Effect of Zinc on A. C. Susceptibility and D. C. Resistivity of Ni1-x Znx Fe2-y EuyO4

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Abstract- The electrical and magnetic behaviour of ferrite system Ni_{1-x} Zn_x Fe_{2-y} Eu_yO_4 as a function of temperature has been studied by means of d. c. resistivity and a. c. susceptibility. D.C. resistivity is found increased after substitution of Eu^{3+}. Curie temp obtained from log (ρ) versus (1000/T) graph in this system is found decreased with increase in Zn concentration x. This is supported by the similar findings from a. c. susceptibility measurements. Curie temperatures obtained from d. c. resistivity measurement and a. c. susceptibility measurements are in good agreement. Curie temperature is found decreased due to Eu^{3+} substitution.

Keywords: Ferrites, susceptibility & resistivity

Introduction

Ferrites are characterised by high electrical resistivity, high dielectric constants and low losses [1]. Due to wide range technological applications especially at high frequency ranges; the ferrites have been attracting the researchers in large number [2,3,4]. $ZnFe_2O_4$ is a normal spinel ferrite [5,6] whereas $NiFe_2O_4$ is an inverse spinel ferrite. Substituted Ni ferrites have been the subject of extensive investigations because of their microwave applications. Ni-Zn ferrites are used in high frequency and pulse field applications [7]. It is observed that incorporation of diamagnetic, tetravalent and pentavalent ions in these ferrites sufficiently improve their electrical properties, whereas these ions reduce magnetization [8]. Magnetization study of Zn substituted spinels show the canted spin arrangement on the octahedral site. This canting of spins gives rise to Y-K angles. Many workers have studied the a. c. susceptibility for mixed ferrites and concluded that there are three types of ferromagnetic particles viz. multidomain (M.D.) single domain (SD) and superparamagnetic (SP) exist within the material [9]. Present communication reports studies on compositional variation of lattice constant, X-ray density, temperature variations of d. c. resistivity and a. c. susceptibility of rare earth (Eu^{3+}) doped Ni-Zn spinel ferrite.

Experimental Procedure

The six Polycrystalline ferrite samples of Ni_{1-x} Zn_x $Fe_{2-y}Eu_yO_4$ (where x= 0.0,0.1,0.2,0.3,0.4,0.5 and y=0.05) were prepared by the standard ceramic route using A. R. grade NiO, ZnO, Fe_2O_3 and Eu_2O_3 compounds with 99% purity. They were mixed in their stoichiometric proportion, ground with acetone base in agate mortar for about two hours to get fine powder. The pre sintering was carried out at 900^0 C for 16 hours in the furnace and samples were allowed to furnace-cool at the rate of 2^0 C/min. These sintered powders were then pressed into pellets of desired thickness with the help of hydraulic press by applying a pressure of 5-6 tons/sq.inch for 10 minutes on each pellete. The polyvinyl acetate was used as a binder during the pelletization. Further these pellets

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were finally sintered at 1100^0 C for 24 hours in the same furnace and allowed to cool at the rate of 2^0 C/min up to room temperature. The phase purity of the samples was analysed by using X-ray diffraction method with Cu-Kα radiation.

The a. c. susceptibility measurements were made by using a double coil set up at the frequency 263 Hz in the r. m. s. field of 7 oersted described by Murthy et. at. (1984). The d. c. resistivity (ρ) as a function of temperature was studied by using two probe method in the temperature range of 300 K to 900 K. the pellets were gently polished and uniform silver paste was applied on both the surfaces of pellets to have the good ohmic contact. Such pellets were held in between the two electrodes of a sample holder designed specially for d. c. resistivity measurements. The pellets were gradually heated above critical temperature and then cooled up to room temperature in the first cycle. In the second cycle of heating, pellets were heated above curie temperature and then allowed to cool up to room temperature. The fixed voltage applied was recorded and the different values of current were noted in the second cycle in steps of 10 K, from which resistance and hence the resistivity (ρ) of each sample was calculated.

Results and discussion

A : XRD Analysis

X-ray diffractograms of the ferrite series show the completion of the solid state reaction and the formation of cubic spinel compounds. The x-ray diffraction pattern of the samples are shown in Fig 1. It is observed from this figure that there exists one small extra unidentified peak on the lower angle side of (311) plane. The appearance of such peak may be due to high reactivity at high temperature between Eu and Fe which results into the formation of perovoskite phase. The similar phase was reported by J. L. Bhosale et. al. [10] in Mg-cd. ferrite substituted with Gd^{3+} ion and by C. B. Kolekar et al. [11] in Gd^{3+} substituted Cu-Cd mixed ferrite. In all samples, the widths of half of maximum intensity peak of (311) planes are almost the same in magnitude, indicating that the substituents have occupied the corresponding lattice sites [12]. The observed peaks in all the samples are sharp defined and intense which confirms the formation of cubic spinel structure.

