

SUMMARY AND CONCLUSIONS

The physical properties of ferrites with spinel type crystal structure have been the subject of many investigations. High electrical resistivity and easy preparation make these materials widely usable for the cores of intermediate and high frequency electromagnetic devices.^{1,2} Being technologically important they have been extensively studied from the point of view of their magnetic and electrical properties to check the suitability for certain applications and they were also subjected to rigorous investigations using the techniques like X-ray diffraction,³ neutron diffraction⁴ and mossbauer spectroscopy,⁵ etc. in order to understand structure property relationship.

Recently to increase the resistivity of materials, the substitution like Ti, Zr, Sn in mixed ferrites were undertaken by many workers. The 'Mg' ferrites appeared to be interesting because it possess high electrical resistivity at room temperature⁶ and sensitive to most of the conditions of preparation including quenching. Therefore, in order to unravel the role of 'Ti' substitution, cation distribution and other properties the following studies on

$\text{Mg}_{1+t}\text{Ti}_t\text{Fe}_{2-2t}\text{O}_4$ ferrites have been undertaken.

- i) Preparation of $Mg_{1+t}Ti_tFe_{2-2t}O_4$ ferrites with $t = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$ by ceramic method at an appropriate temperature.
- ii) X-ray diffraction studies of ferrite samples for finding the Bravais lattices and lattice parameter (a).
- iii) D.C. electrical resistivity and thermo emf for finding out conduction mechanism involved in ferrites.
- iv) Dispersion of dielectric constant and resistivity behaviour with frequency for finding out nature of dielectric constant, \tan and resistivity at different frequency range.
- v) Magnetization study at room temperature and at liquid nitrogen temperature and Curie temperature measurement were carried out for finding out the effect of Ti^{4+} substitution on 'Mg' ferrite system.

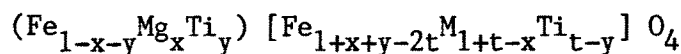
In Chapter I the brief review of the ferrite properties such as magnetization, anisotropy, conductivity, dielectric constant and structure of ferrite is given. The Neels theory for ferrites is also discussed.

In Chapter II part A is devoted to the method of preparation and part-B deals with the X-ray diffraction study. In part A the methods of preparation of ferrites are reviewed and microstructure development during the sintering process is discussed. The possibility of obtaining high density ferrites by hot pressing technique is also discussed. The procedural details of ceramic method followed in this work have been also included in part A of this chapter. Pellets were prepared applying 6 to 7 tonns pressure and sintered

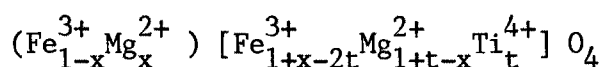
at 950°C temperature for 24 hours. They were then furnace cooled. The rate of cooling of the furnace was roughly 125°C/hour for first 2 to 3 hours and 75°C/hour for intermediate stage dropping to very low value asymptotically as the room temperature was approached within a span of about 10 hours.

In part B of Chapter II details of experimental techniques, indexing of the powder patterns are presented. From X-ray diffraction analysis it is observed that all the samples show the spinel structure and they form complete solid solution. Additional phases have been observed in the sample with $t = 0.4$ and $t = 0.5$. These lines have been identified to be of TiO_2 phases. No definite trend is observed due to the compositional variations on lattice parameter. However, except for the case corresponding to $t = 0.5$ the lattice parameter for all samples is greater than that for $MgFe_2O_4$.

In our system when Ti^{4+} ions are substituted by an amount 't', the Fe^{3+} ion concentration decreases by $(2-2t)$ while the 'Mg' ion concentration increases by $(1+t)$. Since the ionic volumes of Mg^{2+} and Ti^{4+} are greater than that for Fe^{3+} the lattice parameter is found to increase when Fe^{3+} are replaced by Ti^{4+} ions. The change in lattice parameter can be explained on the basis of change on A-site and modelung constant where it is $(b/M)^{1/9}$ of the system. However, it is observed that most of Ti always goes to B-site. For our system $Mg_{1+t}Ti_tFe_{2-2t}O_4$ the general formula for cation distribution may be given,



in which the cation enclosed by () occupy the A-site while those enclosed by [] occupy the B-site. However, there are evidences⁷ indicate that the value of 'y' should be small owing to the maximum charge neutralization. In other words the tetrahedral Fe³⁺ ions are mainly replaced by Ti⁴⁺ ions. Therefore it is reasonable to consider the cation distribution to be of the form,



Further, it is seen that the bond lengths both R_A and R_B of all samples are greater than that for Mg-ferrite except the R_B value for t = 0.5. The theory of ionocovalent bonding in ferrite was explained by Levine on the basis of variation of bond length in the spinel structure. Thus it may be concluded that addition of Ti⁴⁺ ions has an effect of decreasing the iono-covalent character of the ferrite.

