Chapter – 4

RESULTS AND DISCUSSIONS

FOR Mg$_{1+x}$Pb$_x$Fe$_{2-2x}$O$_4$ SYSTEM

4.1 X-ray Diffraction :

The single phase formation for all the samples of the present system was confirmed from X-ray diffraction patterns as shown in figures (4.1 to 4.5). The values of the lattice parameter “a” of all the samples have been determined by using X-ray data with an accuracy of ± 0.002 Å for all the samples having X = 0.0 to X = 0.4 and are listed in table (4.1). On the X-ray diffraction pattern, diffraction maxima for the reflections (220), (311), (400), (422), (511), (440) etc. were induced for the spinel structure. The variation of lattice parameter “a” with increase of concentration (x) in the composition is shown in the figure (4.6). From the table (4.1) and the fig. (4.6), it is found that the lattice parameter increases with increase in x, reaches saturation for x = 0.2 and then decreases for higher values of x and there is continuously change in lattice parameter of the present system presumably due to the closeness of
the ionic radii of Mg$^{2+}$ (0.65 Å) and Fe$^{3+}$ (0.64 Å) and Pb$^{4+}$ (0.70 Å) [1]. The variation in the lattice parameter with concentration is linear and obeys the Vegard’s law and the linear slow decrease in lattice constant may be due to the replacement of smaller Fe$^{3+}$ ions (0.64 Å) by larger Mg$^{2+}$ (0.65 Å) and Pb$^{4+}$ (0.70 Å) in the system [2]. The Mg$^{2+}$ and Pb$^{4+}$ cations have strong preference for octahedral sites. The ionic radii $r_A$ and $r_B$ have been determined by considering cation distribution. It can be observed from the table (4.2) that calculated tetrahedral radii ($r_A$) increase with increase of Mg$^{2+}$ & Pb$^{4+}$ concentration in the composition $x = 0.0$ to $x = 0.4$ , octahedral radii ($r_B$) increases with increasing composition $x = 0.0$ to $x = 0.4$. Knowing the values of $r_A$ and $r_B$, theoretical values of lattice parameter ($a^{th}$) for all compositions were calculated on the basis of estimated cation distribution as discussed below in (4.1.4) by using the relation suggested by Mazen et.al. [3],

\[
a^{th} = \frac{8}{3\sqrt{3}} \left[ (r_A + R_0) + \sqrt{3} (r_B + R_0) \right] \]

(4.1)

where $R_0$ is the radius of oxygen ions (1.35 Å) and $r_A$ and $r_B$ are ionic radii of tetrahedral site and octahedral site respectively. The magnitude of
the theoretical and observed values of the lattice parameter(a) as given in
the table (4.3) and are found to be in good agreement. Therefore, it can be
presumed that the estimated cation distribution is in agreement with real
distribution in that range [4].

The octahedral site plays a dominant role rather than the tetrahedral site
due to the values of lattice parameter. Due to increase in the
concentration x, the average ionic radii increases slowly.

(4.1.1) X-ray density:

The bulk density is defined as the mass per unit volume of the
system. The density of the ferried material influences bulk magnetic
properties. The material which having higher density possess higher
permeability, higher remanance and lower coercivity  [5]. The X-ray
density of all the samples is calculated by using the relation. [6].

\[ d_x = \left( \frac{8M}{Na^3} \right) \text{gmcm}^{-3} \] \hspace{1cm} (4.2)

where M is the molecular weight of composition, a is the lattice
parameter of the spinel ferrite, N is the Avogadro's number. The
calculated values of X-ray density and bulk density of each of the
samples are given in table (4.1). The variation of bulk density and X-ray density with the composition is shown graphically in the fig.(4.8). From the table (4.1) and fig. (4.8) it is found that both the X-ray density and Bulk density increase with concentration(x). This increase in density may be ascribed to the density and the atomic weight of Mg( 24.30, 1.738 gm/cm³) and lead (207.2, 11.34 gm/cm³) which are higher than those of iron (55.847, 7.87 gm/cm³). The increase in the X ray density is consistent with the decrease in the lattice constant.

4.1.2 Particle size :

The sharpness in the diffraction peak in XRD pattern depends on the particle size. Srinivasan et.al [7] and Mehta [8], have employed the XRD technique for the determination of particle size. In the present work, particle size for all the samples was estimated by Scherrer’s formula [9] given by,

$$ t = \frac{0.9 \lambda}{\beta \cos \theta} \quad \text{..................................................(4.3)} $$

Where $\lambda$ is the wavelength of the target used. (here cuK$\alpha = 1.54056$ Å$^0$) and
\( \beta \) is the full width at half maxima (FWHM). From XRD peak (311) the particle size was estimated. The values of particle sizes for the samples are listed in table (4.1). The particle size is observed to vary in the range from 542.156 \( A^0 \) to 897.838 \( A^0 \) with average particle size 762.9 \( A^0 \) which is consistent with the particle size of ceramically prepared systems.

**4.1.3 Porosity:**

The percentage porosity (P) of all samples has been calculated by using the formula given by Standly K. J. [10]

\[
\text{Percentage porosity} = \left[ 1 - \left( \frac{d}{dx} \right) \right] \times 100 \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } \text{ } (4.4)
\]

where \( d \) is the bulk density, \( dx \) is the X-ray density and the values of the calculated percentage porosity are listed in the table (4.1). From the table (4.1) it is observed that porosity (%) for all the samples is found in the range 4.05 to 14.52 percent and these values are found to be in good agreement with the values reported by R. G. Doric et. al [11].
4.1.4 Determination of cation distribution by using X-ray diffraction method:

The X-ray intensity has been determined by using the formula given by Buerger [12]

\[ I_{hkl} = |F_{hkl}|^2 P.Lp \]  \( (4.5) \)

where \( I_{hkl} \) is the relative integrated intensity, \( F_{hkl} \) is structure factor, \( P \) is the multiplicity factor and \( Lp \) is lorentz polarization factor \( (1 + \cos^2 \theta / \sin^2 \theta \cdot \cos^2 \theta) \)

