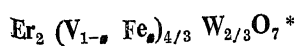


## Solid state studies on rare earth mixed oxide pyrochlores



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**Abstract.** Complete series of solid solutions exist in the mixed oxide pyrochlore system,  $\text{Er}_2(\text{V}_{1-x}\text{Fe}_x)_{4/3}\text{W}_{2/3}\text{O}_7$ , with the crystal structure changing from cubic to rhombohedral at  $x = 0.25$ . The compounds are semiconductors at 300 K exhibiting *p*- or *n*-type behaviour depending on the value of  $x$ . The observed resistivity and Seebeck coefficient data as a function of temperature have been interpreted in terms of a hopping mechanism.

**Keywords.** Mixed pyrochlores; electrical properties; mechanism of conduction.

### 1. Introduction

Oxide pyrochlores of the general formula  $\text{Ln}_2\text{B}_2\text{O}_7$ , where Ln = rare earth or Y, B = transition metal, form an important class of compounds exhibiting a wide variety of interesting physical properties. These have been extensively studied in the literature (Sleight 1968; Rao and Subba Rao 1970). However, rare earth pyrochlores with mixed cations at the B site (B, B') are relatively unknown.  $\text{Ln}_2(\text{BSb})\text{O}_7$ , B = Fe, Cr and Ga (Knop *et al* 1968; Bongers and Van Meurs 1967) and  $\text{Ln}_2(\text{B}_{4/3}\text{W}_{2/3})\text{O}_7$ , B =  $\text{Fe}^{3+}$  (Basile *et al* 1977),  $\text{V}^{3+}$  (Subramanian *et al* 1979) are some of the known series of compounds. This is because in addition to the charge neutrality, ionic radius ratio of the A and B (B') ions is also an important criterion for the occurrence of pyrochlore structure.  $\text{Ln}_2(\text{V}_{4/3}\text{W}_{2/3})\text{O}_7$ , Ln = Gd-Lu, Y, compounds possess the cubic pyrochlore structure and are semiconductors whereas the  $\text{Ln}_2(\text{Fe}_{4/3}\text{W}_{2/3})\text{O}_7$  series are insulators and exhibit rhombohedral structure (Subramanian *et al* 1979). As part of an extensive programme of work on rare earth pyrochlores undertaken in our laboratory, we present some results on mixed pyrochlores of the type,  $\text{Er}_2(\text{V}_{1-x}\text{Fe}_x)_{4/3}\text{W}_{2/3}\text{O}_7$  ( $0 \leq x \leq 1.0$ ). Synthesis, characterisation and electrical properties of the above compounds are described and discussed.

\* Forms part of the Ph.D. Thesis to be submitted by MAS to IIT, Madras.

## 2. Experimental

High purity starting materials were employed ( $\text{Ln}_2\text{O}_3$ , 99.99%, Indian Rare Earths Co. or Ventron, USA;  $\text{WO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$ , J and M Specpure).  $\text{V}_2\text{O}_3$  was prepared by  $\text{H}_2$  reduction of  $\text{V}_2\text{O}_5$  at 850–900° C for 6 hr. The constituent oxides in stoichiometric proportions (e.g.,  $\text{Er}_2\text{O}_3 + 2/3 ((1-x)\text{V}_2\text{O}_3 + x\text{Fe}_2\text{O}_3) + 2/3 \text{WO}_3$ ) were thoroughly ground in an agate mortar, pelletised and sealed in evacuated ( $> 10^{-4}$  torr) quartz tubes. These were then heated to 1,200–1,300° C for 24–36 hr and slowly cooled or quenched. X-ray powder diffraction data were obtained with  $\text{CuK}_\alpha$  radiation (Ni filter) using a Philips unit. Accurate lattice parameters were obtained by the least square fitting procedures using computer programs. Powder densities were determined at 25° C using nitrobenzene as the immersion fluid and a pycnometer.  $\text{V}^{3+}$  and  $\text{Fe}^{3+}$  content in the sample was estimated by the standard chemical methods of analysis. Electrical resistivity ( $\rho$ , by 2-probe method) and Seebeck coefficient ( $\alpha$ , by the static method) measurements were made in  $\text{N}_2$  atmosphere (in air for  $x = 1.0$ ; 300–600; –1000 K) on vacuum-sintered polycrystalline pellets. Conducting silver paint was used to make electrical contacts. Details of the equipment and measurement techniques have been described elsewhere (Subramanian *et al* 1979, 1980).

