

Electron transport in hot pressed $Y_{3-x}Gd_xFe_5O_{12}$

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Abstract. Electron transport properties of a few hot-pressed garnets of the series $Y_{3-x}Gd_xFe_5O_{12}$ (where $x = 0, 1$ and 2.4) have been measured. For comparison, a normal sintered YIG has been studied to see the effect of porosity and microstructure. The electron transport properties have been discussed on the basis of the model suggested by Austin and Mott keeping in view the distortion caused by the substitution.

Keywords. Hot pressing; hopping conduction; porosity; activation energies.

1. Introduction

The electron transport properties in metal oxides have been extensively studied (Parker 1975; Mott and Davis 1979; Rao and Subba Rao 1970). However, these properties in garnets are relatively less understood. A few compounds of the series which have been studied in detail are single crystal or polycrystalline-sintered pellets of the pure REIG where RE is yttrium or rare earth ion (Elwell and Dixon 1968; Larsen and Metselaar 1976; Yadav and Lal 1979). It is found that the electron transport properties depend very much on the preparative conditions. This has been explained on the basis of microstructure and density. To get further insight into the role of porosity and microstructure, we have studied a few hot-pressed garnets of the series $Y_{3-x}Gd_xFe_5O_{12}$ where $x = 0, 1$ and 2.4 along with normal sintered YIG. Gd^{3+} like Y^{3+} or Lu^{3+} has no orbital angular momentum and consequently does not interact strongly with the crystal fields of the lattice as do most of the rare-earth ions. However, the spin angular momentum is not zero as in the case of Y^{3+} or Lu^{3+} . Therefore, it was considered worthwhile to study the effect of gadolinium substitution on the electron transport properties.

2. Experimental

The samples of $Y_{3-x}Gd_xFe_5O_{12}$ were prepared by hot pressing at 1160°C for an hour the pre-fired sample mixtures of suitable composition (for details see Prakash and Srivastava 1979). The normal sintered YIG was prepared by

the usual method of mixing and sintering at 1350°C. These samples were characterised by x-ray diffractometer (XRD-6) for a single phase. The pellet was painted on both sides with conducting platinum paint. It was mounted between two platinum foils in a cell fabricated at this laboratory. The DC and AC resistivity were measured using impedance bridge, RC oscillator, tuned amplifier and null detector (all made by General Radio, USA). Thermoelectric power (TEP) was measured using a millivolt potentiometer (Leeds and Northrup). Sufficient time was given after applying temperature gradient for stability. The overall accuracy of the thermoelectric power measurement is about 10% and the AC and DC resistivity about %.

3. Results and discussion

X-ray diffraction patterns of all the samples show the presence of a single garnet phase in these systems. The electrical resistivity (AC and DC) and thermoelectric power measurements have been carried out between 450 and 1000 K. The log of resistivity (DC) is plotted against inverse of temperature in figure 1. Room temperature DC resistivity was very high and the time-dependent resistivity was observed below 450 K indicating significant contribution due to ionic conduction. Resistivity behaviour of all the samples is similar. For comparison, we have also plotted the data for normal sintered YIG prepared by us. The resistivities in different regions are found to obey an Arrhenius type of relation. The activation energies in different temperature regions are given in table 1. It is interesting that the activation energies change in the vicinity of T_c . Activation energies of conduction do not seem to change much as Y^{3+} is replaced by Gd^{3+} in the second and third temperature range.

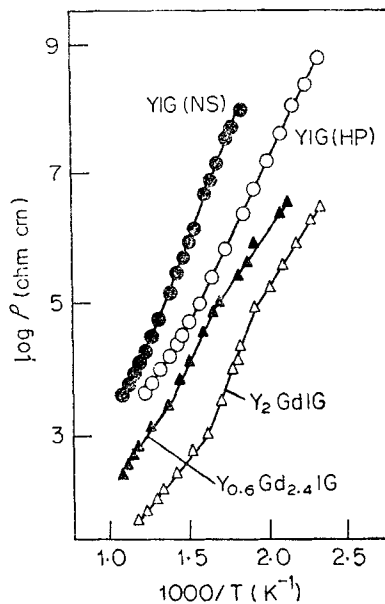


Figure 1. Plot of $\log \rho$ versus inverse of temperature for $Y_{3-x}Gd_xFe_5O_{12}$

Table 1. Activation energies in different temperature regions for $Y_{3-x}Gd_xFe_6O_{12}$

Sample	Region ($^{\circ}K$)			Activation energy (eV)		
	I	II	III	I	II	III
YIG (HP)	425-625	625-835		1.09	0.61	
Y_2GdIG (HP)	415-560	560-620	620-860	0.72	1.20	0.60
$Y_{0.9}Gd_{0.1}IG$ (HP)	450-580	580-740	740-940	1.68	1.02	0.62
YIG (NS)	530-710	710-900		1.20	0.95	

HP--Hot pressed; NS--Normal sintered.

