ionized oxygen vacancies as the predominant defects (Kofstad 1971). The trivalent iron ions may be incorporated in the V_2O_5 lattice either interstitially or substitutionally or both ways. The electroneutrality conditions corresponding to these three conditions may be written as follows:

$$(i) \quad 2(Fe_v'') + (V_v') = 2(V_o'') \dots \text{only substitution}$$

$$(ii) \quad (V_v') = 2(V_o'') + 3(Fe_i''') \dots \text{only interstitial}$$

$$(iii) \quad 2(Fe_v'') + (V_v') = 2(V_o'') + (Fe_i''')$$

where V_o'' = doubly ionized oxygen vacancies; V_v' = V^{4+} site ($V^{5+} + e'$); Fe_v'' = Fe^{3+} at V^{5+} site (substitution) two effective negative charges at the site; Fe_i''' = interstitial Fe^{3+} i.e., three effective positive charges at the site.

(Note: All defect notation are according to Kröger-Vink, solid state physics. According to equations (i), (ii) and (iii) it may be said σ increases with interstitial Fe^{3+} content while it decreases with substitutional Fe^{3+} . When both the type of dissolution of Fe_2O_3 in V_2O_5 occurs, the outcome depends on the relative concentrations of Fe_v'' and Fe_i''').

In view of the above, it may be said that up to 3 mole % Fe_2O_3 , the Fe^{3+} ions enter into interstitial positions. The initial slope of figure 2 seems to lend support to this statement. On increasing the Fe_2O_3 content, however, some of the Fe^{3+} ions start occupying normal lattice sites (forming Fe_v''), thus decreasing n . It would be interesting to assess the fraction of Fe ions on the two types of site. From the present data, it is rather difficult to get at the value of the $(Fe_v'')/(Fe_i''')$ ratio. But a qualitative analysis of figure 2 shows that among the materials considered in this study, V_2O_5

has the highest resistivity. In other words, even at 25 mole % Fe_2O_3 some extra charge carriers have been 'pumped' into the lattice, in addition to those present due to initial oxygen deficiency of V_2O_5 . Therefore, $[\text{Fe}_v^{2+}]/[\text{Fe}_i^{3+}] < 3/2$. The correct value of this ratio may be estimated by determining the Po_2 dependence of σ and/or by Mössbauer spectroscopy.

4.2. Are these materials quasi-amorphous?

One can visualize that for complete charge compensation $[\text{Fe}_v^{2+}]/[\text{Fe}_i^{3+}] = 3/2$; but Burzo and Stanescu (1976) observed a ratio of about one. This discrepancy was accounted by the interpretation that the compounds were 'quasi amorphous', in which case we need not introduce compensating charges. In fact, a similar situation prevails in the $\text{WO}_3\text{--V}_2\text{O}_5$ system also, wherein Burzo *et al* (1976) found that $[\text{W}^{6+}]/[\text{V}^{4+}] < 1$.

Such a quasi amorphous nature of these polycrystalline samples containing appreciable amounts of impurities is not at all surprising! Earlier, Haemers *et al* (1973) measured σ (both ac and dc) of V_2O_5 single crystals at 90–350 K. It was observed that i) $\sigma \sim T^{-1/4}$ at $T < 140$ K and ii) $\sigma_{ac}(\omega)$ where $\omega = \text{ac frequency}$, which are characteristic of variable range hopping suggested by Mott (1967) for noncrystalline materials. These observations lead to the plausible conclusion that the samples in the $\text{Fe}_2\text{O}_3\text{--V}_2\text{O}_5$ system could be quasi amorphous or highly disordered. Our IR absorption data may be invoked to support this interpretation.

The IR spectra (figure 4) consist of two bands at 1020 cm^{-1} and 825 cm^{-1} similar to that of V_2O_5 (Frederickson and Hausen 1962; Kera and Hirota 1969; Febbri and Baraldi 1972). Accordingly, these refer to stretching vibrations of $V=O$ group

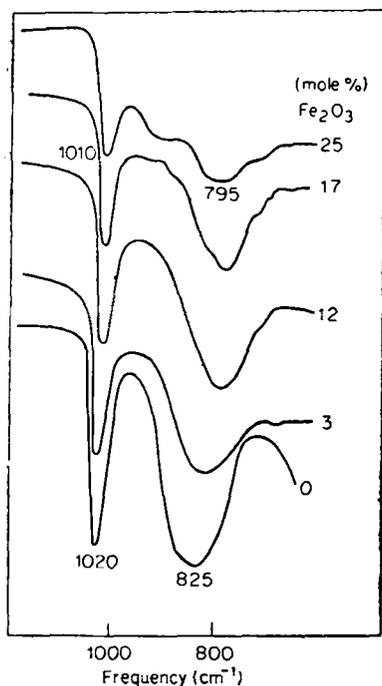


Figure 4. IR spectra for $\text{Fe}_2\text{O}_3\text{--V}_2\text{O}_5$.

perpendicular to and V—O—V group in (010) net plane, respectively. Addition of Fe_2O_3 appears to reduce the relative intensity of the 1020 cm^{-1} band due to decrease in the number of V=O oscillators. More important, however, is the high distortion and broadening, bordering on the appearance of small satellite peaks, of the 825 cm^{-1} band. Similar phenomena have been reported by Zaitsev *et al* (1966) in the case of $MoO_3-V_2O_5$, $Co_2O_3-V_2O_5$ and $P_2O_5-V_2O_5$ systems. These authors attributed this to the large degree of disorder brought about by the incorporation of the foreign ions into the V_2O_5 lattice. Thus it may not be incorrect to conclude that our IR data indicate a large degree of disorder in the $Fe_2O_3-V_2O_5$ lattice. Further confirmation may be obtained by low temperature ac and dc conductivity measurements. In that case, if our interpretations are correct, we may observe the same kind of 'Anderson localisation'. We are contemplating on such experiments.

Acknowledgements

The authors should like to thank Dr M D Sastry of Radiochemistry Division, BARC, for help in ESR experiments. ALS is indebted to CSIR (New Delhi) for financial support.

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