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Structural and Magnetic Studies on Pb^{4+} Substituted Cobalt Ferrite System

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ABSTRACT

The polycrystalline samples of $Co_{1+x}Pb_xFe_{2-2x}O_4$ with x = 0.0,0.1,0.2,0.3,0.4, and 0.5 varying in the steps of 0.1 were prepared by using solid state reaction technique. The structural and magnetic properties have been investigated by means of X-ray diffraction, high field magnetization and a. c. susceptibility measurements. The X-ray analysis confirmed the single-phase formation of the samples. The distributions of divalent, trivalent and tetravalent cations among the tetrahedral (A) and octahedral [B] sites have been obtained from the observed and calculated intensity ratios. The X- ray intensity indicates that tetravalent Pb^{4+} ions occupy both A and B sites replacing iron ions. The added Co^{2+} ions also occupy at A sites with replacing iron ions for x = 0.0, 0.1 and 0.2 and there after very small amount of Co^{2+} migrate from A sites to B sites replacing Fe^{3+} ions for the composition x = 0.3, 0.4, 0.5. The variation of saturation magnetic moment per formula unit at room temperature with Pb^{4+} content is satisfactorily explained on the basis of Neel's collinear spin ordering model for all the samples. The Curie temperatures decreases almost linearly with increase of Pb^{4+} content from x = 0.0 to 0.5.

Keywords: Co-Pb Ferrite, Structural Properties, Cations Distribution, Magnetic Properties.

I. INTRODUCTION

Ferrites are widely used in microwave and electrical industries. These are technologically important material because of their interesting physical and chemical properties, which arise due to their ability to distribute the cations among the tetrahedral A and octahedral B sites. The magnetic properties of spinel ferrites are governed by the types of magnetic ions on A and B sites and the strength of magnetic interaction.

Cobalt ferrite is well known hard magnetic material which has been studied extensively due to their high coercivity and moderate saturation magnetization. Survey of literature shows that cobalt ferrite possesses an inverse spinel structure the degree of inversion depends upon method of preparation and heat treatment [1]. The additions of tetravalent ions like Ti^{4+}, Ge^{4+}, Si^{4+} and Pb^{4+} in cobalt, manganese and nickel ferrites influence structural and magnetic properties of ferrite systems [2-7]. No work has been reported regarding Pb^{4+} substituted cobalt ferrite exist in the literature so far. In the present work the effect of Pb^{4+} substitution on structural and magnetic properties of $Co_{1+x}Pb_xFe_{2-2x}O_4$ spinel ferrites system using X-ray diffraction, magnetization and susceptibility has been studied.

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II. METHODS AND MATERIAL

The six samples of $Co_{1+x}Pb_xFe_{2-2x}O_4$ with x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 were prepared by solid-state reaction technique. The starting materials were analytical reagent grade CoO, PbO_2 and Fe_2O_3. These oxides were mixed in proportion to yield desired stoichemetric compositions then each composition was ground for one hour in an agate mortar. The mixture was then presintered at 950 ^{0}C for 24 h and then slowly cooled to room temperature. The presintered powder was milled again to a fine powder. The powder was pressed under the pressure of 5 tones per square inch to form the pellets by using acetone as a binder. The pellets were finally sintered in an air at 1000 ^{0}C for 24 h and then they were naturally cooled to room temperature. The X-ray diffraction (XRD) pattern of all the samples were obtained on computerized Siemen's 500 D diffractometer at the rate of scanning speed 2 deg per minutes using Cu-Kα radiation (λ = 1.5418Å). The saturation magnetization of each sample in the form of pellets at room temperature was carried out using high field hysterisis loop technique [8]. The low field a. c. susceptibility measurements on powder samples were carried out in the temperature range 300–800 K using double coil setup [9] operating at frequency of 236 Hz and in the r.m.s. field of 39.8 ampere per meter or Am^{-1}.

III. RESULTS AND DISCUSSION

The single phase spinel nature of the samples was confirmed from X-ray diffraction pattern as shown in Fig.1. a and b.