The distribution of divalent, trivalent and tetravalent cations among tetrahedral and octahedral sites in the \( \text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4 \) Ferrite samples is determined from the ratio of intensities of X-ray diffraction lines \( I_{220/440}, I_{400/422}, I_{220/400} \) which are considered to be sensitive to the cation distribution parameters(x) [13]. The observed and calculated X-ray intensity ratios \( I_{220/440}, I_{400/422}, I_{220/400} \) for different cations distributions are given in the table (4.4). It is evident from the table (4.4) that tetravalent \( \text{Pb}^{4+} \) ions occupy both A and B sites replacing iron ions \( \text{Fe}^{3+} \) and also added \( \text{Mg}^{2+} \) ions are substituted for \( \text{Fe}^{3+} \) in both the sites. The
approximate cation distributions derived by using X-ray intensities calculations and site preference energies of the cations can be written as.

\[(\text{Mg}^{2+}_{0.20}\text{Fe}^{3+}_{0.80}) \quad (\text{Mg}^{2+}_{0.80}\text{Fe}^{3+}_{1.20})\]

\[(\text{Mg}^{2+}_{0.57}\text{Pb}^{4+}_{0.32}\text{Fe}^{3+}_{0.11}) \quad (\text{Mg}^{2+}_{0.94}\text{Pb}^{4+}_{0.07}\text{Fe}^{3+}_{0.98})\]

\[(\text{Mg}^{2+}_{0.16}\text{Pb}^{4+}_{0.84}\text{Fe}^{3+}_{0.74}) \quad (\text{Mg}^{2+}_{1.04}\text{Pb}^{4+}_{1.01}\text{Fe}^{3+}_{0.89})\]

\[(\text{Mg}^{2+}_{0.22}\text{Pb}^{4+}_{0.78}\text{Fe}^{3+}_{0.62}) \quad (\text{Mg}^{2+}_{1.07}\text{Pb}^{4+}_{1.71}\text{Fe}^{3+}_{0.75})\]

\[(\text{Mg}^{2+}_{0.29}\text{Pb}^{4+}_{0.53}\text{Fe}^{3+}_{0.55}) \quad (\text{Mg}^{2+}_{1.10}\text{Pb}^{4+}_{2.45}\text{Fe}^{3+}_{0.65})\]
where the parenthesis ( ) and brackets [ ] indicate A site and B site respectively. The tetrahedral and octahedral site radii have been calculated using the following relations

\[ r_A = C_A \text{Mg} r(\text{Mg}^{2+}) + C_A \text{Fe} r(\text{Fe}^{3+}) + C_A \text{Pb} r(\text{Pb}^{4+}) \] ........................ (4.6)

\[ r_B = \frac{1}{2} [C_B \text{Mg} r(\text{Mg}^{2+}) + C_B \text{Fe} r(\text{Fe}^{3+}) + C_B \text{Pb} r(\text{Pb}^{4+})] \] ........................ (4.7)

where, \( r(\text{Mg}^{2+}), r(\text{Pb}^{4+}), r(\text{Fe}^{3+}) \), are ionic radii of \( \text{Mg}^{2+}, \text{Pb}^{4+} \) and \( \text{Fe}^{3+} \) ions respectively. While concentration at A site \( C_A \text{Mg}, C_A \text{Fe} \) and \( C_A \text{Pb} \) are the concentrations of the \( \text{Mg}^{2+}, \text{Pb}^{4+} \) and \( \text{Fe}^{3+} \) ions on A sites , \( C_B \text{Mg}, C_B \text{Fe} \) and \( C_B \text{Pb} \) are the concentrations of \( \text{Mg}^{2+}, \text{Pb}^{4+} \) and \( \text{Fe}^{3+} \) ions on B sites. Using these formulae, the values of mean tetrahedral(\( r_A \))and octahedral(\( r_B \))ionic radii for \( x = 0.0 \) to \( x = 0.4 \) compositions have been calculated and are listed in table (4.2). It can be observed that tetrahedral ionic radius gradually increases with increasing X. It is also observed that ionic radius of octahedral sites increases with increasing X. The result of increase in both the radii(\( r_A \))and (\( r_B \)) is that the lattice constant “a” decreases with x. Calculated \( r_A \) and \( r_B \) given in the table (4.4) it can be
seen that calculated tetrahedral $r_A$ and $r_B$ increase gradually in all the samples with increasing $x$.

### 4.1.5 Oxygen Positional Parameter ($u$):

The oxygen positional parameter ($u$) for each composition was calculated by using the formula[25]

$$u_{3n} = \frac{1}{4} R^2 - \frac{2}{3} + \left( \frac{11 R^2 - \frac{1}{18}}{48} \right)^{\frac{1}{2}}$$

(4.8)

where $R = \frac{B - O}{A - O}$ The bond lengths B-O and A-O are average bond lengths calculated based on the cation distribution listed in Table( 4.2 ). B-O = < $r_B + r(O^2)$> and A-O = < $r_A + r(O^2)$> The values of oxygen positional parameter of each sample obtained from equ.(4.8) are in very good agreement with those deduced from the value of $u$ for two end members Mg Fe$_2$O$_4$ (x=0.0) (u= 0.262) and Mg$_{1.5}$Pb$_{0.5}$FeO$_4$ (x=0.5) (u= 0.262) and given in table (4.8).

