Our Heritage (UGC Care Listed)
ISSN: 0474-9030 Vol-68, Special Issue-12
National Conference on Recent Trends in Physics, Chemistry and Mathematics (RTPCM-2020)
Held on 4th February 2020
Organised by: Department of Physics, Chemistry and Mathematics, Sunderrao Solanke Mahavidyalaya, Majalgaon, MS

Electrical, Dielectric And Thermoelectric Power Studies Of Pb^{4+} Ions Substituted Cobalt Ferrites

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Abstract: The variation of ac resistivity (ρ_{ac}) and other parameter such as dielectric constant (ε'), dielectric loss (ε''), loss tangent (tanδ) and thermoelectric power studies of $Co_{1+x}Pb_xFe_{2-2x}O_4$ ferrite system has been carried out as a function of temperature and composition. The variation of ac resistivity (ρ_{ac}) with temperature shows unusual metal like behavior up to approximately 375^0K thereafter shows conventional behavior of ferrites. Dielectric constant (ε'), dielectric loss (ε'') and loss tangent (tanδ) increases very slowly in the beginning till the temperature reaches 520^0K and then increases very rapidly. These observed variations have been explained on the basis of electronic exchange between $Fe^{2+}\Leftrightarrow Fe^{3+}$, $Co^{2+}\Leftrightarrow Co^{3+}$ cations on (A) and [B] sites and local displacement of electrons in the direction of electric field..

Thermoelectric power (TEP) studies of prepared compositions were carried out from temperature 300 to 700^0K using differential method. The variation of Seebeck coefficient (α) with temperature indicated p-type semiconducting nature of the composition at higher temperature and further increasing temperature shows n-type semiconducting nature indicating the conduction due to electron. The Curie temperature

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(T_C) of the prepared compositions measured from the Arrehenius plots of logρ versus $10^3/T$ and shows a decreasing trend with the increasing Pb^{4+} concentration.

Keywords: Ferrites; Electrical properties; Dielectric Properties; thermoelectric power; Seebeck coefficient;

1. Introduction:

The spinel ferrites have attracted considerable interest due to their uses in microwave devices, magnetic data storage and bio-medical applications [1-3]. These ferrites have general formula $(A^{2+})\ [B^{3+}]_2O_4^{2-}$ where A^{2+} and B^{3+} are the divalent and trivalent ions occupying tetrahedral (A) and octahedral [B] sites . FCC structure of the spinel ferrites is result of cations and oxygen anions formulation. Divalent cations occupies either tetrahedral or octahedral sites when it occupies tetrahedral sites normal spinel is formed. On the other hand when the divalent cation occupies both tetrahedral as well as octahedral sites inverse spinel is formed [4].

The electrical, dielectric and thermoelectric properties of ferrites depend on several factors such as method of preparation, sintering condition and distribution of cations among tetrahedral (A) and octahedral [B] sites. $CoFe_2O_4$ and $NiFe_2O_4$ are extensively studied spinel ferrites due to their large number of application [5-6]. $CoFe_2O_4$ is most versatile hard magnetic material with cubic spinel structure having Fd3m space group which exhibits high coercivity (~5400 Oe) high magneto crystalline anisotropy and moderate saturation magnetization [7-8]. Survey of literature shows that the physical properties of Pb^{4+} ions substituted ferrites have not been studied therefore an attempt has

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been made to study the effect of Pb^{4+} ions substitution on electrical, dielectric and thermoelectric power of $CoFe_2O_4$ system.

2. Experimental:

Samples with composition $Co_{1+x}Pb_xFe_{2-2x}O_4$ (x = 0.0 to 0.5) were prepared by standard ceramic technique. The starting materials were of analytical reagent grade Cobalt oxide CoO (Riedel), lead dioxide PbO_2 (CDH) and ferric oxide Fe_2O_3 (Riedel). These oxides were mixed in proper proportion to yield desired stoichiometric composition. Each composition was ground for half an hour in an agate mortar. The mixture was presintered at 950^0C for 24 hrs and slowly cooled to room temperature. The presintered compositions were ground for one hour to get homogeneous powder. The pellets were made from the presintered powder under the pressure of 5 tones per square inch using acetone as a binder. These pellets were finally sintered in air at 1000^0C for 24 hours and naturally cooled to room temperature. X-ray diffraction patterns of all the samples of present systems confirm the single-phase cubic spinel structure formation. The detail regarding sample preparation, structural and magnetic properties have been studied in our reported research paper [9].