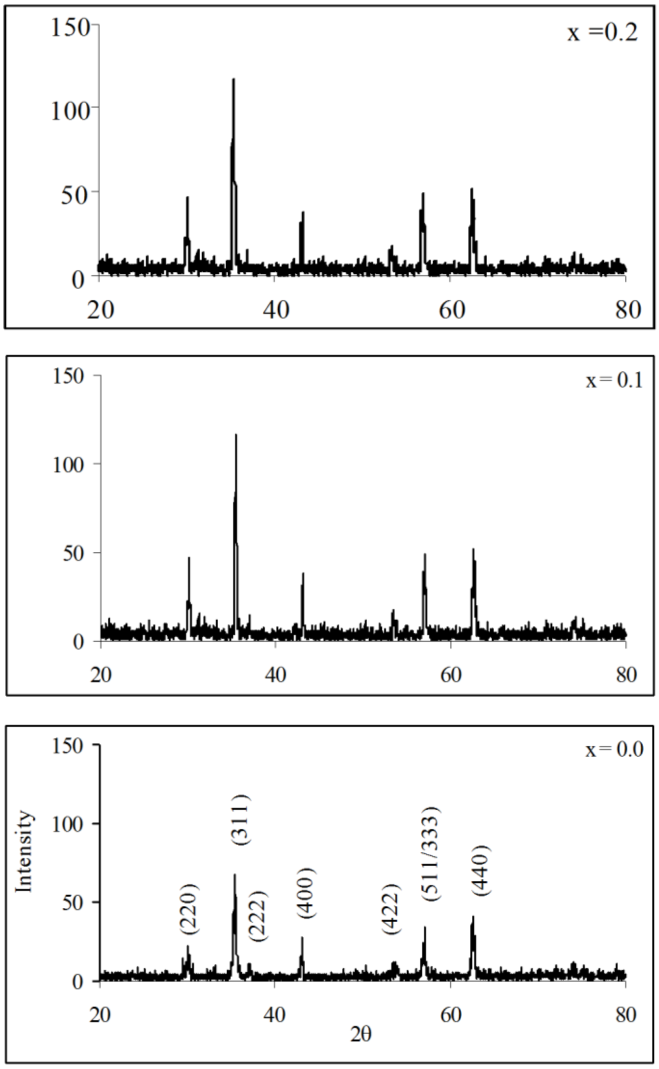
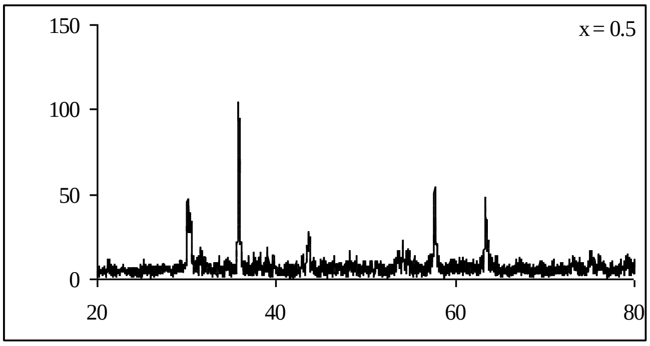


Figure 1 (a) X-ray diffraction pattern of $Co_{1+x}Pb_xFe_{2-2x}O_4$ system



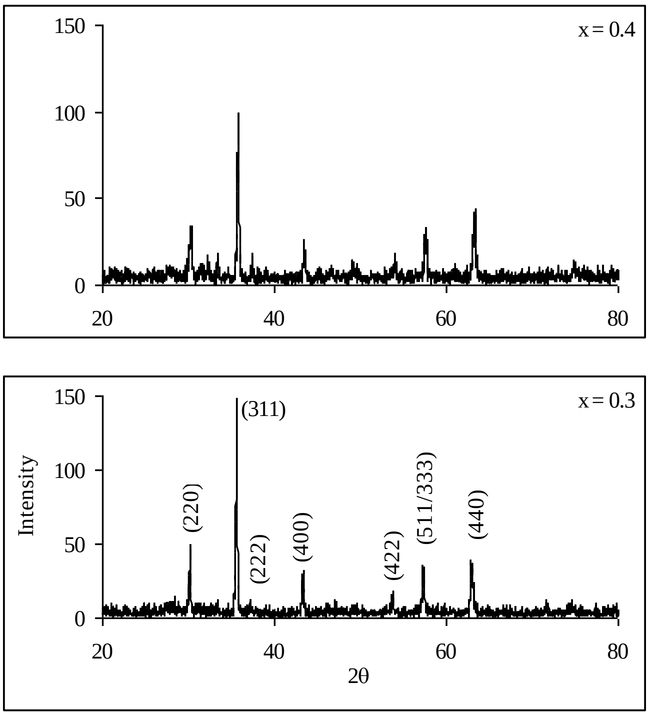


Figure 1(b) X-ray diffraction pattern of $Co_{1+x}Pb_xFe_{2-2x}O_4$ system

Lattice parameter of each of the samples was calculated from XRD data with an accuracy of ± 0.002 Å and are listed in the table 1.