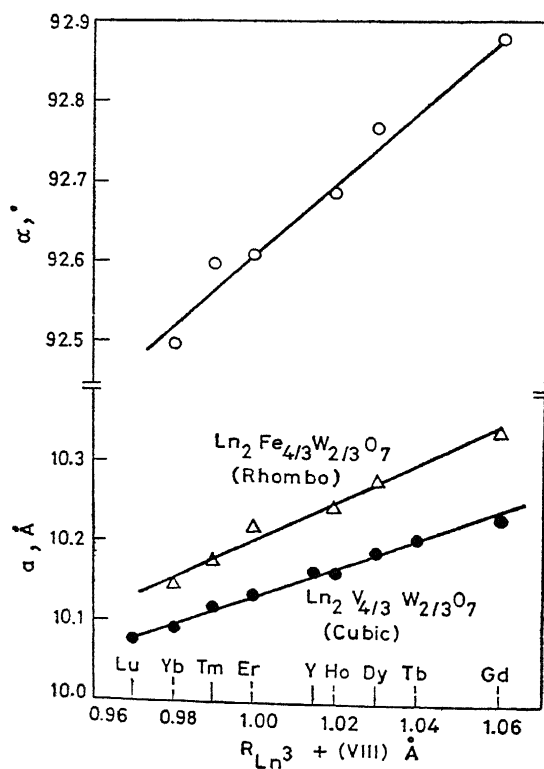


Figure 1. Unit cell size vs ionic radii of  $\text{Ln}^{3+}$  for mixed pyrochlores.

### 3. Results and discussion

#### 3.1. Structure and stability

Single phase materials,  $\text{Er}_2(\text{V}_{1-x}\text{Fe}_x)_{4/3}\text{W}_{2/3}\text{O}_7$ , have been obtained for various  $x$  under the preparative conditions employed. We have also synthesised  $\text{Ln}_2\text{Fe}_{4/3}\text{W}_{2/3}\text{O}_7$  ( $\text{Ln} = \text{Gd}-\text{Yb}, \text{Y}$ ) and find that the rhombohedral lattice parameters are in good agreement with those of Basile *et al* (1977). The data, along with those for the V-containing (cubic) pyrochlores (Subramanian *et al* 1979), are given in figure 1. It is to be noted that compounds with  $\text{Ln} = \text{La}-\text{Eu}$  do not form for  $\text{B}' = \text{Fe}$  and V. Further, there is a linear relationship between the  $a$  lattice parameter and the ionic radius of  $\text{Ln}^{3+}$  ion (8-fold coordination, Shannon and Prewitt 1969, 1970) as has been noted in other  $\text{Ln}_2\text{B}_2\text{O}_7$  pyrochlores (Sleight 1968). However, the reason for the rhombohedral distortion from cubic structure (space group  $\text{Fd}\bar{3}\text{m}$ ) when  $\text{B}'$  is changed from  $\text{V}^{3+}$  to  $\text{Fe}^{3+}$  (both having nearly identical ionic radius for 6-fold coordination, (Shannon and Prewitt 1969, 1970) is not known. Probably, factors due to the changes in electronic configuration ( $d^3$  vs  $d^5$ ) and local site symmetry play a significant role. In the solid solutions,  $\text{Er}_2(\text{V}_{1-x}\text{Fe}_x)_{4/3}\text{W}_{2/3}\text{O}_7$ , a change from cubic-to-rhombohedral structure occurs for  $x = 0.25$ . However, slight but systematic changes in  $a$  parameter occur for  $0 \leq x \leq 0.25$  and for  $0.25 \leq x \leq 1.0$ . The relevant data are given in table 1.