### 4.1.6 Bond Lengths:

The X-ray diffraction data was used to calculate the bond length $R_A$ (i.e. the shortest distance between A-site cation and oxygen
ion) and $R_B$ (i.e. the shortest distance between B-site cation and oxygen ion) were calculated by using the relation[14].

$$R_A = a(3)^{1/2} \left( \delta + 1/8 \right)$$ ...........................................(4.8)

$$R_B = a \left( 3\delta^2 + \frac{1}{16} - \frac{\delta}{2} \right)^{1/2}$$ ...........................................(4.9)

where, $\delta = u_{\text{system}} - u_{\text{ideal}}$, $u_{\text{system}}$ = oxygen parameter = $(u_1 + u_2)/2$ and $u_{\text{ideal}} = 0.250$ Å, and $u_1$ and $u_2$ are anion parameter of the two end members of the system respectively (Table 4.10). The values of bond lengths $R_A$ and $R_B$ are given in table (4.5) and their variation with the concentration(x) is shown in the figure(4.9). From the figure it can be observed that both $R_A$ and $R_B$ decrease slightly with the concentration. This behaviour can be attributed to the fact that the lattice parameter (a) decreases with the concentration.

**4.1.7 IR Spectra :**

IR spectra of all the samples of the system $\text{Mg}_{1-x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$ with $x = 0.0$ to $x = 0.4$ in step of 0.1 system are shown in the figures [4.10 to 4.14]. The spectra of all the compositions have been used to locate the bands positions in order to determine the absorption frequency. There are
two frequency bands in the IR spectra in the present system. It is observed that the range of the higher frequency band $\nu_1$ is from 600 to 610 cm$^{-1}$ and that of the lower frequency band $\nu_2$ is from 410 to 430 cm$^{-1}$ [14-15]. This difference in the band position is expected because of the difference in the Fe$^{3+}$ - O$^{2-}$ distances for the octahedral and tetrahedral complexes. Figures (4.10 – 4.14) and Table (4.3) clearly show that the bands $\nu_1$ and $\nu_2$ shift towards the lower energy with increasing Pb$^{4+}$ substitution for Fe$^{3+}$ ions. This may be explained on the basis of decreasing the concentration of Fe$^{3+}$ ions amongst the A and B sites. Which cause the decreasing the metal Oxygen stretching vibrational energies and cause increasing the A and B sites ionic radius.

The higher frequency band and lower frequency band of IR spectra are assigned to the intrinsic vibrations of tetrahedral and octahedral complexes [16-17]. The slight variation in $\nu_1$ and $\nu_2$ is due to the method of preparation, the grain size and sintering temperature can influence the band positions. The molecular weight of tetrahedral site ($M_A$) and that of octahedral site ($M_B$) have been calculated by using cation distribution
obtained from X-ray diffraction and magnetizations measurements. The values of force constant \( k_t \) and \( k_0 \) were calculated by using Waldron’s analysis [18]. According to Waldron, the force constants, \( k_t \) and \( k_0 \) for respective sites are given by,

\[
k_t = 7.62 \times M_1 x \nu_1^2 x 10^{-7} \text{ N/m} \tag{4.10}
\]

\[
k_0 = 10.62 \times M_2 / 2 x \nu_2^2 x 10^{-7} \text{ N/m} \tag{4.11}
\]

where, \( M_1 \) and \( M_2 \) are the molecular weights of cations on A and B sites respectively. The variation of force constant with \( \text{Pb}^{4+} \) concentration (x) is presented in table (4.3). From the figures (15-16) the force constant is found to increase with (x), and this suggests the strengthening of the inter atomic bonding. This facts is in agreement with the result that the bond lengths decrease with x.

The bond length \( R_A \) and \( R_B \) have been calculated using formula given by Smith Jain [19]. The values of \( \nu_1, \nu_2, k_t, k_0 \), are found in good agreement with the reported ones.
4.1.8 Magnetic Properties:

Magnetic properties of all the samples of the present system were studied by obtaining the magnetic hysteresis loops at 300 K. The magnetic hysteresis loops of all the samples indicate that these samples are all ferrimagnetic in nature. The saturation magnetization ($\sigma_s$) was calculated from hysteresis loop for all the samples of the series and magnetic moments per formula unit (magneton number) $n_B$ were calculated by using the following relation [20].

$$n_B^{obs} = \frac{\sigma_s M}{5585} \quad (4.8)$$

Where $M$ is molecular weight of the sample and $\sigma_s$ is saturation magnetization in (emu/gm). According to Neel’s two sublattice model of ferrimagnetism [21], Neel’s magnetic moment per formula unit in $\mu B$, $n_s^N$, is given by

$$n_s^N = M_B - M_A \quad \text{................................................................. (4.9)}$$

where $M_B$ and $M_A$ are the B (octahedral site) and A (tetrahedral site) sublattice magnetic moments in $\mu B$. The theoretical values of magnetic moments per formula unit in Bohr’s magneton unit ($n_s^N$) have been
estimated by using the cation distribution. By taking the ionic magnetic moments of Fe$^{3+}$, Mg$^{2+}$ and Pb$^{4+}$ as 5 µB, 0 µB and 0 µB respectively, $n_B^N$ values for all the samples of present system were calculated using equation (4.9). The values of $\sigma$, $n_B^{obs}$ and $n_B^N$ as a function of the concentration x are listed in the table (4.6). From the above table it can be observed that the observed (experimental) values $n_B^{obs}$ and the theoretical values $n_B^N$ are in good agreement for all the samples. Saturation magnetization $\sigma$, as listed in table (4.6), decreases as the concentration x increases. This may be due to the replacement of magnetic ions Fe$^{3+}$ by nonmagnetic ions Pb$^{4+}$ as Mg$^{2+}$. The variation $n_B^{obs}$ and $n_B^N$ with the concentration x is shown graphically in the fig.(4.17). It is found from the fig. that the nature of variation of both $n_B^{obs}$ and $n_B^N$ is the same i.e. both $n_B^{obs}$ and $n_B^N$ decrease with the concentration x. This decrease in $n_B^{obs}$ and $n_B^N$ with the concentration x can be explained by using equation (4.9). When non-magnetic Zn$^{2+}$ and Pb$^{4+}$ ions are substituted in the samples, Fe$^{3+}$
ions on A site are replaced by Zn$^{2+}$ ions and by a small proportion of Pb$^{4+}$ ions. Also the Fe$^{3+}$ ions on B site are replaced solely by nonmagnetic ions Pb$^{4+}$. The result of this is that both $M_A$ and $M_B$ decrease and as a result $n_s^N$ which is given by equation (4.9) decreases.