Table 1. Variation of lattice parameter, X-ray density, bulk density crystallite size and percentage porosity for $Co_{1+x}Pb_xFe_{2-2x}O_4$ system.

Composition (x)	Lattice parameter, a (Å)	X-ray density, dx (gm/cm^3)	Bulk density, d (gm/cm^3)	Crystallite size, t (Å)	% porosity, P
0.0	8.378	5.28	4.58	355	14
0.1	8.380	5.61	4.36	407	23
0.2	8.382	5.99	4.19	407	31
0.3	8.383	6.35	4.62	630	28
0.4	8.322	6.82	4.19	420	29
0.5	8.311	7.21	5.08	531	30

From the table 1, it can be seen that initially lattice parameter increases, it becomes maximum for (x) = 0.3 and then decreases for higher value of (x). Increase in lattice parameter for (x) = 0.0 to 0.3 is attributed to the replacement of smaller Fe^{3+} (0.64Å) by a large ions Pb^{4+} (0.70Å) and Co^{2+} (0.78Å). Lattice parameters value for pure ferrites (x = 0.0) agree well with the value given in the literature [10-12].

X-ray density was calculated by using the formula [13]

$$dx = \frac{ZM}{NV} gm/cm^3 \qquad (1)$$

where Z is the number of molecules per unit cell (Z = 8), M is the molecular weight of the sample, N is the Avogadro's number and V is the unit cell volume.

The X-ray densities (dx) are tabulated in the table 1. From the table 1, it can be seen that X-ray densitiy (dx) increases linearly with composition (x). It can be ascribed to the density and atomic weight of cobalt (8.85 gm/cm^3, 58.933) & lead (11.34 gm/cm^3, 207.19) which are higher than those of iron ions (7.87gm/cm^3, 55.847). The bulk density (d) is determined from mass per unit volume of the pellet samples and is given in the table 1. It is observed from the table 1, that bulk density decreases with compositions up to (x) = 0.2 and then increases for higher values of (x).

The crystallites size for all the compositions was estimated by Scherrer's formula [13] given by

$$t = \frac{0.9\lambda}{B cos\theta} \qquad (2)$$

where t is the diameter of the crystallites, λ is the wavelength of target used (here Cu K_α = 1.5418 Å), B is the full width at half the maximum intensity (FWHM) of diffracted line in radian.

The crystallites size for all the composition is observed in the range 355–630 Å and is in agreement with crystallite size prepared by ceramic method. Percentage porosity of all the samples was calculated using the formula given by [14]

Percentage porosity,

$$P = \left[1 - \frac{d}{dx}\right] \times 100\% \qquad (3)$$

where d is the bulk density and dx *is* the x-ray density.

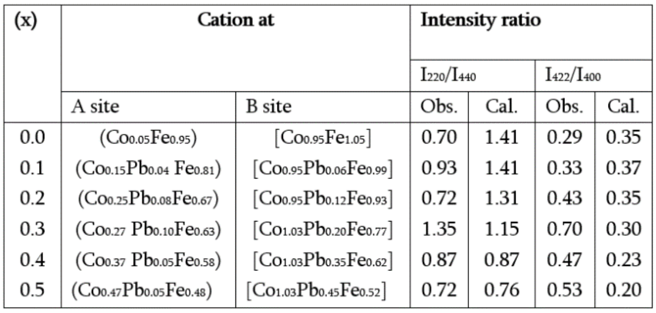
The values of percentage porosity are given in the table 1. From table 1, it can be seen that percentage porosity of all the sample varies in the range 14% to 31% and are good agreement with those obtained by the same method reported else where [6,15].

In order to determine cations distribution, XRD intensities were calculated using formula given by Burger [16]

$$I_{hkl} = \left|F_{hkl}\right|^2 PL_P \qquad (4)$$

where the notations have their usual meanings. The distribution of divalent, trivalent and tetravalent cations among the tetrahedral and octahedral sites in the $Co_{1+x}Pb_xFe_{2-2x}O_4$ ferrite samples are determined from the ratio of intensity of X-ray diffraction lines I_{220}/I_{440} and I_{422}/I_{400} [17].