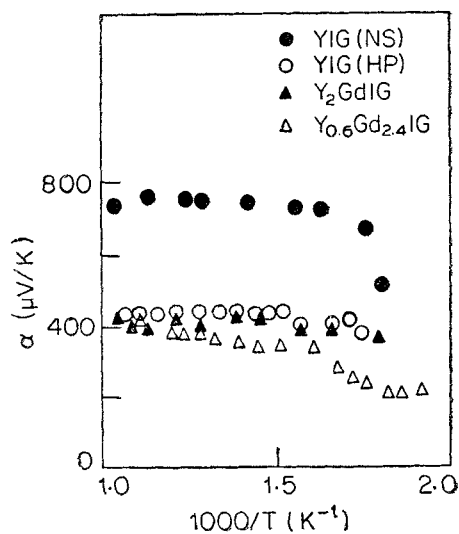


Figure 2. Plot of α versus inverse of temperature for $Y_{1-x}Gd_xFe_6O_{12}$.

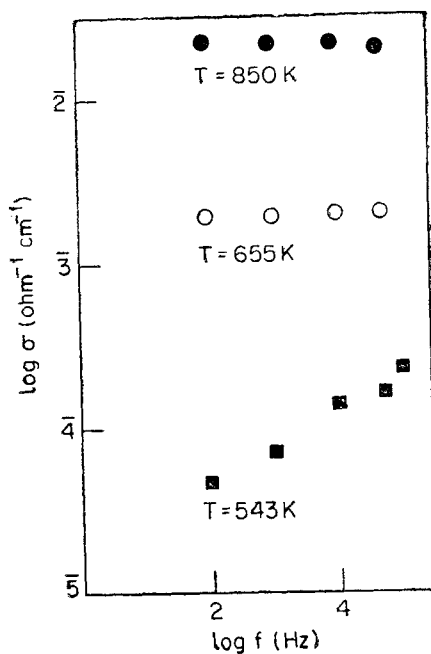


Figure 3a. Plot of $\log \sigma$ versus $\log f$ for $Y_2GdFe_6O_{12}$.

However, the activation energy in the first region is different for Gd-substituted YIG. For pure YIG, activation energy does not change for the first and second temperature regions. Thermoelectric power versus inverse of temperature is plotted in figure 2. Again, for comparison, we have given the data for our

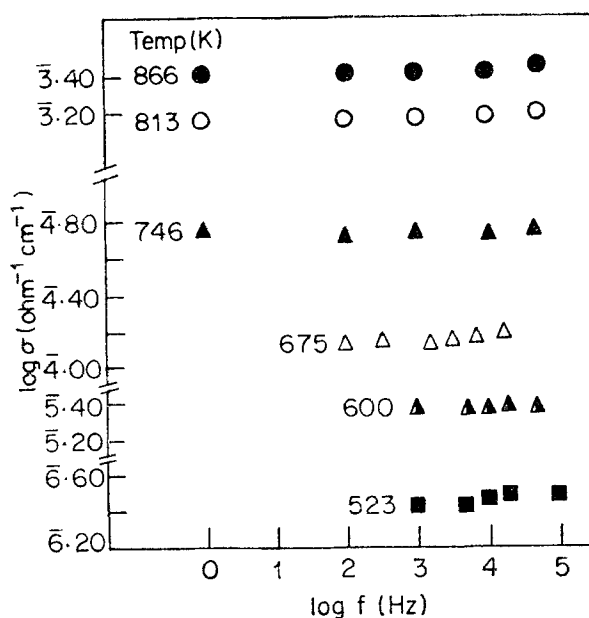


Figure 3b. Plot of $\log \sigma$ versus $\log f$ for $Y_{0.6}Gd_{2.4}Fe_6O_{12}$.

normal sintered YIG also. This plot shows that α is positive and it increases with temperature in the vicinity of T_c , though the increase is very small. Apart from this change, α remains essentially constant throughout the temperature. α seems to decrease with increase in x . The positive value of α indicates that the holes are majority charge-carriers. This plot of α versus $1000/T$ further indicates a hopping type of behaviour in this system. To get further insight into the conduction mechanism, the frequency dependence conductivity measurements have been plotted in figure 3. The conductivity is frequency-dependent at a lower temperature. However, this frequency dependence decreases with temperature and at a high temperature, it is essentially independent of frequency. Such a behaviour is usually observed in hopping conduction.