### 4.1.9 Interatomic distances and Bond angles:

The configuration of ion pairs in spinel ferrites with favourable distances and angles for effective magnetic interactions are shown in fig.(4.21) and the bond lengths between the cations (b,c,d,e, and f) i.e. (Me-Me) lengths and between the cations and anions (p,q,r and s) i.e. (Me-O) lengths were calculated by using the experimental values of lattice constant 'a' and the oxygen positional parameter (u) by the following relation(27-28)

\[
\begin{align*}
\text{Me-O} & \\
p &= a(1/2-u) & b &= (a/4)2^{1/2} \\
q &= a(u-1/8)3^{1/2} & c &= (a/8)11^{1/2} \\
r &= a(u-1/8)11^{1/2} & d &= (a/4)3^{1/2} \\
s &= a/3(u+1/2)3^{1/2} & e &= (3a/8)3^{1/2}
\end{align*}
\]
From Table (4.7) it is seen that both the distances (Me-Me) and (Me-O) decrease with increasing concentration (x). This result is in accordance with decrease in the bond angles ($\theta_1$, $\theta_2$, $\theta_3$, $\theta_4$, $\theta_5$) in table (4.7) were calculated by simple trigonometry principles using the values of interionic distances. It is observed from the table(4.7) that angles ($\theta_1$, $\theta_2$, $\theta_3$) decreases while ($\theta_3$, $\theta_4$) increases with concentration x and the observed increase $\theta_3$ and $\theta_4$ angles suggests weakening of A-B interaction while decrease in $\theta_1$, $\theta_2$, $\theta_5$ suggests strengthening B-B and A-A interaction on Mg$^{2+}$ and Pb$^{4+}$ substitution in the system.

4.1.10 D.C. resistivity:

The variation of d.c. electrical resistivity of sintered pellets of all the samples for the system Mg$_{1+x}$Pb$_x$Fe$_{2-2x}$O$_4$ was measured as a function of temperature in the range 300K to 460K. Log $\rho_{dc}$ has been plotted as a function of 1000/T as shown in the figures (18-20). From these figures it can be observed that, the d.c. electrical resistivity of all the samples is
found to decrease with increase in temperature and obeys the Arrhenius relation[24].

\[ \rho_{dc} = \rho_0 \exp\left( \frac{\Delta E}{K_B T} \right) \] .................................. (4.10)

Where \( \rho_{dc} \) is the resistivity at temperature \( T \)

\( \rho_0 \) is the temperature independent constant

\( \Delta E \) is the activation energy,

\( K_B \) is the boltzman constant

\( T \) is absolute temperature

By using the above relation, the values of activation energies are determined for ferrimagnetic and paramagnetic regions and is given in the table (4.9). The plots of \( \log \rho_{dc} \) verses \( 1000/T \) shows a kink near the curie temperature which is indicative of the magnetic phase change from ferrimagnetic region to paramagnetic region due to thermal energy and such behaviour has also been observed in many ferrites systems[ ] . The activation energies in both the ferrimagnetic and paramagnetic regions have been computed using the slope of \( \log \rho_{dc} \) verses \( 1000/T \) and given in the table(4.8). The activation energy is found to decrease on changing
from ferrimagnetic to paramagnetic regions. The ionization energy required for Fe$^{2+}$ to Fe$^{3+}$ is 0.1 eV. This is much smaller than the activation energy given in the table (4.8) for both ferrimagnetic and paramagnetic regions. The conductivity can be explained on the basis of polaron hopping. Polaron formation can be taken place due to incomplete inner d or f shells. The polaron in ferrites do not introduce a significant strain in ionic lattice as the d electrons contribute to the polaron. The hopping of both electrons are required to migrate polaron and the polarized the atomic configuration from one site to an adjacent one. In ferrites the cations occupy both sites namely A-site and B- site and the electrons are localized due to ionic bonding. The distance between two metal ions at B-site is smaller than the distance between two metal ions at A-site. Under normal conditions it is observed that the probability of electrons hopping between B-A sites is very small as compared to that of B-B- sites. The electrons hopping between A-A sites do not exist due to the most of Fe$^{3+}$ ions occupy A-sites and Fe$^{2+}$ ion formed during sintering.
preferably occupy B-sites only. Thus the hopping probability depends up
on the distance between the metal ions and also on the activation energy.

The conduction mechanism for the present system may be given as

\[ \text{Fe}^3 \leftrightharpoons \text{Fe}^{2+} \]

4.1.11 Thermoelectric Power studies:

Thermoelectric power measurements of all the samples for the
ferrite system \( \text{Mg}_{1-x}\text{Pb}_{x}\text{Fe}_{2-2x}\text{O}_4 \) \((x=0.0 \text{ to } 0.4)\) have been carried out
from room temperature to 473 K temp. The values of the seebeck
coefficient \( \alpha \) is given by the relation:

\[ \alpha = \frac{\Delta V}{\Delta T} \ldots \ldots\ldots\ldots(4.15) \]

where \( \Delta V \) is the voltage measured across the sample and \( \Delta T \) is the
temperature difference across the the sample. Figure( ) shows the
temperature variation of seebeck coefficient \( \alpha \) for all the samples. The
common feature for all the compositions is that \( \alpha \) is negative over the
whole range of temperature indicating that the majority charge carriers
are of n-type, suggesting the conduction mechanism to be predominantly
by electron hopping. It is clear from the figure (22) that the magnitude of $\alpha$ is found to decrease with increasing temperature for all the samples. In the region where conduction is due to one kind of charge carriers, the relations between the seebeck coefficient ($\alpha$) and Fermi energy ($E_F$) is given by [29].

$$E_F = e\alpha T - AKT$$

(4.16)

