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Studies on the Electrical Properties of Tungsten Doped V_2O_5

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The electrical properties of the monophasic $W_xV_2O_5$ samples for $O < x \leqslant 0\cdot03$ (iso-structural with α-V_2O_5) have been investigated. The conduction mechanism of these non-stoichiometric semiconductors involves hopping of electrons through equivalent vanadium lattice sites. It is found from experimental data that W^{6+} ions preferentially occupy interstitial positions influencing the electrical properties of the host system.

PURE V_2O_5 is an electrical insulator. However, non-stoichiometric semiconductors of vanadium pentoxide containing a non-integral number of *d*-electrons per transition element lattice site are known.

Dissolved impurities can be incorporated into the lattice of V_2O_5 either interstitially or substitutionally or by both ways. Metal (M^{n+}) ions occupy interstitial sites similar to that in the case of the corresponding vanadium bronzes, $M_xV_2O_5$ (ref. 1) for a limited range of x. However, occupation of lattice (vanadium) sites by W^{6+} or Mo^{6+} ions is reported in mixed oxide bronzes of vanadium[2,3], a few doped V_2O_5 lattices[4,5] and other tungsten-vanadium oxide compounds[6-8].

The present investigation aims at examining the influence of the added impurity ions (W^{6+}) upto $x \leqslant 0\cdot03$, on the solid state properties of the host V_2O_5 lattice under the conditions of their synthesis.

Materials and Methods

Preparation and characterization of the samples — Different samples of $W_xV_2O_5$ were obtained by the reactions carried out in the molten state at 1120 K for 48 hr between high purity tungsten metal powder and V_2O_5 taken in the desired proportions ($0 < x \leqslant 0\cdot03$, where $x = W/V_2O_5$). The molten mass of the reaction was cooled to room temperature at a rate of 10°/min, pressed into pellets of desired thickness and sintered at 900 K for a few hours to achieve the maximum packing density.

The compounds were characterized by X-ray powder diffraction technique using Cu K_α radiation ($\lambda = 1\cdot517$ Å) and nickel filter.

Electrical conductivity measurements — The D.C. electrical conductivity (σ) of the polycrystalline samples was measured between 300 and 875 K through four probe technique. The samples were in the form of sintered compacts ($\approx 85\%$ packing density) of 18 mm diameter and 2 mm thickness.

The Seebeck coefficient (α) was determined between 300 and 875 K by integral method maintaining a temperature gradient of approximately 10 K between the two ends of the sample.

Results and Discussion

The X-ray analysis shows that the gross V_2O_5 structure is maintained for $x \leqslant 0\cdot03$, called the α-phase[9,10]; the W^{6+} ions are incorporated at well-defined sites of the lattice. Due to similar ionic sizes of W^{6+} (0·54 Å) and V^{5+} (0·58 Å), substitution or the interstitial occupation does not change the lattice parameter to such an extent as to distort the V_2O_5 structure.

The data on the electrical conductivities (σ) of the samples are presented in Fig. 1. The $W_xV_2O_5$ compounds, isostructural with α-V_2O_5, are non-stoichiometric semiconductors. The electrical conductance data presented are characteristic of hopping mechanism of conduction. The sign of the Seebeck coefficient (α) is negative and temperature-independent indicating a constant number of charge carriers (electrons). The electron transfer in such compounds takes place by hopping of electrons on equivalent vanadium sites of the lattice. Figs. 1 and 2 show that the electrical conductivities (σ) of the samples increase with increase in x at a given temperature for $x \leqslant 0\cdot03$, while the value of Seebeck coefficient (α) decreases. However, it is observed that the number of charge carriers do not increase with increase in temperature as to contribute to electrical conductivity. In such cases, the electrical conductivity could be ascribed to thermally activated mobility of the charge carriers. The temperature-dependence of σ then follows the equation

$$\log_{10} \sigma T = \log_{10} \sigma_0 T - \Delta G^*/2\cdot3KT \qquad \ldots(1)$$

where ΔG^* is the free energy of activation for conduction (Table 1). This is further evidenced

TABLE 1 — ELECTRICAL CONDUCTANCE DATA FOR THE SAMPLES

$x = W/V_2O_5$	Seebeck coefficient μV° (*n*-type)	Electrical conductivity, σ ($ohm^{-1}cm^{-1}$)	Activation energy (eV)
0	−200	$1\cdot5 \times 10^{-5}$	0·20
0·005	−50	$2\cdot86 \times 10^{-2}$	0·24
0·01	−48	$3\cdot13 \times 10^{-2}$	0·24
0·02	−40	$3\cdot63 \times 10^{-2}$	0·23
0·03	−30	$4\cdot17 \times 10^{-2}$	0·22