The ac resistivity (ρ_{ac}), dielectric constant (ε'), dielectric loss (ε'') and loss tangent ($\tan\delta$) was measured by means of two probe method at 1 KHz frequency using Aplab made LCR-Q meter . For good electrical contact pellets were polished and silver paste was applied on end surfaces. The resistivity measurements were carried out from room

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temperature to well above the Curie temperature. During the measurement sufficient time was allowed to sample to attain equilibrium temperature. The resistivity (ρ) was calculated by using the relation

$$\rho = \frac{\pi r^2 R}{t} \qquad (1)$$

where *r* is the radius of the pellet, *t* the thickness of the pellet and *R* the resistance.

The activation energy was calculated from the plot of $\log\rho_{ac}$ versus reciprocal of temperature. The dielectric constant (ε) was calculated by using the formula

$$\varepsilon' = \frac{ct}{\varepsilon_0 A} \qquad (2)$$

where *c* is the capacitance of the sample, *t* is the thickness of the pellets, *A* the is area of cross of pellet and ε_0 is permittivity of the free space.

The value of loss tangent (tanδ) were calculated by using the relation,

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad (3)$$

Also $\tan\delta = 1/Q$ where Q is the quality factor.

The Seebeck coefficient was measured as a function of temperature and composition. For its measurement the pellet was kept in heating cell by keeping the temperature difference (Δt) = 20^0c across the pellets. The thermoelectric power or Seebeck coefficient is calculated by using the relation [10],

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$$\alpha = \frac{\Delta E}{\Delta T} \qquad (mV/K) \qquad (4)$$

Where ΔE is thermoemf produced across the two ends of the samples and ΔT is temperature difference between the two surfaces of pellets.

3. Results and Discussion:

3.1. Electrical Properties

Ac electrical resistivity of sintered pellets was measured at various temperatures and at fixed frequency 1KHz and from it specific resistivity (ρ) values were calculated. The temperature dependence of resistivity is given by the Arrehenius equation.

$$\rho = \rho_0 e^{(\Delta E / KT)} \qquad (5)$$

where K is Boltzmann's constant, T is temperature in °K and ΔE is activation energy. The activation energy values for conduction are computed from Arrehenius plots of logρ versus $10^3/T$ and is shown in the figure 1.

The ac resistivity (ρ_{ac}) values of different compositions with x = 0.0 to 0.5 at 200^0C and activation values are given in the table 1. The resistivity for all the compositions lies in the range from 2.07×10^5 to 4.57×10^5 Ω-cm, the activation energy lies in the range from 0.40 to 0.57ev. The values of activation energy with compositions are tabulated in the table 1. The Arrehenius plots (fig.1) for all the compositions show unusual metal like behavior. The resistivity initially increases with increase in the temperature up to approximately 376°K and thereafter it decreases with increases in the temperature, which

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is the conventional behavior of ferrite. The anomalous electrical behavior of resistivity with temperature i.e. the increase in resistivity with increase in temperature is also observed for Sn^{4+} and Zn^{2+} substituted nickel ferrites and has been explained on the basis of electron hopping and current due to the electrons in conduction band [11]. Such metal like unusual characteristics is reported in [12].

3.2. Dielectric Properties:

The variation of dielectric constant (ε) for different compositions with x = 0.0 to 0.5 as a function of temperature at fixed frequency of 1 KHz is shown in the figure 2.
From the figure 2 it appears that the dielectric constant remains constant or increases very slowly in the beginning till the temperature reaches to 525ºK and then increases very rapidly. Since the resistivity of ferrites decreases with increase in temperature, an increase in dielectric constant at high temperature is expected because the resistivity and the dielectric constant are inversely related. Such a behavior has been reported by K. M. Jadhav et.al. [13] in case of Co-Si ferrite system, Shaikh et. al [14] in case of Li-Mg-Zn ferrite system and Bellad et. al [15] in case Li-Cd ferrites.