The interplaner spacing'd' was calculated from Bragg's law $n\lambda = 2d \sin\theta$ and lattice constant 'a' was determined by using the relation $a = d\sqrt{N}$ where $N= h^2+k^2+l^2$ and h, k, l are miller indices. The determined values of lattice constant 'a' are listed in Table 1 and variation of 'a' with Zn concentration 'x' in shown in Fig 2. the lattice constant of pure Ni-ferrite $NiFe_2O_4$ is 8.337 A^0 [13]. In the present work for sample x=0 i.e. for $NiFe_{1.95}Eu_{0.05}O_4$ it is found that lattice constant is 8.327 A^0 indicating that 'a' is decreased by 0.010 A^0. Further the variation of lattice constant with Zn concentration 'x' shows increasing nature obeying Vegards law [14]. This is due to replacement of Ni^{2+} ion of smaller ionic radia (0.74 A^0) by Zn^{2+} ions of larger ionic radia (0.83 A^0). Similar nature of lattice constant in Gd^{3+} substituted Mg. Cd ferrite has been reported by J. L. Bhosale et. al. [10]. X-ray density of each sample was calculated and the values are presented in Table 1. X-ray density is found to be decreased with increase in Zn concentration. The decrease in x-ray density is attributed to increase in lattice constant

The variation of x-ray density with Zn concentration 'x' is shown in Fig.3 which shows decreasing trend. Depending upon the ionic radii, site preference of constituent ions and x-ray intensity ratios for the sensitive planes(220),(400),(422),(440)

cation distribution is confirmed. The assumed cation distribution is shown in Table 1 which shows that Zn^{2+} resides at tetrahedral (A) siteand Eu^{2+}, Ni^{2+} at Octahedral [B] site whereas Fe^{3+} occupies both sites. The cation distribution assumed in this system is given by the formula, $(Zn_xFe_{1-x})[Ni_{1-x}Eu_yFe_{1+x-y}]O_4$

AC susceptibility

The graphs between the ratio of susceptibility at different temperature to room temperature (χ_T / χ_{RT}) and the temperature are plotted and the natures of these plots are shown in Fig. 4. From this figure it is observed that susceptibility suddenly drops to zero at certain temperature this temperature is called curie temperature (Tc). These graphs show normal ferrimagneitc behaviour. The curie temperature determined for all samples are listed in Table 2. Tc of pure Ni ferrite is 858 K [13]. It is observed from Table 2 that Tc is decreased due to Eu^{3+} doping in Ni-Zn ferrite. also Tc is found decreased with increase in Zn concentration x. The variation of Tc. with Zn concentration x is shown in Fig. 5.

This decrease in Tc with increase in Zn concentration is attributed to the decreasing A-B interaction resulting from replacement of Fe^{3+} ions by Zn^{2+} on A-site and as Eu^{3+} occupies B site. The plots do not show peaking behaviour and drops slowly to zero near Tc.

DC resistivity

The variation of resistivity (ρ) studied as a function of temperature (T) is shown in Fig. 6, 7. It is observed from this figure that the resistivity decreases with increase in temperature in all the samples. The resistivity at lower concentration of Zn is greater while that at higher concentration resistivity is found smaller. The graphs of log(ρ) with (1000/T) are plotted for all the samples. The natures of graphs are shown in Fig. 8. These graphs show the two regions of two behaviours of a sample. One corresponds to paramagnetic region and the other to ferrimagnetic region. The graphs are the straight lines of two different slopes indicating that the samples change their magnetic behaviour at curie temperature (Tc). The curie temperature of sample is found to be decreased due to substitution of Eu^{3+} in Ni-Zn ferrite. Also it is found that curie temperature decreases with increase in Zn concentration x. The values of Tc obtained from d. c. resistivity are in good agreement with those obtained from a. c. susceptibility. The values of Tc are shown in Table 2. The variation of Tc with Zn concentration x is shown in Fig. 5. Activation energies (ΔE) in both paramagnetic region and ferrimagnetic regions were calculated by using the relation $\rho = \rho_0 \exp(\Delta E/kT)$ as a function of substituted ion and the values are presented in Table 2. From Table 2, it is noticed that the activation energy in paramagnetic region (E_p) is greater than that in ferromagnetic region (E_f). The resultant activation energy (ΔE) of the samples ($\Delta E = E_p - E_f$) is shown in the Table 2. From this table it is clear that the activation energy (ΔE) goes on decreasing with increase in Zn concentration x upto x = 0.2 beyond which ΔE increases. The variation of (ΔE) with x is shown in Fig. 9. The conduction in paramagnetic region is explained as an impurity conduction, while that in ferrimagnetic region is due to polaron hoping from Fe^{3+} to Fe^{2+} on the B-site [15]. Already it is reported that if substituted ion occupies B-site then the effect on activation energy is greater [16] whereas if it occupies A-site without disturbing B-site, then activation