Table 2. Comparison of intensities ratio for $Co_{1+x}Pb_xFe_{2-2x}O_4$ system



(x)	Cation at		Intensity ratio			
			I_{220}/I_{440}		I_{422}/I_{400}	
	A site	B site	Obs.	Cal.	Obs.	Cal.
0.0	$(Co_{0.05}Fe_{0.95})$	$[Co_{0.95}Fe_{1.05}]$	0.70	1.41	0.29	0.35
0.1	$(Co_{0.15}Pb_{0.04}\ Fe_{0.81})$	$[Co_{0.95}Pb_{0.06}Fe_{0.99}]$	0.93	1.41	0.33	0.37
0.2	$(Co_{0.25}Pb_{0.08}Fe_{0.67})$	$[Co_{0.95}Pb_{0.12}Fe_{0.93}]$	0.72	1.31	0.43	0.35
0.3	$(Co_{0.27}\ Pb_{0.10}Fe_{0.63})$	$[Co_{1.03}Pb_{0.20}Fe_{0.77}]$	1.35	1.15	0.70	0.30
0.4	$(Co_{0.37}\ Pb_{0.05}Fe_{0.58})$	$[Co_{1.03}Pb_{0.35}Fe_{0.62}]$	0.87	0.87	0.47	0.23
0.5	$(Co_{0.47}Pb_{0.05}Fe_{0.48})$	$[Co_{1.03}Pb_{0.45}Fe_{0.52}]$	0.72	0.76	0.53	0.20

In Table 2, the results of X-ray intensity calculations for the compositions (x) = 0.0-0.5 are listed along with the experimental intensity ratios.

It is observed from Table 2 that the tetravalent Pb^{4+}occupies both A and B sites replacing iron ions. The added Co^{2+} ions also occupy at A sites with replacing iron ions for the compositions (x) = 0.0, 0.1 and 0.2 and there after very small amount of Co^{2+}ions migrate from A sites to B sites replacing iron (Fe^{3+}) ions for the compositions with (x) = 0.3, 0.4 and 0.5. The cations distribution is derived using X-ray intensity calculation, magnetization, site preference energies of the cations and earlier studies [18-19] can be written as

$$(Co_{0.05+x}\ Pb_{0.4x}Fe_{0.95-0.4x+x})\ [Co_{0.95}Pb_{0.6x}Fe_{1.05-0.6x}]\ O_4 \qquad (5)$$

For the compositions (x) = 0.0, 0.1 and 0.2.

The cations distribution for the compositions (x) = 0.3, 0.4 and 0.5 can be written as

(x) = 0.3

$$(Co_{0.27}Pb_{0.10}Fe_{0.63})\ [Co_{1.03}Pb_{0.20}Fe_{0.77}]\ O_4 \qquad (6)$$

(x) = 0.4

$$(Co_{0.37}Pb_{0.05}Fe_{0.58})\ [Co_{1.03}Pb_{0.35}Fe_{0.62}]\ O_4 \qquad (7)$$

(x)= 0.5

$$(Co_{0.47}Pb_{0.05}Fe_{0.48})\ [Co_{1.03}Pb_{0.45}Fe_{0.52}]\ O_4 \qquad (8)$$

Saturation magnetization measurements show hysterisis loop for all the compositions of the systems at 300 K. This indicates that they are all ferrimagnetic in nature. The saturation magnetization (σ_s) is calculated from hysrerisis loop for all the compositions and magnetic moment per formula unit (magneton number) η_B is then calculated by using the relation [20]

$$\eta_B = \frac{\sigma_S \cdot Mole.weight}{5585} \qquad (9)$$

The values of magneton number are summarized in table 3.

Table 3. Saturation magnetization (σ_s), magneton number (η_B) and Curie temperature (T_c) for $Co_{1+x}Pb_xFe_{2-2x}O_4$ system.

(x)	Saturation Magnetization, (σ_s) emu/gm	Magneton number, (η_B)		Curie temperature, (Susceptibility) (T_c) K
		Cal.	Obs.	
0.0	71.41	3.20	3.00	795
0.1	71.46	3.30	3.20	747
0.2	69.39	3.39	3.29	712
0.3	59.8	2.98	3.00	677
0.4	41.96	2.18	2.22	650
0.5	32.59	1.88	1.82	622

From which, it can be seen that the η_B increases slowly and reaches to a maximum at (x) = 0.2 and then decreases thereafter for all the compositions. The substitution of non magnetic Pb^{4+} ion ($0\mu_B$) for magnetic Fe^{3+} ($5\mu_B$) in $CoFe_2O_4$ system results in decrease of magnetic moment of A and B sites and therefore η_B decreases with increasing Pb^{4+} concentration for (x) = 0.3, 0.4 and 0.5. According to Neel's two sub-lattice model of ferrimagnetisms [21] magnetic moment per formula unit in (μ_B) η_B^N is expressed as

$$\eta_B = M_B(x) - M_A(x) \qquad (10)$$

where M_B and M_A are B and A sub lattice magnetic moment in μ_B.