In view of the similarity of the structure and conductivity values with those of pure YIG, the intrinsic conduction in these solids may result due to transfer of electrons from field valence band to an empty conduction band. The energy required for this transfer is about 3 eV. The observed activation energies in the present case are much smaller to support the intrinsic conduction. The estimated mobility values are also very small ($\sim 10^{-2} \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$) compared to that expected in the case of band conduction ($\sim 1-100 \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$). Therefore, intrinsic conduction is ruled out. α is almost constant in the temperature region 600 to 1000 K, whereas ρ yields activation energies of $\sim 1.0 \text{eV}$ in the temperature range 550 to 700 K and $\sim 0.6 \text{eV}$ in the range 700 to 900 K. This suggests that the number of charge carriers is almost constant and their drift mobilities are thermally activated. This type of behaviour can be associated with small polaron or hopping of localised charge carriers of impurities.

But these materials are *p*-type semiconductors and there is a strong evidence of broad valence band in garnets (Wemple *et al* 1974). Therefore, formation of small polarons does not seem to be possible.

In YIG, the iron atoms on octahedral sites from a body-centred cubic lattice and nearest neighbour distance are relatively large ($\sim 5.7\text{\AA}$). The nearest neighbour distance will only slightly increase in the Gd-substituted samples we have studied. Thus, electron hopping in the octahedral sites may move most easily by jumping indirectly through a tetrahedral site. Such a model could, in principle, explain temperature-independent thermopower, which is based on the model suggested by Austin and Mott (1969). In this model, two types of centres A (octahedral) and B (tetrahedral) are separated by a constant energy Δu and it is assumed that $\Delta u \ll kT$ and that the conduction is due to hopping between A sites. However in each case, the carrier must hop over an intermediate B site. Thus, the occupation of B site is negligible and E_f is close to the energy level E_a of the A sites.

In general, the conduction mechanism could be explained on this model. However, with gadolinium substitution, we expect a slight distortion of the lattice as ionic radii of $\text{Gd}^{3+} > \text{Y}^{3+}$. This may also reduce the mobility as the effective hopping distance increases. Besides this, the slight distortion of the lattice could cause a change in potential well depth. Also, it could decrease the separation between E_a and E_f and increase the number of charge carriers. Some extra localized energy levels may also be generated.

In view of the above facts, we would now attempt to explain our electron transport data of the system $\text{Y}_{3-x}\text{Gd}_x\text{Fe}_5\text{O}_{12}$. The DC resistivity of Gd-substituted samples does not vary uniformly with x . As separation between E_a and E_f decreases, the occupancy of sites at energy E_a increases. Hence, the resistivity decreases. On the other hand, the mobility of charge carrier will decrease which in turn, increases the resistivity. These two effects are contrary to each other and may not vary uniformly with x . Therefore, the overall effect on the resistivity with X will also be nonlinear. The thermoelectric power value seems to decrease with X , though the decrease is very small. It supports our earlier inference, that is, with increase in x , the number of charge carrier increases.

Since, the activation energies in temperature range II and III are similar in all the hot-pressed samples, the localized sites through which hopping takes place seem to be the same. At low temperatures, however there is a change in activation energy in Gd-substituted samples. Further, this low temperature activation energy is same in both Gd-substituted samples thus indicating that the hopping of carriers takes place between some new localized energy levels which may be generated due to distortion as described earlier. These levels are close to fermi level compared to E_a . Obviously, these levels are absent in pure YIG.

The density of normal sintered YIG is about 50% of the theoretical density where all our hot-pressed garnets are more than 99.5% dense. The average grain size is 15-16 microns for normal-sintered YIG whereas it is 1-2 microns for hot-pressed garnets. Our experimental data show that the resistivity, thermopower and the activation energy in normal sintered YIG are higher than the hot-pressed YIG.

Porosity may, in principle, increase the resistivity by increasing the effective length of the conduction path and decreasing the effective cross-sectional area. If we take into account this change, the dependence of the measured conductivity on the porosity P can be approximated by the formula (Sharon *et al* 1981)

$$\frac{\sigma}{\sigma_0} = \frac{1-P}{1+P}$$

where σ_0 is the true conductivity of the bulk. However, the results show that the increase in porosity of the sample increases the resistivity by a greater extent than is to be expected by the above formula. In fact this observation also is true for hot-pressed MgO (Sharon *et al* 1981). It is therefore obvious that some other factors also cause increase in resistivity which also accounts for increases in thermopower and activation energy. It is likely that the scattering due to pores reduces the mobility which may, in turn, increase the E_a and α . This further increases the resistivity.

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