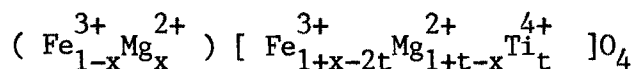
Chapter III deals with conduction mechanism and thermo-electric power measurement. Electrical resistivity measurements are carried out by two probe method from room temperature to 800 (K) Thermo-emf measurements are carried out using sensitive micro-voltmeter.

The resistivity with temperature obeys Arrhenius relation,

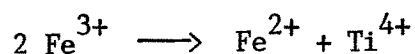
$$\rho = \rho_0 \exp (E/KT) ,$$

where 'E' is activation energy 'K' is Boltzman constant and T is absolute temperature. The temperature at which break in the resistivity curve occurs almost correspondes to the ferrimagnetic Curie temperature. It is also seen that in the range of temperature under consideration the resistivity increases on addition of Ti⁴⁺ in

the system. In our system the addition of $(1+t)$ of Mg^{2+} ions reduces the Fe^{3+} concentration by $(2-2t)$. The cation distribution is to be of the form,



So A-A hopping does not exist as there are only Fe^{3+} ions on this sub-lattice and any Fe^{2+} ions formed during processing preferentially occupy the B-site, B-B hopping is more dominant than A-B hopping. Thus the reduction of Fe^{3+} ions on addition of Ti^{4+} are responsible to increase the resistivity. Ferric ions are also reported to be converted to ferrous ions on addition of Ti^{4+} as follows,



The resistivity is expected to increase due to localization of Fe^{2+} on B-site when Ti^{4+} is added. However, the addition of Ti^{4+} results in overall reduction in Fe^{3+} from the ferrite material and hence the reduction of conductivity or increase in resistivity. It is seen that activation energies in paramagnetic region are greater than those in the ferrimagnetic region. From the range of values of ΔE (0.35 eV to 0.94 eV) the conduction is clearly seen to be intrinsic type. However activation energy also depends on other factors like porosity, grain size, impurity etc. Further the value of ΔE suggest that the hopping process due to polarons is favoured. The theory of conductivity has been explained on the hopping of polarons due to thermal activation.⁸

The activation energy in the paramagnetic region is found to be more than that in the ferrimagnetic region. This can be attributed to the effect of magnetic ordering in the conduction process.⁹ According to strict theoretical considerations the anomalous changes in the activation energy occur at the disordered temperature.

Thus both in ferrimagnetic and paramagnetic region over the range of temperature the conductivity is governed by hopping of polarons as evidenced from the value of ΔE .

In thermoelectric measurements, the Seebeck co-efficient is negative. This suggested that the carriers are of n-type in the entire temperature range. In all the samples as the temperature increases the Seebeck co-efficient increases i.e. there is more generation of n-type carriers, however, after maximum value of Seebeck co-efficient further increase in temperature tends to reduce the Seebeck co-efficient. The effect appears to be more pronounced in the samples with $t=0.3, 0.4, 0.5$. The temperatures where the maximum value of Seebeck co-efficient are observed can roughly be correlated with Curie temperatures. That is, the magnetic ordering has an influence on the Seebeck co-efficient. $MgFe_2O_4$ is known to be n-type. It is also seen that addition of Ti^{4+} enhances the n-type of carriers in the ferrite.

For our sample the increase in the value of ' α ' on addition of Ti^{4+} is indicative of an effect of reducing Fe^{2+} ions on B-site. This is responsible for the increase of resistivity. However, as suggested by Ghani et.al.¹⁰ electrons are generated due to the presence of Fe^{2+} ions. And so the explanation of n-type conductivity

cannot be related with the content of Fe^{3+} ions. The increase of Ti^{4+} is accompanied by increase of Mg^{2+} in the system. Thus, the Mg^{2+} ions are responsible for the n-type behaviour. Mg-ferrites are sensitive to heat treatment and hence unless the cation distribution is accurately known the explanation of n-type behaviour with the content of Mg^{2+} and its variation with temperature will be speculative.

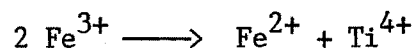
In Chapter IV dielectric properties of our system are presented. Theoretical aspects including Koops theory are discussed in detail. Experimental measurements of dielectric constant, $\tan\delta$ and resistivity with variation of frequency were carried out at ERTL, Bombay. It is found that in the frequency range of 10 KHz to 10 MHz the nature of variation exhibited by three samples ($t=0.2, 0.2, 0.5$) is similar. The dielectric constant is high for low frequencies and as the frequency increases the dielectric constant is found to decrease. It is also observed that the dielectric constant ' ϵ ' decreases on addition of Ti^{4+} in the system. A change in Ti^{4+} ion concentration by ' t ' reduces iron (Fe^{3+}) content by $(2-2t)$ and increases Mg^{2+} ion content by $(1+t)$.

