

5. Lippincott, E. R., Nagarajan, G. and Stutman, J. M., *J. Phys. Chem.*, 1966, 70, 78.
6. Long, T. V. and Plane, R. A., *J. Chem. Phys.*, 1965, 43, 457.
7. Terzis, A. and Spiro, T. G., *Inorg. Chem.*, 1971, 10, 643.
8. Billiner, P. A., Maroni, V. A. and Spiro, T. G., *Ibid.*, 1970, 9, 1887.
9. —, Quicksall, C. O. and Spiro, T. G., *Ibid.*, 1971, 10, 13.
10. Nagarajan, G., *Acta Phys. Pol.*, 1973, 43A, 301.
11. Verma, U. P. and Pandey, A. N., *Z. Naturforsch.*, 1978, 33A, 495.
12. Rao, C. N. R., George, M. V., Mahanty, J. and Narasimhan, P. T., *A Hand-Book of Chemistry and Physics* (East West Press Pvt. Ltd. New Delhi), 1967.
13. Rendell, C. H., Ford, T. A., Mavi's Redshaw, and orville-Thomas, W. J., *J. Mol. Struct.*, 1975, 24, 187.

STUDIES ON THE ELECTRICAL PROPERTIES OF MAGNESIUM METAVANADATE

MAGNESIUM METAVANADATE is one of the members of a series of compounds, MV_2O_6 where $M = Mg, Co, Zn, Ca, Hg$, etc., having brannerite¹ ($ThTi_2O_6$) crystal structure.

The reports²⁻⁶ on the $MgO-V_2O_6$ system indicated a stable phase with composition MgV_2O_6 and the crystal structure studies⁷ of the phase showed space group $C2/m$ of monoclinic symmetry. A recent investigation⁸ of X-ray diffraction and D.T.A. of MgV_2O_6 synthesised under the conditions mentioned elsewhere confirmed a structural transition at 833 K, both polymorphs having brannerite crystal structure.

Except these phase studies and the studies on the crystal structure no other information is available concerning the solid state properties of MgV_2O_6 which has initiated this investigation.

Experimental

A new $M_3V_2O_6$ phase is synthesised by solid state reaction as described elsewhere and matched with

earlier reports^{3,4}. The DC electrical conductivity (σ) of the polycrystalline magnesium metavanadate phase was measured between 300–1000 K by two probe technique. The sample was in the form of a sintered compact (above 85% packing density) of 18 mm diameter and thickness of 2 mm. The Seebeck coefficient (a) of the compound was measured between 300–1000 K by integral method. The ESR spectrum was recorded in a varian x-band instrument operating at 8.82 GHz with DPPH as marker.

Results and Discussion

Stoichiometric MgV_2O_6 is an electrical insulator. However XRD σ and a results of the present work showed that the compound synthesised retained the gross monophasic MV_2O_6 (M is a divalent cation) crystal structure¹ but having nonstoichiometric composition and exhibiting n -type semiconduction. The transport behaviour of magnesium metavanadate is reminiscent of hopping mechanism of conduction. The temperature dependence of σ follows the relationship $\log_{10} \sigma T = \log_{10} \sigma_0 - \Delta G_0^*/2.303 KT$ where ΔG_0^* is the free energy of activation for conduction. This is evidenced by the linearity of $\log_{10} \sigma T$ versus $1/T$ plot (not shown) and the temperature independence of Seebeck coefficient, a . The sign of a is negative and temperature independent, indicating constant number of charge carriers. This is further confirmed by ESR measurement of the phase at 300 K which showed a signal at $g = 1.96$ with a narrow line width. The narrow line width at 300 K pointed out (a) localisation of the d -electron (V^{4+}) at the lattice sites and (b) hopping mechanism of the d -electron between the equivalent vanadium sites.

In magnesium metavanadate, anion vacancies occur leaving behind two electrons per $\frac{1}{2}$ molecule of oxygen leaving the lattice; in other words, the metavanadate can be represented as $Mg^{2+} V_{2-2x}^{5+} V_{2x}^{4+} O_{6-x}$ for small value of x under conditions of its synthesis indicating the reduction of a small amount of V^{5+} to V^{4+} . Thus it becomes established that MgV_2O_6 exhibits n -type conduction due to electron hopping on equivalent $V^{4+} - V^{5+}$ sites in the lattice.