The variation of dielectric loss (ε'') as a function of temperature for all the compositions at a frequency 1 KHz is shown in the figure 3. It is observed from the figure 3, that the dielectric loss (ε'') almost remains constant or varies very slowly up to 600 ºK (approx.) and then increases very rapidly in the same way as the dielectric constant (ε') increases. This behavior of temperature dependence of dielectric constant (ε) and

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dielectric loss (ε'') for $Co_{1+x}Pb_xFe_{2-2x}O_4$ ferrite system is in full agreement with that obtained by V.A. Ioffe et al [16] in spinel ferrites.

Accourding to Rabkin and Novikova [17] in the spinel ferrites the process of dielectric polarization takes place through a mechanism similar to the conduction process. By electronic exchange between $Fe^{2+}\Leftrightarrow Fe^{3+}$ and $Co^{2+}\Leftrightarrow Co^{3+}$, one obtains local displacements of electrons in the direction of applied electric field, these displacement determine the polarization. Both n and p types of carriers contribute the polarization and they depend on temperature. Since the influence of temperature on electronic exchange is more pronounced than on the displacement of p type carriers, hence dielectric constant (ε') and dielectric loss (ε'') increases rapidly with temperature. Certainly these have been observed for various Pb^{4+} compositions in $Co_{1+x}Pb_xFe_{2-2x}O_4$ ferrite system.

The thermal variation of loss tangent (tanδ) for all the compositions at frequency 1 KHz is shown in the figure 4. It can be seen from the figure 4 that loss tangent (tanδ) increases very slowly in the beginning and then increases very rapidly with temperature for all the compositions. This behavior is in good agreement with the, "general rule that is tanδ appreciably increases when the temperature is rise" [18]. The values of dielectric constant (ε'), dielectric loss (ε'') and loss tangent (tanδ) for all the composition at 1 KHz frequency for 200°C are listed in the table 2.

3.3. Thermoelectric Power:

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The thermoelectric power studies of the prepared ferrites composition were measured in the temperature range 300 to 700^0K. The values of Seebeck coefficient (α) of present series at temperature 200^0c are calculated from observed value of thermoemf and are summarize in the table 2. From the table 2 it can be observed that Seebeck coefficient decreases with increase in Pb^{4+} compositions these decrease in the Seebeck coefficient (α) may be attributed to replacement of Fe^{3+} ios on B sites by adding Pb^{4+} concentrations. Similar results have been reported for rare earth elements substitution in Mg-Cd ferrites by Bhosale et al [19] and Cu-Cd ferrites by Kolekar et al [20]. The fig. 5 shows the variation of Seebeck coefficient (α) with temperature for all the prepared compositions.

From the figure 5 it can be seen that, the values of Seebeck coefficient (α) was positive at high temperature except composition x = 0.4. By increasing temperature Seebeck coefficient attain negative values for all the ferrite samples under investigation. This indicates that, at high temperature these prepared compositions have p-type semiconductor. By increasing the temperature further the Seebeck coefficient reverses its sign and becomes negative at about the temperature greater than 550^0K these indicates that the predominant conduction mechanism in these ferrites was due to the electrons and it behaves like the n-type semiconductors. Such type of conductivity is attributed to the hopping of electrons between Fe^{2+} and Fe^{3+} ions at octahedral sites. The n-type conducting mechanism can be written as follows

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$$Fe^{2+} \Leftrightarrow Fe^{3+} + e^{-1}$$

4. Conclusion

The addition of Pb^{4+} ions causes appreciably changes in the electrical, dielectric and thermoelectric power of cobalt ferrites system. High value of resistivity (2.07×10^5 to 4.57×10^5 Ω-cm) and low value of dielectric loss tangent are obtained. This shows that the present ferrite systems are suitable for potential application in microwave devices. At high temperature Seebeck coefficient was positive which indicates p-type semiconducting behavior of ferrites and further increasing the temperature Seebeck coefficient becomes negative and they act like n-type semiconductor.