Where $A$ is a term connected with the kinetic energy of charge carriers, $e$ is the electronic charge, $k$ is the Boltzmann constant and $T$ is the absolute temperature. The calculated values of $E_F$ as a function of temperature for two values of $A$ ($A=0$ and 2) are shown in figure (23-25). The extrapolated value of $E_F$ to $T=0 K$ yields the values of $E_F(0)$ table (4.9). Comparing the activation energy of ferromagnetic region ($E_f$) with $E_F(0)$, it is seen that $E_f > E_F(0)$. The difference between two values can be attributed to an activation energy associated with the drift mobility of electrons. Thus, the activation energy consists of one part associated with the generation of electrons and the other part associated with the hopping of the polarons between equivalent sites.
4.1.12 Dielectric Studies:

The variation of dielectric constant $\varepsilon'$, dielectric constant $\varepsilon''$, loss tangent $\tan \delta$, a.c. conductivity were studied for $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$ system where $[x = 0.0, 0.2, 0.4]$. This is carried out by applying frequencies from $10^2$ to $10^5$ Hz, and the results of each compositions are displayed in figures 4.26(a) to 4.26(c), 4.27(a) to 4.27(c), 4.28(a) to 4.28(c) and 4.29(a) to 4.29(c). The real part ($\varepsilon'$) of the dielectric constant and dielectric loss tangents ($\tan \delta$) have been calculated by using the following formula.

$$\varepsilon' = C t / (\varepsilon_0 A) \quad \text{.............}$$

and

$$\delta = \frac{\varepsilon''}{\varepsilon'} \quad \text{...............}$$

were $C$ is the capacitance due to the presence of the sample between the two electrodes of the sample holder, $t$ is the thickness of the sample, $A$ is its crossectional area, $\varepsilon_0$ is the free space permittivity, and the a.c. conductivity of the system was calculated according to the formula.

$$\sigma_{\text{a.c.}} = 2 \pi f \tan \delta \varepsilon_0 \varepsilon_r \quad \text{...............}$$
This equation is used to calculate the a.c. conductivity using dielectric constant and \( \tan \delta \) at a given frequency. It is to be noted that both \( \tan \delta \) and \( \varepsilon_r \) were available from dielectric measurements.

4.1.13 Frequency dependence of the dielectric constant \( \varepsilon' \):

The frequency variation of the dielectric constant at room temperature for the composition \( x = 0.0, 0.2, 0.4 \) are shown in the figure 4.26(a) to 4.26(c). The trend of the decreasing dielectric constant with increasing frequency is observed in the range of \( 10^2 \) to \( 10^5 \) Hz. for the above mentioned compositions.

Above mention figures clarifies two important points

1) There is no example of presence of P-type charge carriers at room temperature.

2) The distribution of Pb in A and B sites is reasonably valid. Because, it can be seen from figure that the values of dielectric constant \( (\varepsilon) \) decreases with increasing \( \text{Pb}^{4+} \) substitution.

[ ] Finally, as the \( \text{Pb}^{4+} \) content increases more (at \( x=0.4 \)) on the expense of the iron content the dielectric constant decreases again
as a result of decreasing the n-type charges in the sample as a whole, and the formation of number of Fe$^{2+}$ions on B sites.

4.1.14 Frequency dependence of the dielectric losses (tanδ)

The variation of tanδ with log frequency for the composition x=0.0, 0.2 and 0.4 is shown in the figure 4.28(a) to 4.28(c). From the figure it is manifested that the samples show dispersion in tan(δ). When the frequency of hopping charge carriers equal or nearly equal with the frequency of external applied electric field, a maximum in the dielectric loss can be obtained. The samples of the present system does not exhibit the peak in the plot of tan δ versus frequency indicating that the frequency at which maximum dielectric loss occurs is beyond 1MHz.
Conclusions

1) The system Mg_{1+x}Pb_xFe_{2-2x}O_4 with x=0 to x=0.4 (with step of 0.1) has single phase spinel structure.

2) The lattice parameter increase up to x=0.1 and then decreases from x=0.2 to x=0.4 with increase in Mg^{2+} and Pb^{4+} content. The variation of lattice parameter is due to the closeness of the ionic radii of Mg^{2+} (0.65 Å) ions, Fe^{3+} (0.64 Å) and Pb^{4+} (0.70 Å) ions.

3) The particle size of the system is between 542.156 Å to 897.838 Å.

4) The percentage porosity of the sintered pellets is between 4.05 to 14.52%.

5) The cation distribution suggests that Mg^{2+} and Pb^{4+} have less preference for A site and strong preference for B site respectively.

6) The saturation magnetization and magneton number decrease with the increase in Mg^{2+} and Pb^{4+} content in the system.
7) The values of magnetic moment indicate that the system obeys Neel’s two sublattice collinear model for ferrimagnetism.

8) The IR spectrum of Mg\(^{2+}\) and Pb\(^{4+}\) substituted cobalt ferrite is found to exhibit two major bands in the wave number range 410-610 cm\(^{-1}\). No absorption bands were observed above 610 cm\(^{-1}\).

9) The d.c. electrical resistivity of all the samples of the system decreases with increase in temperature indicating the semiconductor behavior of the system and obeys the Arrhenius relation.

10) At a particular temperature the system changes from ferrimagnetism to paramagnetism.

11) The thermoelectric power study indicates that the n-type majority charge carriers are accountable for the conduction mechanism.

12) The both inter ionic distances between the cation anion and between cations, decrease with increasing Mg\(^{2+}\) and Pb\(^{4+}\) concentration (x), but the distance between anion and A site
cation (p,q,r,s) also decreases on substitution of $\text{Mg}^{2+}$ and $\text{Pb}^{4+}$ in the system.