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energy almost remains unaltered [17]. Also it is reported that hoping between ions of different metals on B site requires higher value of activation energy than for ions of same metal [18]. In the present work Zn^{2+} ions have a preference to A-site so that they cannot take part in affecting A. E. therefore change in activation energy can be attributed to Eu^{3+} occupying octahedral [B] site.

Conclusion

The investigations of the system Ni_{1-x} Zn_x Fe_{2-y} Eu_yO_4 leads to the following conclusions.

1. Lattice Constant is found slightly decreased due to substitution of Eu^{3+}.
2. Also it is found that lattice constant increases with increase in Zn concentration x.
3. x-ray density is observed to be decreasing.
4. As per cation distribution it is noticed that Zn diverts to A site and Ni, Eu resides on B-site. Fe occupies both A & B sites.
5. The graphs between susceptibility and temperature show normal ferrimagnetic behaviour. Curie temperature Tc is decreased due to Eu3+ doping in Ni-Zn ferrite. Also Tc decreases with increase in Zn concentration x due to decreasing A-B interaction.
6. D. c. resistivity at lower concentration of Zn is found greater than that at higher concentration. The resistivity decreases with increasing temperature. The graphs between (log) and (1000/T) show two regions corresponding to paramagnetic and ferrimagnetic behaviour through straight lines. Curie temperature obtained by d. c. resistivity are in good compromise with those obtained by a. c. susceptibility. Activation energies are found greater in paramagnetic region than those in ferrimagnetic region. Resultant activation energy is observed decreased with increase in Zn concentration x upto x = 0.2 beyond which it increases.

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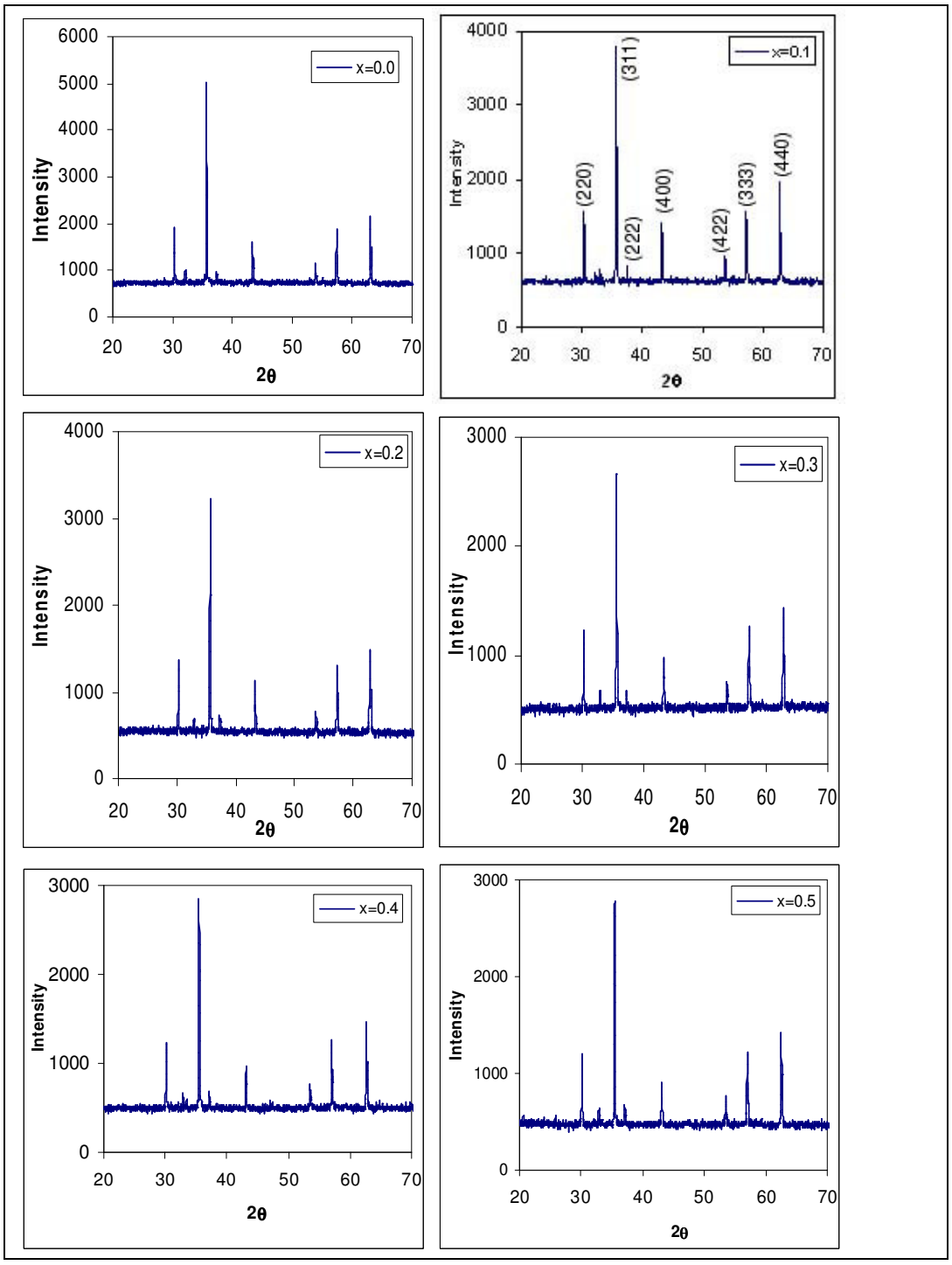
Table 1-