Acknowledgments

The authors are also thankful to N. R. Shamkuwar, Ex. Prof. and Head, Department of Physics, Dr. Babashed Ambedkar Marathwada University, Aurangabad (M.S.) India for valuable suggestions and guidance. One of the authors (BKL) is indebted to UGC-WRO Pune for supporting this work under the tenure of teacher fellowship.

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Table 1

Resistivity ρ_{ac}, activation energy ΔE and transition temperature (T_C) for $Co_{1+x}Pb_xFe_{2-2x}O_4$ system at 200^0c for 1 KHz frequency

Composition x	ac resistivity (Ω-cm)	Activation energy ΔE (in ev)	Transition Temperature $(T_C)\,^0K$
0.0	9.45x105	0.40	795
0.1	5.71x105	0.48	747
0.2	4.57x105	0.57	717
0.3	7.87x105	0.50	677
0.4	1.26x105	0.55	650
0.5	2.07x105	0.44	622

Table 2

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Dielectric constants (ε'), dielectric loss (ε''), loss tangent (tan δ) and Seebeck coefficient for $Co_{1+x}Pb_xFe_{2-2x}O_4$ system at 200^0c

Composition (x)	Dielectric constants (ε)	Dielectric loss (ε'')	Loss tangent (tan δ)	Seebeck Coefficient (α) in ($mV/^0K$)
0.0	2.37x105	3.00x105	72	24.7
0.1	4.19x105	2.20x107	52	14.9
0.2	2.26x105	7.08x106	31	6.98
0.3	1.55x105	5.53x106	35	17.48
0.4	3.48x105	5.12x105	13	-5.4
0.5	5.37x105	2.54x105	04	17.37

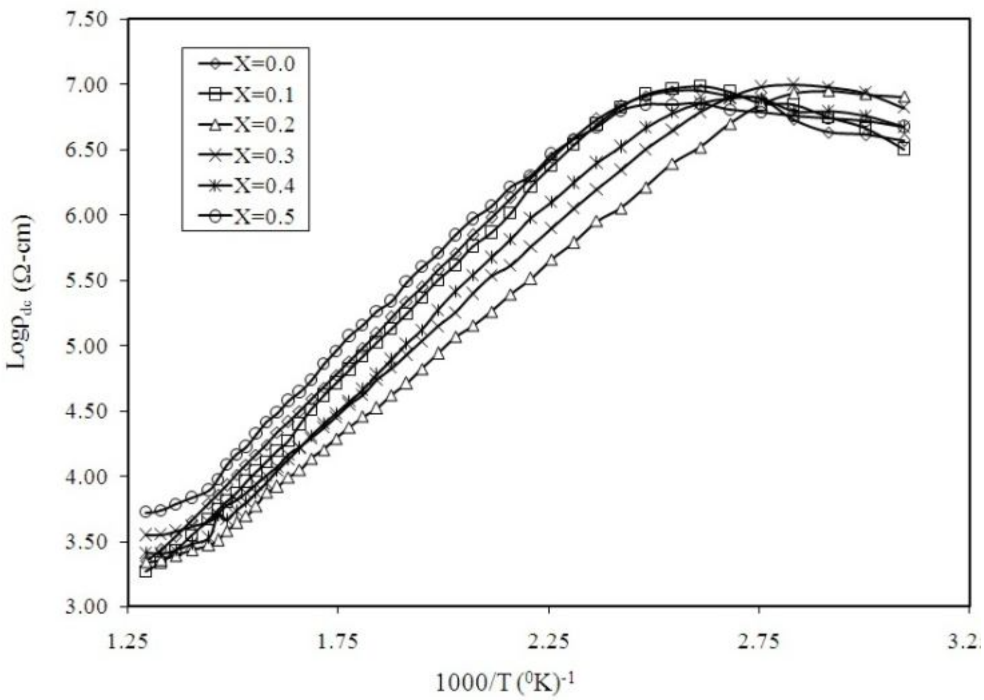

Figure 1 Variation of resistivity Logρ_{ac} with temperature for $Co_{1+x}Pb_xFe_{2-2x}O_4$ ferrite system