The magnitude of Seebeck coefficient in the cubic phase is given by,

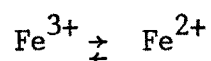
$$\alpha = \frac{\text{total number of iron ions of B-site}}{\text{total number of } \text{Fe}^{2+} \text{ ions on B-site}}$$

From our studies of the Seebeck co-efficient we found that ' α ' increases with the addition of Ti^{4+} in the system. This suggests that the Fe^{3+} ion concentration increases and Fe^{2+} ion content

decreases, so the ' α ' increases according to the above equation. Ferric ions are also reported¹¹ to be converted to ferrous ions on addition of Ti^{4+} as,



The decrease in the dielectric constant on addition of Ti^{4+} may thus be associated with the reduced number of electronic exchange of the type,



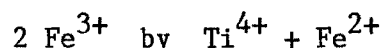
Also increase of Ti^{4+} is associated with the increase of Mg^{2+} ions. The distribution of Mg^{2+} ions on the A-site and B-site will differ from one ferrite to the other and hence to understand the role of Mg^{2+} ions on the dispersion of dielectric constant, will entail exact computation of the distribution of cation and valance states of various cations involved, although Mg^{2+} ions appear to obstruct the electronic exchange contributing to the conductivity.

All the samples revealed dispersion due to Maxwell¹² and Wagner¹³ interfacial polarization in agreement with Koops phenomenological theory. The variation of relaxation intensity i.e. difference between high and low frequency dielectric constants with Ti^{4+} content is therefore primarily governed by the change in the dielectric constant at low frequencies. It decreases with increasing Ti^{4+} concentration.

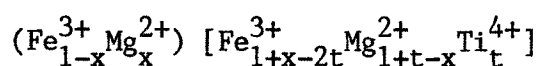
The loss tangent ($\tan \delta$) goes on decreasing with increasing frequency. The resistivity increases with increase in Ti^{4+} content and frequency. The increase in resistivity on addition of Ti^{4+}

implies that the flow of space charge carriers is abstracted and thus the build up of space charge polarization is impeded. No peaks have been observed in the dispersion of loss tangent. A maximum in dielectric loss is observed when the jump frequency is approximately equal to that of the external field.¹⁴

Magnetization and Curie temperature measurements are reported in chapter V. Magnetization measurements are carried at room temperature and also at liquid nitrogen temperature. It is seen that except for $t = 0.4$ the values of ' n_B ' decreases almost linearly on addition of Ti^{4+} in the system. In the sample corresponding to $t = 0.4$ there is sudden increase in the value of ' n_B '. The nature of variation at 300 (K) and 77 (K) is identical. Addition of Ti^{4+} in the system causes the replacement of Fe^{3+} by Ti^{4+} and Fe^{2+} as



But the increase in resistivity on addition of Ti^{4+} suggest that there is no formation of Fe^{2+} ions. The addition of Ti^{4+} by an amount ' t ' reduces ' Fe^{3+} ' ion concentration by $(2-2t)$ while increases Mg^{2+} ion concentration by $(1+t)$. Hence reduction of magnetic moment can be directly associated to Fe^{3+} ions. However, to understand the role of Mg^{2+} ions the distribution of cations must be known precisely. In the system containing 'Cu' and 'Mg' this task is not easy as these ferrites are sensitive to heat treatment. For our system it is reasonable to consider the cation distribution to be of the form,

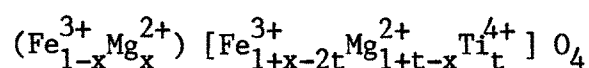


Whatever amount of Ti^{4+} or Mg^{2+} ions are added to the system there is a reduction of Fe^{3+} ions. Also occupation of B-site by Ti^{4+} ions has an effect of forcing Fe^{3+} ions from B-site to A-site. Thus addition of Ti^{4+} reduces A-B interaction and hence n_B .

In Curie temperature measurement it is seen that Curie temperature decreases on addition of ' Ti^{4+} '. There is close agreement between the experimentally measured Curie temperature and that obtained from thermal variation of resistivity. The fact that Curie temperature decreases linearly on addition of Ti^{4+} suggests that A-B interaction reduces in the system. A detail understanding of this phenomenon can be had from neutron diffraction studies. But in our system triangular spin arrangement may not be favourable. The Curie temperature is roughly proportional to the product of the concentration of the Fe^{3+} ions on A-site and B-site. Accordingly Curie temperature T_c varies with t and x as

$$(1-x)(1+x-2t) = (1-x)^2 - 2t(1-x)$$

The temperature at which the break in the $\log \rho$ vs $1/T$ curves takes place satisfy the above mentioned relation. From the cation distribution suggested for the system,



It is reasonable to state that the decrease in T_c on addition of Ti^{4+} reduces the A-B interaction. This fact is supported by the observed reduction in n_B with the addition of Ti^{4+} . Jadhav et.al.¹⁵

have reported the effect of substitution of 'Ti⁴⁺' on Curie temperatures of Cu-Zn ferrites. They attributed the variation in T_c to the change of A-B-interaction. It is very difficult to predict the nature of magnetization at intermediate temperatures eventhough the Curie point and saturation moments are precisely known.

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