x	a (A^0)	d_x (A^0)	Cation Distribution				
			A site	B-site			
			Zn	Fe	Ni	Fe	Eu
0.0	8.327	5.502	0.0	1	1	0.95	0.05
0.1	8.340	5.492	0.1	0.9	0.9	1.05	0.05
0.2	8.352	5.484	0.2	0.8	0.8	1.15	0.05
0.3	8.362	5.479	0.3	0.7	0.7	1.25	0.05
0.4	8.374	5.467	0.4	0.6	0.6	1.35	0.05
0.5	8.387	5.461	0.5	0.5	0.5	1.45	0.05

Table 2-

x	T_c(sus)	T_C(res)	E_p	E_f	ΔE(e.v.)
0.0	850	847	0.238	0.171	0.067
0.1	805	800	0.228	0.165	0.063
0.2	775	767	0.071	0.050	0.021
0.3	670	680	0.065	0.040	0.025
0.4	620	610	0.058	0.028	0.030
0.5	550	515	0.054	0.022	0.032



Plot. 1- XRD patterns for all the samples of the system $Ni_{1-x}Zn_xFe_{2-y}Eu_yO_4$

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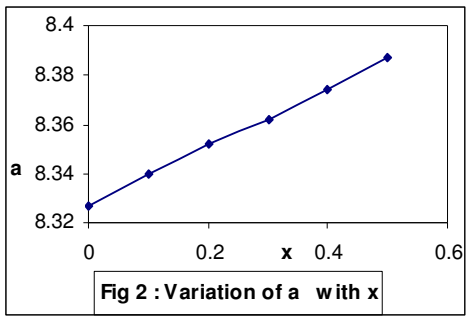

Fig 2 : Variation of a with x

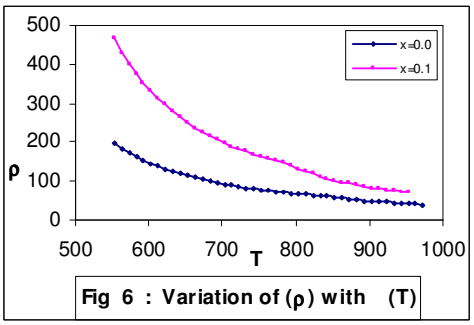

Fig 6 : Variation of (ρ) with (T)