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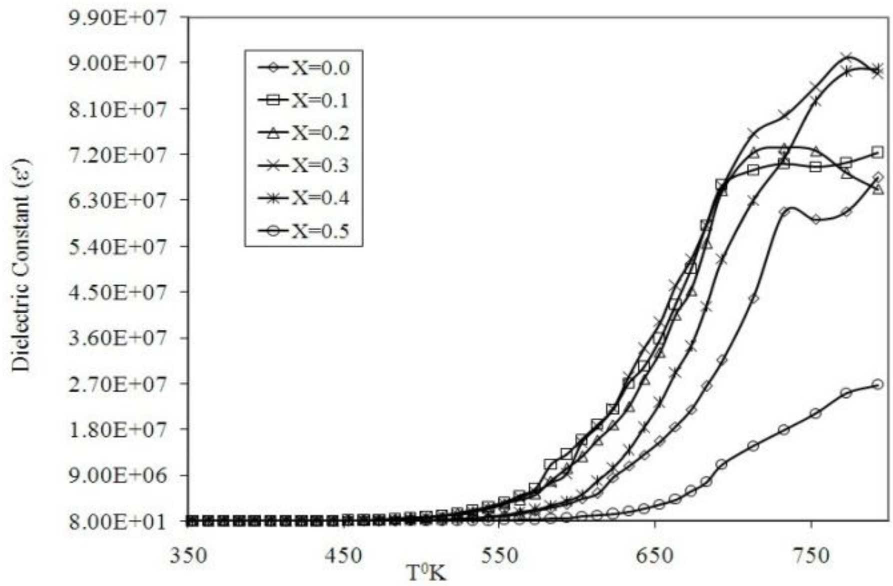

Figure 2 Variation of dielectric constants (ε') with temperature for $Co_{1+x}Pb_xFe_{2-2x}O_4$ ferrite system

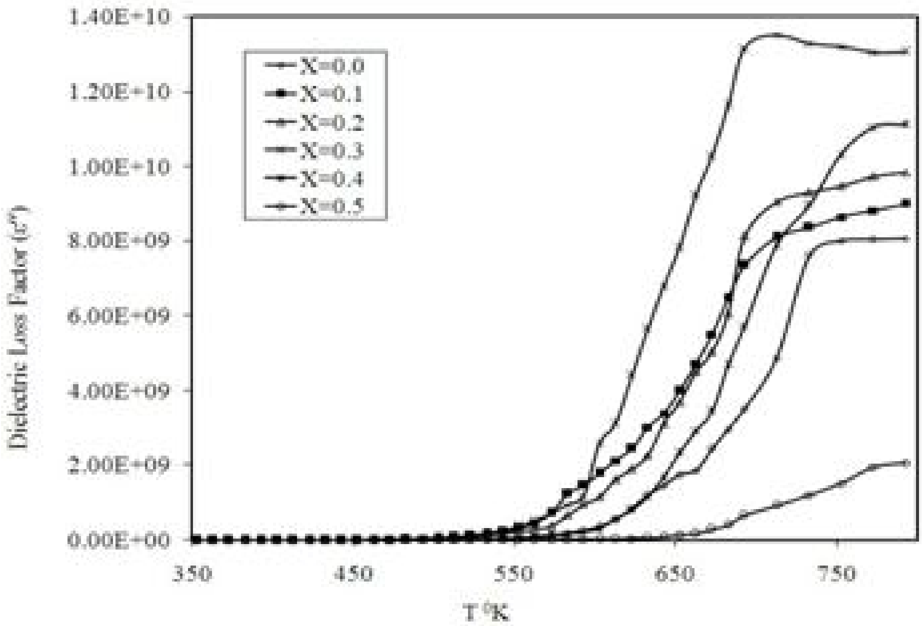

Figure 3 Variation of dielectric loss (ε'') with temperature for $Co_{1+x}Pb_xFe_{2-2x}O_4$ ferrite system