The experimental and calculated values of η_B from cations distribution equation and spin only moment of Fe^{3+}($5\mu_B$), Co^{2+}($3\mu_B$) and Pb^{4+}($0\mu_B$) are plotted with composition (x) in fig.2.

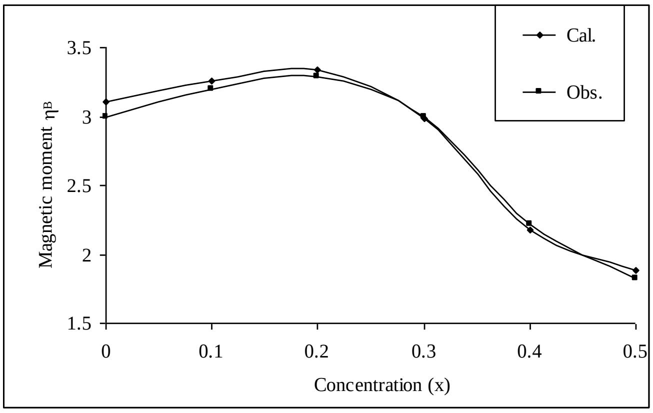


Figure 2. Variation of magnetic moment with concentration(x) for

$Co_{1+x}Pb_xFe_{2-2x}O_4$ system

It can be seen that estimated η_B values agree well with experimentally observed values for all the compositions confirming collinear spin order.

Figure 3 shows the temperature variation of normalized a. c. susceptibility (χ_T/χ_{RT}).

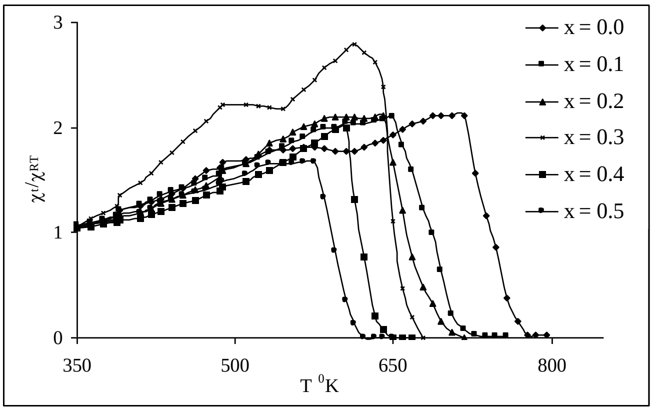


Figure 3. Variation of a.c. susceptibility with temperature for $Co_{1+x}Pb_xFe_{2-2x}O_4$ system

The compositions (x) = 0.0, 0.1, 0.2, 0.3 and 0.4 show peaking behavior near Curie temperature (Tc). χ_T/χ_{RT} drops sharply near the Curie temperature (Tc). A peak at Tb, blocking temperature, in normalized χ_T/χ_{RT} curve is due to the transition of magnetic particle from single domain (SD) to superparamagnetc (SP) state. The blocking temperature is a temperature at which a ferromagnetic substance changes to a super paramagnetic substance.

The normalized a.c. susceptibility, for all the samples, changes with temperature. This shows that all the samples have SD state. The blocking temperature Tb decreases with increases Pb^{4+} content indicates that the formation of SD particle is gradually suppressed by the addition of Pb^{4+} content.

The Curie temperature of the ferrite samples were determined from the plots of normalized a. c. susceptibility verses temperature, and listed in the table 3. It is observed that Curie temperature decreases linearly with addition of Pb^{4+} contents. The decrease in the Curie temperature may be attributed to the decrease in A-B interaction.

IV. CONCLUSION

Lattice parameter increases with increase in Pb^{4+}concentration. The intensity calculation shows that Pb^{4+} occupies both A and B sites replacing iron Fe^{3+} ions. The added Co^{2+} ions occupy at A sites with replacing iron Fe^{3+} ions for x = 0.0, 0.1 and 0.2 thereafter very small amount of Co^{2+} ions migrate from A to B sites.

Magnetization measurement exhibits Neel's collinear spin ordering for all the samples, which is further supported by Curie temperature data.

V. ACKNOWLEDGMENTS

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