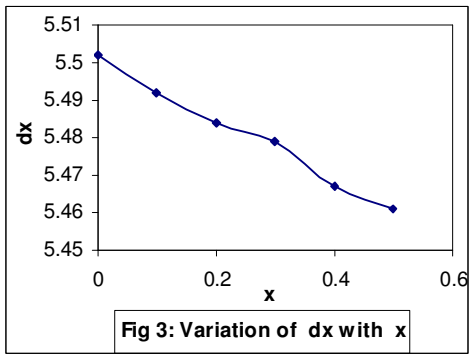

Fig 3: Variation of dx with x

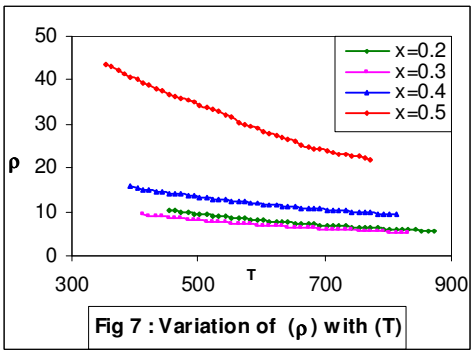

Fig 7 : Variation of (ρ) with (T)

50

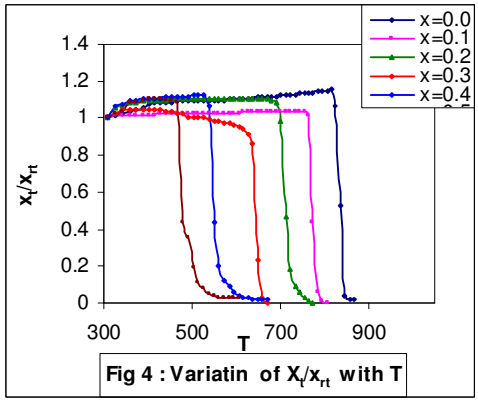

Fig 4 : Variatin of X_t/x_{rt} with T

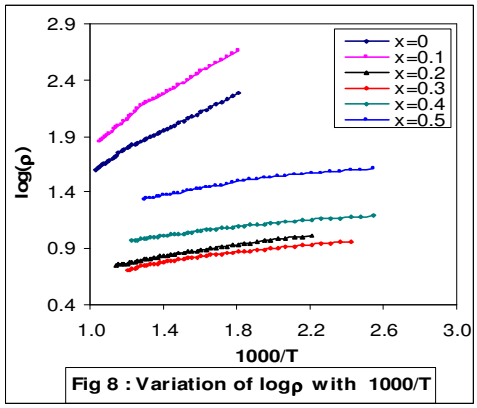

Fig 8 : Variation of logρ with 1000/T

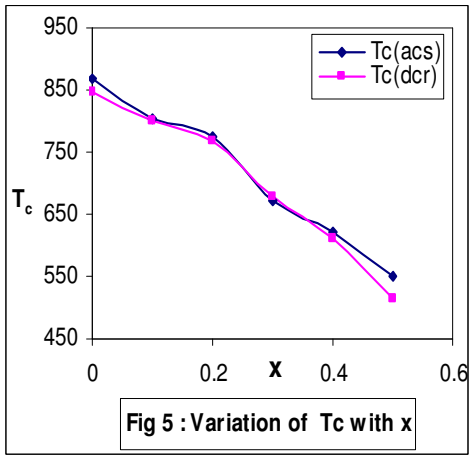

Fig 5 : Variation of Tc with x

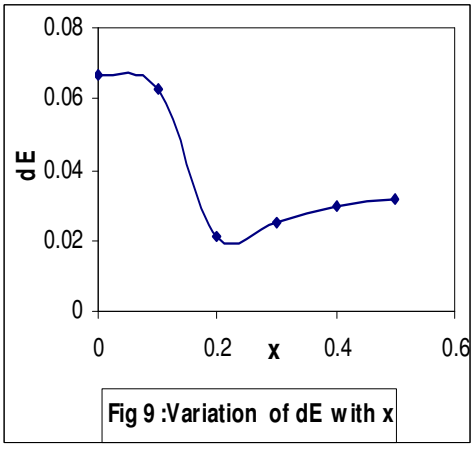

Fig 9 :Variation of dE with x

Plot. 2-

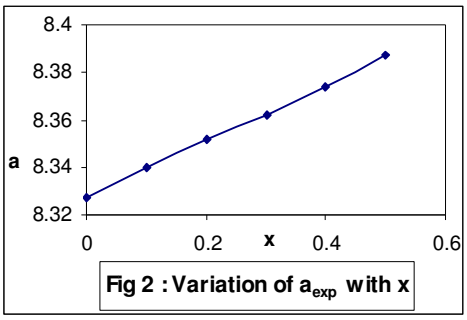

Fig 2 : Variation of a_{exp} with x