13) The observed increase $\theta_3$ and $\theta_4$ angles suggests weakening of A-B interaction while decrease in $\theta_1$, $\theta_2$, $\theta_5$ suggest strengthening B-B and A-A interaction on increase $\text{Mg}^{2+}$ and $\text{Pb}^{4+}$ substitution in the system.
<table>
<thead>
<tr>
<th>Composition (X)</th>
<th>Lattice Parameter</th>
<th>X-ray Density</th>
<th>Bulk Density</th>
<th>Partical size t.A</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a_{\text{exp.}} ) ( ^0 )</td>
<td>( a_{\text{cal.}} ) ( ^{03924} )</td>
<td>dx- ( \text{gm/cm}^3 )</td>
<td>gm/cm(^3)</td>
<td>( ^0 )</td>
</tr>
<tr>
<td>0.0</td>
<td>8.3645</td>
<td>8.3694</td>
<td>4.4906</td>
<td>3.6082</td>
<td>897.838</td>
</tr>
<tr>
<td>0.1</td>
<td>8.3722</td>
<td>8.3682</td>
<td>4.7614</td>
<td>4.0235</td>
<td>888.163</td>
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<tr>
<td>0.2</td>
<td>8.3727</td>
<td>8.3688</td>
<td>5.0323</td>
<td>4.5368</td>
<td>878.752</td>
</tr>
<tr>
<td>0.3</td>
<td>8.3705</td>
<td>8.3665</td>
<td>5.4126</td>
<td>4.7074</td>
<td>851.911</td>
</tr>
<tr>
<td>0.4</td>
<td>8.3642</td>
<td>8.3602</td>
<td>5.5848</td>
<td>4.6894</td>
<td>542.156</td>
</tr>
</tbody>
</table>

Table 4.1 Variation of lattice parameter, x-ray density, particle size and porosity for 
\( \text{Mg}_{1+x} \text{Pbx Fe}_{2-2x} \text{O}_4 \) system
<table>
<thead>
<tr>
<th>(X)</th>
<th>Cation distribution</th>
<th>Intensity Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A-Site</td>
<td>B-Site</td>
</tr>
<tr>
<td>0.0</td>
<td>(Mg\textsuperscript{2+}\textsubscript{.10}Fe\textsuperscript{3+}\textsubscript{.90})</td>
<td>(Mg\textsuperscript{2+}\textsubscript{.90}Fe\textsuperscript{3+}\textsubscript{.10})</td>
</tr>
<tr>
<td>0.1</td>
<td>(Mg\textsuperscript{2+}\textsubscript{.157}Pb\textsuperscript{4+}\textsubscript{.032}F\textsuperscript{3+}\textsubscript{.811})</td>
<td>(Mg\textsuperscript{2+}\textsubscript{.943}Pb\textsuperscript{4+}\textsubscript{.072}Fe\textsuperscript{3+}\textsubscript{.985})</td>
</tr>
<tr>
<td>0.2</td>
<td>(Mg\textsuperscript{2+}\textsubscript{.16}Pb\textsuperscript{4+}\textsubscript{.099}F\textsuperscript{3+}\textsubscript{.741})</td>
<td>(Mg\textsuperscript{2+}\textsubscript{1.04}Pb\textsuperscript{4+}\textsubscript{.10}Fe\textsuperscript{3+}\textsubscript{.859})</td>
</tr>
<tr>
<td>0.3</td>
<td>(Mg\textsuperscript{2+}\textsubscript{.229}Pb\textsuperscript{4+}\textsubscript{.129}F\textsuperscript{3+}\textsubscript{.642})</td>
<td>(Mg\textsuperscript{2+}\textsubscript{1.07}Pb\textsuperscript{4+}\textsubscript{.17}Fe\textsuperscript{3+}\textsubscript{.758})</td>
</tr>
<tr>
<td>0.4</td>
<td>(Mg\textsuperscript{2+}\textsubscript{.29}Pb\textsuperscript{4+}\textsubscript{.15}F\textsuperscript{3+}\textsubscript{.55})</td>
<td>(Mg\textsuperscript{2+}\textsubscript{1.10}Pb\textsuperscript{4+}\textsubscript{.24}Fe\textsuperscript{3+}\textsubscript{.65})</td>
</tr>
</tbody>
</table>

Table 4.2 Cation Distribution and intensity ratios for Mg\textsubscript{1+x}Pb\textsubscript{x}Fe\textsubscript{2-2x}O\textsubscript{4} system

111
<table>
<thead>
<tr>
<th>$x$</th>
<th>$V_1 \text{ cm}^{-1}$</th>
<th>$V_2 \text{ cm}^{-1}$</th>
<th>$R_A \text{ nm}$</th>
<th>$R_B \text{ nm}$</th>
<th>$K_t \times 10^2 \text{ N/m}$</th>
<th>$K_0 \times 10^2 \text{ N/m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>600</td>
<td>420</td>
<td>0.19918</td>
<td>0.20028</td>
<td>1.4454</td>
<td>0.7803</td>
</tr>
<tr>
<td>0.1</td>
<td>590</td>
<td>430</td>
<td>0.19915</td>
<td>0.20026</td>
<td>1.4784</td>
<td>0.9116</td>
</tr>
<tr>
<td>0.2</td>
<td>600</td>
<td>430</td>
<td>0.19913</td>
<td>0.20024</td>
<td>1.8046</td>
<td>0.9246</td>
</tr>
<tr>
<td>0.3</td>
<td>610</td>
<td>420</td>
<td>0.19911</td>
<td>0.20021</td>
<td>1.9322</td>
<td>0.9722</td>
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<tr>
<td>0.4</td>
<td>590</td>
<td>410</td>
<td>0.19896</td>
<td>0.20007</td>
<td>1.8568</td>
<td>1.0167</td>
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Table 4.3 Vibration frequency, Bond lengths and force constant for Mg$_{1+x}$Pb$_x$Fe$_{2-2x}$O$_4$ system
<table>
<thead>
<tr>
<th>x</th>
<th>a exp</th>
<th>rA</th>
<th>rB</th>
<th>r=rA+rB/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.3942</td>
<td>0.6410</td>
<td>0.6445</td>
<td>0.6428</td>
</tr>
<tr>
<td>0.1</td>
<td>8.3930</td>
<td>0.6435</td>
<td>0.6469</td>
<td>0.6452</td>
</tr>
<tr>
<td>0.2</td>
<td>8.3928</td>
<td>0.6475</td>
<td>0.6482</td>
<td>0.6479</td>
</tr>
<tr>
<td>0.3</td>
<td>8.3913</td>
<td>0.6500</td>
<td>0.6505</td>
<td>0.6503</td>
</tr>
<tr>
<td>0.4</td>
<td>8.3850</td>
<td>0.6523</td>
<td>0.6529</td>
<td>0.6526</td>
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</tbody>
</table>