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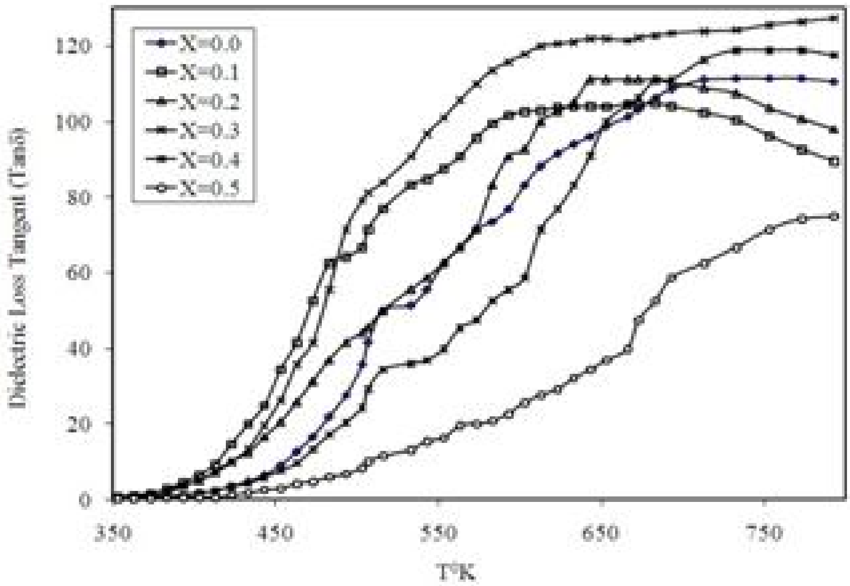

Figure 4 Variation of dielectric Loss tangent (tanδ) with temperature for $Co_{1+x}Pb_xFe_{2-2x}O_4$ ferrite system

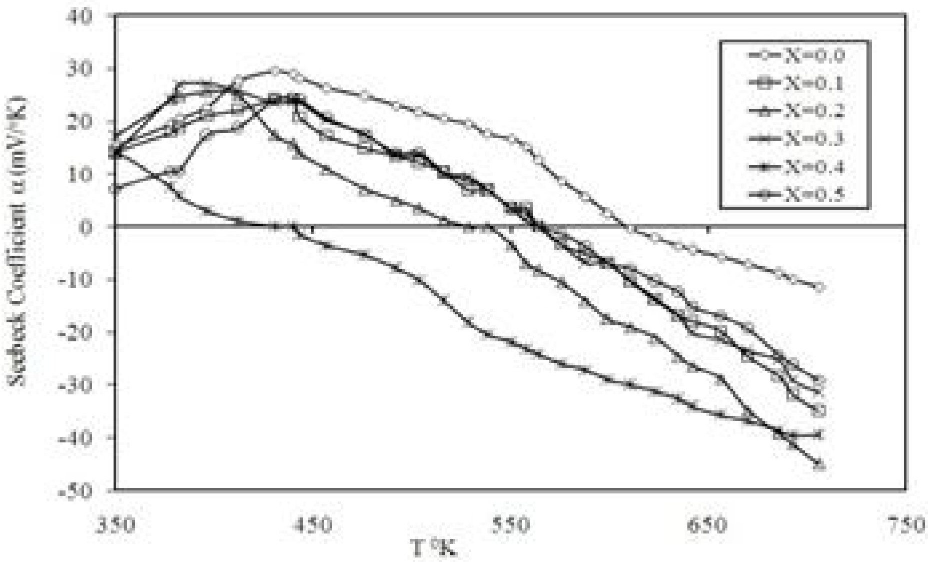

Figure 5 Variation of Seebeck coefficient α (mv/^{0}K) with temperature for $Co_{1+x}Pb_xFe_{2-2x}O_4$ ferrite system

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