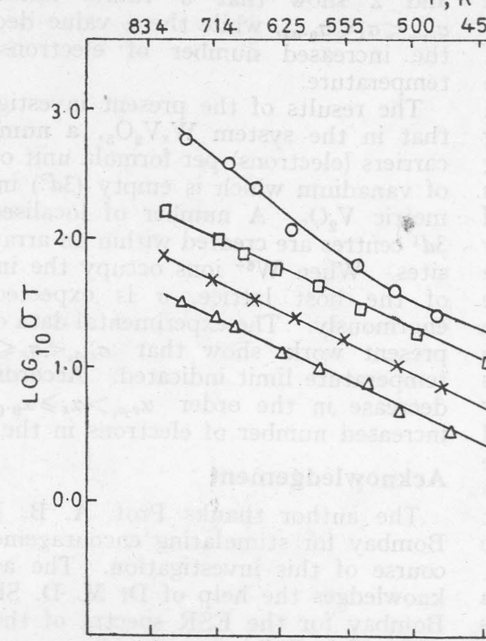

Fig. 1 — Plots of $\log_{10} \sigma T$ versus $10^3/T$ for $W_xV_2O_5$ samples [Curve 1, $x=0{\cdot}005$; curve 2, $x=0{\cdot}01$; curve 3, $x=0{\cdot}02$; curve 4, $x=0{\cdot}03$]

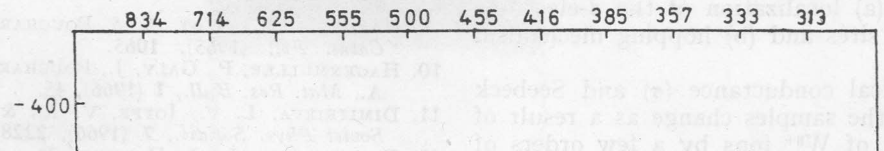

Fig. 2 — Plots of Seebeck coefficient (α) versus $10^3/T$ for $W_xV_2O_5$ samples [Curve 1, $x=0{\cdot}005$; curve 2, $x=0{\cdot}01$; curve 3, $x=0{\cdot}02$; curve 4, $x=0{\cdot}03$]

by the linearity of $\log_{10} \sigma T$ versus $1/T$ plots, and temperature-independence of α (Figs. 1 and 2).

Investigation of V_2O_5, weakly doped with WO_3[4,5], and also of a few mixed oxide bronzes of the type $M_xV_{2-y}W_yO_5$[2,3] for $x>0{\cdot}33$, indicated the occupation of lattice sites by the W^{6+} ions, in each case causing localization of the $3d^1$ electron at one neighbouring vanadium site. This substitution of tungsten ions for vanadium would result in the formation of $W^{6+}{-}O{-}V^{4+}$ pairs within the vanadium array of the host lattice. In this case the excess negative charge of the V^{4+} is bound to the excess positive charge of the W^{6+} and hence does not participate in the current transfer[11]. In addition, it can be shown that with the increased number of W^{6+} ions at the vanadium lattice sites, the $V^{4+}{-}O{-}V^{5+}$ distance is enhanced for hopping of electron and thus, the conduction takes place through the lattice with higher activation and σ would vary as $\sigma_{V_2O_5} > \sigma_x \geqslant \sigma_{0{\cdot}03}$. This behaviour, however, is not in agreement with the results observed in the present work.

On the contrary, the present investigation of a weakly doped V_2O_5 sample with W^{6+} ions indicates that for $0<x\leqslant 0{\cdot}03$, the incorporated tungsten ions preferentially occupy interstitial/tunnel sites of the host lattice giving rise to an α-phase. This is supported by the following experimental data:

(i) The XRD data indicates that the samples are monophasic and isostructural with V_2O_5 lattice with no appreciable change in the lattice parameters of the unit cell.

(ii) A characteristic IR bands of V_2O_5[12] is observed which shows no change in the local symmetry and nature of the bonds in the lattice.

(iii) An ESR signal at $g = 1{\cdot}96$ is observed with a narrow line width. The narrowing line width at 300 K indicates (a) localization of the *d*-electrons at the vanadium sites and (b) hopping mechanism of *d*-electrons[13].

(iv) The electrical conductance (σ) and Seebeck coefficient (α) of the samples change as a result of the incorporation of W^{6+} ions by a few orders of magnitude depending on the mode of addition and the amount of impurity (W^{6+}) present. Figs. 1 and 2 show that σ values follow the order: $\sigma_{V_2O_5} < \sigma_x \leqslant \sigma_{0{\cdot}03}$, while the α value decreases due to the increased number of electrons at a given temperature.

The results of the present investigation indicate that in the system $W_xV_2O_5$, a number of charge carriers (electrons) per formula unit occupy *d*-states of vanadium which is empty ($3d^\circ$) in the stoichiometric V_2O_5. A number of localised, yet mobile $3d^1$ centres are created within an array of vanadium sites. When W^{6+} ions occupy the interstitial sites of the host lattice, σ is expected to increase enormously. The experimental data obtained in the present work show that $\sigma_{V_2O_5} < \sigma_x \leqslant \sigma_{0{\cdot}03}$ for the temperature limit indicated. Accordingly, α values decrease in the order $\alpha_{V_2O_5} > \alpha_x \geqslant \alpha_{0{\cdot}03}$ due to an increased number of electrons in the V_2O_5 lattice.

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