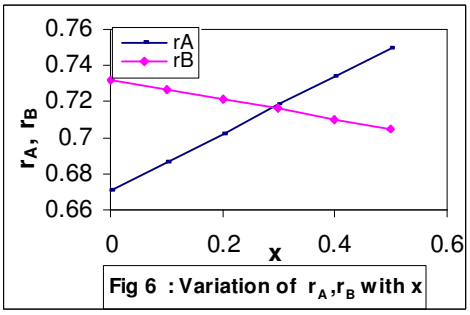

Fig 6 : Variation of r_A, r_B with x

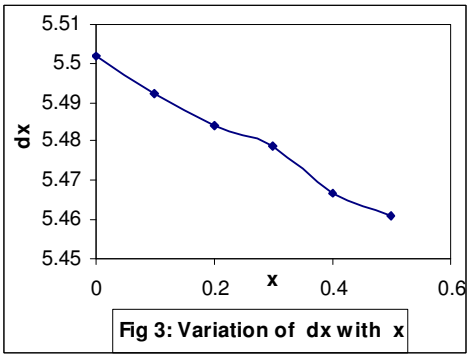

Fig 3: Variation of dx with x

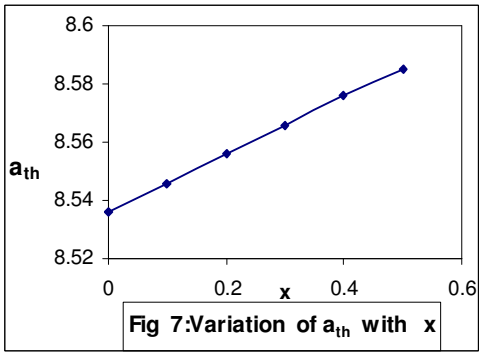

Fig 7:Variation of a_{th} with x

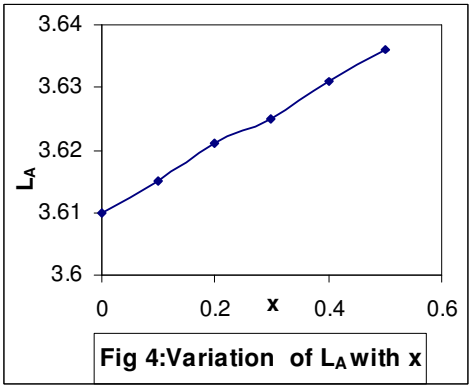

Fig 4:Variation of L_A with x

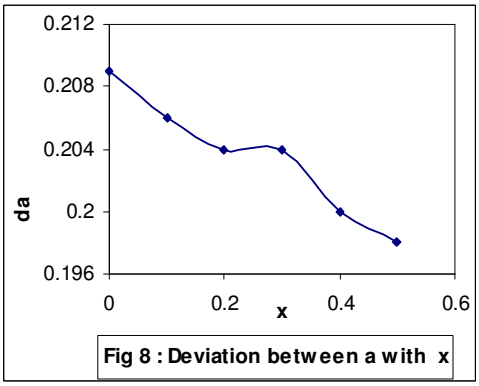

Fig 8 : Deviation between a with x

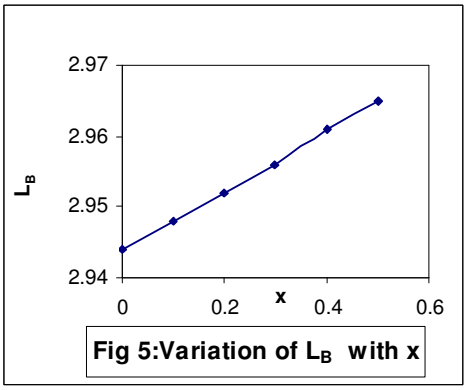

Fig 5:Variation of L_B with x

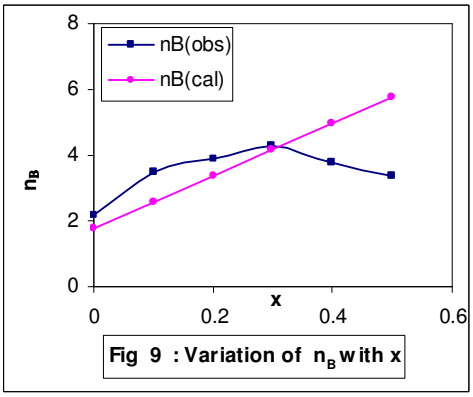

Fig 9 : Variation of n_B with x

Plot. 3-

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