$\text{Ln}-\text{Fe}$ -containing compounds are brown whereas ( $\text{Ln}-\text{V}$ - and  $\text{Ln}-\text{V}-\text{Fe}$  ( $x > 0.0$ ) oxide phases are black or brownish-black in color and are stable towards exposure to air and moisture.  $\text{V}^{3+}$ -containing compounds decompose (oxidation of  $\text{V}^{3+}$  to  $\text{V}^{5+}$ ) on heating in air to  $T > 600^\circ\text{C}$ . Density and wet chemical analysis are in accordance with the expected pyrochlore structure and composition of the phases obtained.

Table 1. Crystallographic and electrical data on  $\text{Er}_2(\text{V}_{1-x}\text{Fe}_x)_{4/3}\text{W}_{2/3}\text{O}_7$  pyrochlores

$x$ in $\text{Er}_2(\text{V}_{1-x}\text{Fe}_x)_{4/3}$ $\text{W}_{2/3}\text{O}_7$	Rhombohedral parameters		$\rho_{500\text{K}}$ $\Omega\text{cm}$	$E_g$ , eV	$\alpha_{300\text{K}}$ $\mu\text{V}/^\circ\text{K}$
	$a_R$ , Å	$a_R^\circ$			
0	10.137	90	75	0.24	
0.1	10.140	90	30	0.22	+ 115
0.2	10.140	90	33	0.22	+ 70
0.3	10.201	92.58	64	0.27	+ 73
0.4	10.205	92.54	88	0.32	..
0.5	10.208	92.62	105	0.32	+ 20
0.6	10.214	92.60	210	0.33	- 20
0.8	10.213	92.62	600	0.39	- 65
1.0	10.219	92.61	$6.3 \times 10^5$	0.49	-100 -400

## 3.2. Electrical properties

The  $V^{3+}$  containing compounds are semiconducting with  $\rho_{300K} \sim 10^3 \Omega \text{ cm}$  whereas the corresponding  $Fe^{3+}$  containing rhombohedral pyrochlores are almost insulators ( $\rho_{300K} \sim 10^7 \Omega \text{ cm}$ ). Appreciable conductivity sets in  $Er_2(Fe_{4/3}^{3+}W_{2/3}^{6+})O_7$  only for  $T > 500 \text{ K}$ . However, doping with  $V^{3+}$  ( $x = 0.8$ ) brings about a thousand-fold reduction in resistivity. From the data shown in figure 2 and table 1 for the solid solutions,  $Er_2(V_{1-x}Fe_x)_{4/3}W_{2/3}O_7$ , it is clear that there is a gradation in  $\rho_{500K}$  and energy of activation ( $E_a$ ) values with varying  $x$ , the lowest values