Table 4.4 Variation of ionic radii and tetrahedral and octahedral site and average of ionic radii

<table>
<thead>
<tr>
<th>x</th>
<th>rA</th>
<th>rB</th>
<th>a exp</th>
<th>a th</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6410</td>
<td>0.6445</td>
<td>8.3942</td>
<td>8.3839</td>
</tr>
<tr>
<td>0.1</td>
<td>0.6435</td>
<td>0.6469</td>
<td>8.3930</td>
<td>8.3940</td>
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<tr>
<td>0.2</td>
<td>0.6475</td>
<td>0.6482</td>
<td>8.3928</td>
<td>8.4040</td>
</tr>
<tr>
<td>0.3</td>
<td>0.6500</td>
<td>0.6505</td>
<td>8.3913</td>
<td>8.4136</td>
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<td>0.4</td>
<td>0.6523</td>
<td>0.6529</td>
<td>8.3850</td>
<td>8.4234</td>
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</tbody>
</table>

Table 4.5 Variation of ionic radii and lattice parameter [theoretical and observed] for Mg$_{1+x}$Pb$_x$Fe$_{2-2x}$O$_4$ system
| r no. | saturation Magnetization $\sigma_s$(emu/gm) | $\eta_B (\mu_B)$ | $|CA-CB|$ | Tc (K) |
|-------|------------------------------------------|-----------------|-----------|--------|
|       |                                          | Cal. | Obs.       |        |        |
| 0.0   | 34.965                                   | 1    | 1.252      | 0.25   | 713    |
| 0.1   | 25.334                                   | 0.87 | 0.961      | 0.09   |        |
| 0.2   | 19.552                                   | .59  | .784       | 0.19   | 703    |
| 0.3   | 17.303                                   | .58  | 0.746      | 0.17   |        |
| 0.4   | 11.684                                   | 0.50 | 0.519      | 0.02   | 693    |

Table 4.6 Saturation magnetization, Bhors magneton and Curie temperature for $Mg_{1+x}Pb_xFe_{2-2x}O_4$ system
<table>
<thead>
<tr>
<th>x</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>2.96728</td>
<td>2.96693</td>
<td>2.96693</td>
<td>2.966219</td>
<td>2.9641</td>
</tr>
<tr>
<td>c</td>
<td>3.47931</td>
<td>3.4789</td>
<td>3.4789</td>
<td>3.47807</td>
<td>3.47558</td>
</tr>
<tr>
<td>d</td>
<td>3.6346</td>
<td>3.63417</td>
<td>3.63417</td>
<td>3.633303</td>
<td>3.63071</td>
</tr>
<tr>
<td>e</td>
<td>5.4519</td>
<td>5.45125</td>
<td>5.45125</td>
<td>5.449955</td>
<td>5.44606</td>
</tr>
<tr>
<td>f</td>
<td>5.13923</td>
<td>5.13861</td>
<td>5.13861</td>
<td>5.13739</td>
<td>5.13372</td>
</tr>
<tr>
<td>p</td>
<td>1.99491</td>
<td>1.99463</td>
<td>1.9936</td>
<td>1.993036</td>
<td>1.99167</td>
</tr>
<tr>
<td>q</td>
<td>1.99672</td>
<td>1.99656</td>
<td>1.99834</td>
<td>1.998017</td>
<td>1.99648</td>
</tr>
<tr>
<td>r</td>
<td>3.82281</td>
<td>3.82251</td>
<td>3.82592</td>
<td>3.825302</td>
<td>3.82235</td>
</tr>
<tr>
<td>s</td>
<td>3.69441</td>
<td>3.69399</td>
<td>3.69459</td>
<td>3.693758</td>
<td>3.69108</td>
</tr>
<tr>
<td>1</td>
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<td>121.3</td>
<td>121.265</td>
<td>121.2585</td>
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<td>2</td>
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<td>136.85</td>
<td>136.71</td>
<td>136.7</td>
<td>136.7</td>
</tr>
<tr>
<td>3</td>
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<td>96.1</td>
<td>96.17</td>
<td>96.17</td>
<td>96.17</td>
</tr>
<tr>
<td>4</td>
<td>126.575</td>
<td>126.576</td>
<td>126.59</td>
<td>126.591</td>
<td>126.586</td>
</tr>
<tr>
<td>5</td>
<td>69.325</td>
<td>69.32</td>
<td>69.225</td>
<td>69.217</td>
<td>69.211</td>
</tr>
</tbody>
</table>

Table 4.7 Interatomic distances and bond angles for Mg$_{1+x}$Pb$_x$Fe$_{2-2x}$O$_4$ system. (Distances in Å and angles in degree)
<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Activation Energy $\Delta E$ in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ferrimagnetic Region MF</td>
</tr>
<tr>
<td>0.0</td>
<td>0.995</td>
</tr>
<tr>
<td>0.2</td>
<td>0.481</td>
</tr>
<tr>
<td>0.4</td>
<td>1.262</td>
</tr>
</tbody>
</table>

Fig. 4.8  The variation of ferrimagnetic and paramagnetic region with composition $x$ for the system.