TABLE I

Electrical transport data for MgV_2O_6

Compound	Temperature	Sign of Seebeck coefficient a	Electrical conductance σ , $\text{Ohm}^{-1} \text{Cm}^{-1}$	Activation energy ΔG^* (eV)
α - MgV_2O_6	300–830 K	n -type	10^{-6} to 10^{-3}	0.25
β - MgV_2O_6	833–1000 K	n -type	10^{-4} to 10^{-3}	0.50

The electrical transport behaviour of MgV_2O_6 showed anomaly at the phase transition temperature as one would expect, with no change in the carrier concentration and or transport mechanism. For reasons given, in isotypic $CdV_2O_6^{10}$, it is evident that the vanadium-vanadium distance increase during structural transition. This could be one of the plausible explanations for the anomaly observed at 833 K for MgV_2O_6 in which case the electron hopping on equivalent vanadium sites need higher activation energy (Table I).

The author expresses his sense of gratitude to late Dr. A. B. Biswas, IIT, Bombay and to Dr. C. N. R. Rao, IISc., Bangalore, for their encouragement. The financial support from UGC, New Delhi, is gratefully acknowledged.

Solid State Laboratory,
Department of Chemistry,
St. Philomena College,
Puttur 574 215,
September 24, 1979.

O. G. PALANNA,

1. Wadseley, A. D. and Ruh, R., *Act. Cryst.*, 1966, 21, 974.
2. Pollard, A. J., *NASA. Acess No.* 65/17008, 6038, 1969.
3. Matveevicheva, V. A., Ezhkova, Z. I., Zaitsev, B. E. and Lyubarskii, A. G., *Russ. J. Phy. Chem.*, 1969, 43, 143.
4. Galy, J. and Pouchard, M., *Bull. Soc. Chim. Fr.*, 1967, 1, 261.
5. Eke, M. and Brett, N. H., *Trans. Brit. Ceram. Soc.*, 1973, 72, 195.
6. Clark, G. M. and Pick, A. N., *J. Therm. Anal.*, 1975, 7, 289.
7. Calvo, C. and Ng, H. N., *Can. J. Chem.*, 1972, 50, 3619.
8. Palanna, O. G., *Proc. Indian Acad. Sci.*, 1979, 88A, 19.
9. Sperlich, G., *J. Solid. St. Chem.*, 1975, 12, 360.
10. Bouloux, J. C., Peruz, G. and Galy, J., *Bull. Soc. Fr. Mineral. Cryst.*, 1972, 95, 130.

RAPID SEPARATION OF SOME ALKALOIDS OF PHARMACOLOGICAL AND TOXICOLOGICAL INTEREST ON HYDROUS ZIRCONIUM OXIDE PAPER

VERY few reports¹⁻³ are available on the use of papers impregnated with inorganic ion exchangers for the separation of alkaloids. Several cation separations of analytical and radiochemical interest were reported from this laboratory with hydrous zirconium oxide paper⁴. In the present communication, the chromatographic behaviour of opium and strychnos alkaloids along with atropine and quinine has been studied on

hydrous zirconium oxide papers using aqueous solvent systems only. On the basis of the R_f values, separations of the four components have been achieved.

EXPERIMENTAL

Preparation of hydrous zirconium oxide paper :

Whatman No. 1 paper strips (14 × 3 cm) were first dipped in 0.1 M zirconium oxychloride solution, blotted to remove excess solution and then air dried at $25^\circ \pm 3^\circ$ C. The strips were then dipped in 3 M ammonia solution in a glass trough for 30 seconds. The paper was dried, washed with distilled water and air dried at room temperature for twelve hours.

Development of chromatograms and separations :

Samples of alkaloids (10–20 μ g) were spotted on the papers by micropipettes. These papers were then run in closed chambers (25 × 12 × 25 cm) conditioned for 10–15 minutes with solvent and the solvent was allowed to ascend to develop the chromatograms. The papers were dried with an air blower and alkaloids visualized by spraying with Dragendorff's reagent⁵.

RESULTS AND DISCUSSION

The hR_f values of 9 alkaloids in 10^{-3} N hydrochloric acid and sodium hydroxide are given in Table I. As apparent from the table, morphine and narcotine are selectively retained on hydrous zirconium oxide paper in 10^{-3} N NaOH medium, thus facilitating their separation from other alkaloids. In addition, numerous separation of mixtures containing upto four alkaloids of pharmaceutical and toxicological importance have been achieved on these papers. Some representative quaternary separations of important alkaloids are presented in Table II. All the separations were accomplished within 15–20 minutes.

TABLE I
($R_f \times 100$) values of alkaloids on hydrous zirconium oxide paper

Alkaloid	hR_f value	
	HCl, 10^{-3} N	NaOH, 10^{-3} N
Codeine	72	94
Morphine	85	00
Thebaine	95	55
Narcotine	55	00
Papaverine	84	57
Strychnine	78	78
Brucine	90	78
Atropine	98	92
Quinine	62	84