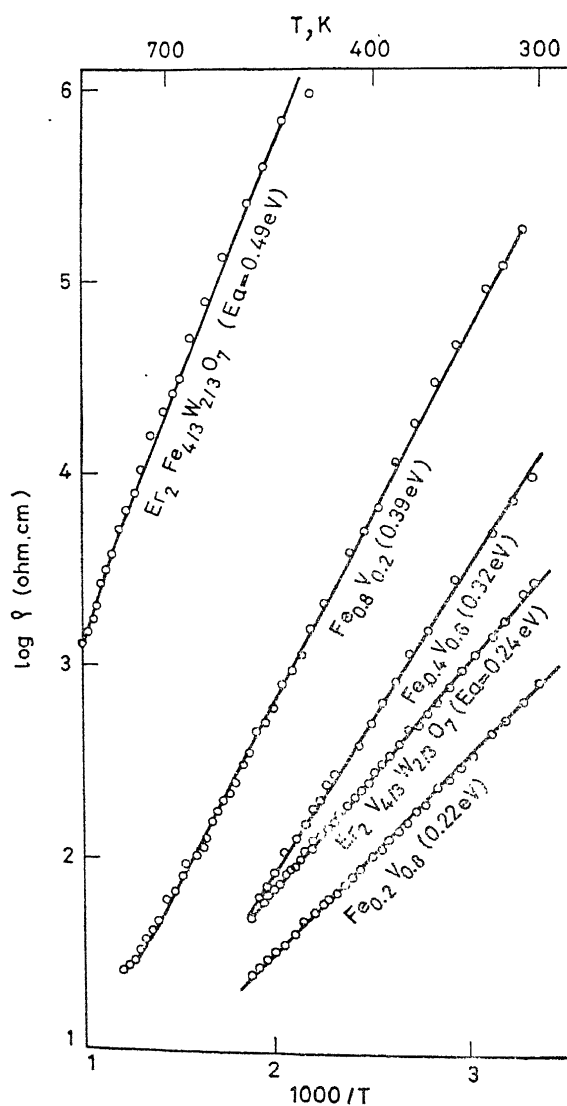


Figure 2. Electrical resistivity vs temperature plots for  $Er_2(V_{1-x}Fe_x)_{4/3}W_{2/3}O_7$  pyrochlores.

being encountered at around the composition where crystal structure change is noted. Seebeck coefficients are positive and negative respectively for the end members of the solid solution series ( $x = 0.0$  and  $1.0$ ), the absolute values being fairly large (table 1). As expected, there is a switchover from  $p$ -to- $n$ -type behaviour with increasing  $x$  (at a given temperature, 300 K) but, surprisingly this occurs at  $x = 0.45-0.50$ .  $\alpha - T$  data on two solid solutions, viz.,  $x = 0.2$  and  $0.6$  (table 1) indicate that  $\alpha$  decreases (become less positive) and increases (more negative) respectively with rise in temperature (300-500 K).

The observed resistivity and Seebeck coefficient behaviour of the compounds can be explained by assuming mixed conduction (Rao and Rao 1978; Goodenough 1972). Electrical conductivity in the  $\text{Ln}_2(\text{V}_{4/3} \text{W}_{2/3})\text{O}_7$  compounds can arise due to the creation of  $\text{V}^{4+}$  sites (and  $\text{W}^{5+}$ ) and hopping of 'holes' within the localised levels as is shown by the  $p$ -type behaviour and low energies of activation (table 1). This is because V can readily exist in  $3^+$  and  $4^+$  oxidation states in oxides (Rao and Subba Rao 1974; Subramanian *et al* 1979). On the other hand, realisation of  $\text{Fe}^{4+}$  in oxides is more difficult and we expect  $\text{Er}_2(\text{Fe}_{4/3} \text{W}_{2/3})\text{O}_7$  to be insulating as is indeed found experimentally. Introduction of a small amount of  $\text{V}^{3+}$  increases the conductivity as expected. The observed  $n$ -type behaviour and semiconduction in  $\text{Fe}^{3+}$  (high  $x$ ) containing samples must be due to the thermal excitation of electrons from the localised  $t_{2g}$  to the  $e_g$  levels of the  $\text{Fe}^{3+}$  ions (Rao and Subba Rao 1970; Parker 1975). The predominance by way of number and/or mobility of each type of carrier (viz., thermally excited electron and  $\text{V}^{4+}$  'hole') will determine the overall  $n$ - or  $p$ -type behaviour at ordinary temperatures. And, as expected the switch over occurs for  $x = 0.45-0.50$  in the solid solutions. For a given composition of the solid solution, increase in temperature increases the  $n$ -type carriers produced by thermal excitation (and probably these are more mobile than holes at a given  $T$ ) and gives rise to the decreased  $+ \alpha$  as is indeed observed experimentally.

#### 4. Conclusion

In conclusion we state that complete series of solid solutions exist in the mixed pyrochlore systems containing V, Fe and W metals at the B site ( $\text{Er}_2(\text{V}_{1-x} \text{Fe}_x)_{4/3} \text{W}_{2/3} \text{O}_7$ ). The structure changes from cubic to rhombohedral for  $x = 0.25$  at 300 K. Electrical conductivity and Seebeck coefficient data as a function of temperature can be satisfactorily explained by invoking hopping mechanism. Preliminary magnetic susceptibility studies indicate interesting magnetic order in these compounds. Detailed studies are in progress and will be reported elsewhere.

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