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Extrapolated values $E_f(0)$ eV</th>
<th>Activation energy in Ferrimagnetic region in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>$-9.138 \times 10^{-5}$</td>
<td>0.995</td>
</tr>
<tr>
<td>0.2</td>
<td>$-9.932 \times 10^{-5}$</td>
<td>0.481</td>
</tr>
<tr>
<td>0.4</td>
<td>$-9.138 \times 10^{-5}$</td>
<td>1.262</td>
</tr>
</tbody>
</table>

Fig. 4.9  The difference between extrapolated values and activation values in ferrimagnetic region.
Figure 4.1 X-Ray Diffraction pattern of the system $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$ for $x = 0.0$
Figure 4.2  X-Ray Diffraction pattern of the system $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$ for $x = 0.1$
Figure 4.3 X-Ray Diffraction pattern of the system $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$ for $x = 0.2$
Figure 4.4 X-Ray Diffraction pattern of the system $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$
for $x = 0.3$
Figure 4.5  X-Ray Diffraction pattern of the system Mg$_{1-x}$Pb$_x$Fe$_{2-2x}$O$_4$ for $x = 0.4$
Fig. 4.6 Variation of lattice constant $a(A^0)$ with concentration ($x$) for $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$ system.
Fig. 4.7 Variation of Ionic radii rA and rB with composition x
Figure 4.8 Variation of X-ray density and bulk density with concentration (x)
Fig. 4.9 variation of $R_A$ and $R_B$ with concentration ($x$)
Figure 4.10 IR Spectra of $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$ System for $x=0.0$
Figure 4.11 IR Spectra of Mg$_{1+x}$Pb$_x$Fe$_{2-2x}$O$_4$ System for x=0.1
Figure 4.12  IR Spectra of Mg$_{1+x}$Pb$_x$Fe$_{2-2x}$O$_4$ System for x=0.2
Figure 4.13  IR Spectra of Mg_{1+x}Pb_{x}Fe_{2-2x}O_{4} System for x=0.3
Figure 4.14  IR Spectra of $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$ System for $x=0.4$
Fig. 4.15 Variation $K_t$ with $R_A$ for the system
Fig. 4.16 Variation of $K_n$ with $R_\theta$ for $\text{Mg}_{1.6} \text{Pb}_{0.4} \text{Fe}_{2.2} \text{O}_4$
Fig 4.17 Variation of $nB(\mu B)$ with $Pb^{4+}$ with concentration, $x$
Fig. 4.18 Thermal variation of d.c. resistivity for the composition $x=0.0$ for the system
Fig. 4.19 Thermal variation of dc resistivity for the composition $x=0.2$, for $\text{Mg}_{1+x} \text{Pb}_x \text{Fe}_{2-2x} \text{O}_4$. 
Fig. 4.20 Thermal variation of dc resistivity for the composition $x=0.4$ for the system
Figure 4.21 Configurations of the ion pairs in spinel ferrites with favourable distances and angles for effective magnetic interactions.
Figure 4.22: Thermal variation of seebeck coefficient for $x=0.0, 0.1, 0.2, 0.3, 0.4$ composition of $M_{1+x}Pb_xFe_{2-x}O_4$. 
Fig 4.23 Graph of Fermi energy $E_F$ (eV) against temp(K) for $A=0$ and $2$ for composition $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$ for $x=0.0$
Fig 4.24 Graph of Fermi energy $E_f(eV)$ against temp(K) for $A=0$ and 2 for composition $\text{Mg}_ {1-x} \text{Pb}_ x \text{Fe}_{2+2x} \text{O}_4$ for $x=0.1$.

$E_f(0) eV = 9.9323 \times 10^{-2} eV$
Fig 4.25 Graph of Fermi energy $E_f$(eV) against temp(K) for A=0 and 2 for composition $\text{Mg}_{1-x}\text{Pb}_x\text{Fe}_{2x}\text{O}_4$ for $x=0.2$.
Fig 4.26 Graph of Fermi energy $E_f(\text{eV})$ against temp(K) for $A=0$ and $2$ for composition for $x=0.4$
Fig 4.27(a) Frequency dependence of the dielectric constant ($\varepsilon'$) at room temperature for the system Mg$_{1-x}$Pb$_x$Fe$_{2-2x}$O$_4$. 

$x = 0.0$
Fig 4.27(b) Frequency dependence of the dielectric constant ($\varepsilon'$) at room temperature for the system $\text{Mg}_{1+x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$
Fig 4.27(c) Frequency dependence of the dielectric constant ($\varepsilon'$) at room temperature for the system Mg$_{1+x}$Pb$_x$Fe$_{2x}$O$_4$
Fig 4.28(a) Frequency dependence of the dielectric loss tangent (tan$\delta$) for the system Mg$_{1+x}$Pb$_x$Fe$_{2.2x}$O$_4$
Fig 4.28(b) Frequency dependence of the dielectric loss tangent ($\tan\delta$) for the system $\text{Mg}_{1-x}\text{Pb}_x\text{Fe}_{2-2x}\text{O}_4$. $x = 0.2$
Fig 4.28(c) Frequency dependence of the dielectric loss tangent \( \tan(\delta) \) for the system \( \text{Mg}_{1-x} \text{Pb}_x \text{Fe}_{2+2x} \text{O}_4 \)
Fig 4.29(a) Complex dielectric constant versus frequency curves for the system Mg$_{3+x}$ Pb$_x$ Fe$_{2-x}$ O$_4$
Fig 4.29(b) Complex dielectric constant versus frequency curves for the system $\text{Mg}_{1+x} \text{Pb}_x \text{Fe}_{2-2x} \text{O}_4$
Fig 4.29(c) Complex dielectric constant versus frequency curves for the system Mg$_{1+x}$Pb$_x$Fe$_{2-2x}$O$_4$
Fig 4.30(a) The experimental a.c. conductivity $\sigma V/s$ Frequency for $x = 0.0$
Fig 4.30(b) The experimental a.c. conductivity $\sigma V/s$ Frequency for $x = 0.2$
Fig 4.30(c) The experimental a.c. conductivity $\sigma V/s$ Frequency for $x = 0.0$
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