EFFECT OF TEMPERATURE OF SYNTHESIS ON X-RAY, IR PROPERTIES OF MG-ZN FERRITES PREPARED BY OXALATE CO-PRECIPITATION METHOD

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ABSTRACT

The magnetic properties of $Mg_{1-x}Zn_xFe_2O_4$ (where x = 0.3,0.4,0.5,0.6) ferrites have been studied. Magnesium Zinc Ferrites was synthesized by oxalate co-precipitation method at different synthesis temperature and characterized by X-ray diffraction and far IR absorption techniques, scanning Electron microscopy .Far infrared absorption spectra show two significant absorption bands ,first at about 600 cm^{-1} and second at about 425 cm^{-1},which were respectively attributed to tetrahedral (A) and octahedral (B) sites of the spinel .The positions of the bands are found to be composition dependent and dependent on the temperature of synthesis. The force constants K_T and K_0 were calculated and plotted against zinc concentration and temperature of synthesis. Composition dependent of force constants is explained on the basis of cation-oxygen bond distances of respective sites and cation distribution.

KEYWORDS: Polycrystalline ferrites, Oxalate precursor, IR absorption, X-ray diffraction, Cation distribution, force constants.

I. INTRODUCTION

Polycrystalline ferrite materials have wide application range in the field of electronic and communication industries due to their interesting electrical and magnetic properties [1]. Infrared absorption spectroscopy is an important and non-destructive characterizing tool, which provides qualitative information regarding structural details of crystalline materials [2,3]. The results from IR absorption study can be used to interpret the electrical and magnetic properties of the ferrites [4]. The absorption bands from which the details regarding functional groups and their linkages can be explored, are found to be dependent on atomic mass, cation radius, cation-anion bond distances, cation distribution etc. Infrared spectral analysis have been carried out for several ferrites by Woldron (1955)[5] who reported two absorption bands within the wave numbers 800 – 200 cm^{-1}, which could respectively attributed to the tetrahedral and octahedral group complexes of the spinel structure. El Hitti et al (1996) [6] studied the IR absorption spectra of Ni-Zn-Mg ferrites and reported four absorption bands, out of which ν_1 and ν_2 are due to tetrahedral and octahedral sites and ν_3 and ν_4 are assigned to the vibrations in divalent metal ion-oxygen group complexes in octahedral site.[7] and mass of divalent cations [8] respectively. Kolekar et al (1994)[9] studied the Gd^{3+} substituted cd-cu ferrite system by using IR absorption spectroscopy and the results showing the compositional dependent behaviour of force constant are attributed to the cation oxygen bond distances. The structural distortion in case of chromium substituted nickel ferrites was studied by Ghatage et al

(1996) [10] . The IR spectra of Cd, Co, Mg, Ni, Zn, Cu etc. containing ferrites have been reported (Srivastav and Srinivasan 1982; Nathwani and Darshane 1987) [11,12]. The synthesis of ferrites can be carried out using different methods but the low temperature synthesis and molecular level mixing is reported to be useful in obtaining desired magnetic properties and the reaction kinematics in a chemical process dependent on the temperature at which it is carried out.

The present study reports on the synthesis of Mg-Zn ferrite powders of controlled composition by oxalate co-precipitation method. The effect of synthesis temperature and process parameters on particle size and crystallinity has been investigated. In the present communication the results regarding IR absorption spectral analysis, magnetic properties and XRD of Mg-Zn ferrites are discussed.

II. EXPERIMENTAL SETUP

The Mg Zn ferrites having general formula $Mg_{1-x}Zn_xFe_2O_4$ (where x= 0.3,0.4,0.5,0.6) were prepared by co-precipitation method at different reaction temperatures – room temperature (38^0C), below room temperature (10^0C) and above room temperature (70^0C). The AR grade Magnesium sulphate, zinc sulphate, and ferrous sulphate were weighed carefully on single pan microbalance (make – Conteque and L.C. – 0.001 gm) to have proper stoichiometric proportion required in the final product. The synthesis was carried out at room temperature (38^0C), in which 200ml distilled water was taken and sulphates of magnesium (mg), zinc (Zn), and ferrous (Fe) were added in stoichiometry proportion to the water at that temperature. A clear solution was obtained. Ammonium oxalate was taken in burette and was added drop by drop until the precipitation was completed. The chemical reactions can be given as,

1. $MgSO_4 + 2H_2O + C_2O_4 \longrightarrow MgC_2O_4 2H_2O + SO_4$

2. $ZnSO_4 + 2H_2O + C_2O_4 \longrightarrow ZnC_2O_4 2H_2O + SO_4$

3. $FeSO_4 + 2H_2O + C_2O_4 \longrightarrow FeC_2O_4 2H_2O + SO_4$

The precipitate was filtered through whatman filter paper No. 41. The filtrate was washed with distilled water to remove unreacted chemicals. The residue was checked for the absence of sulphates using Barium chloride test. The solution was maintained at same temperature. Similar reaction was carried out using ice bath below room temperature at 10^0C and above room temperature at 70^0C where the magnetic stirrer was maintained at 70^0C to carry out the reaction. The precipitate was dried using electric lamp. The solid state reaction was carried out in muffle furnace maintained at 600^0C for 6 hours, and the powders so obtained were finely ground using agate mortar to obtain fine powders. The pellets of diameter 1 cm and thickness 0.5 cm were formed with the hydraulic press at the pressure of 9 kg/cm^2 for five minutes, for the study of saturation magnetization. The palletized samples were finally heated in a furnace at 700^0C for 7 hours, for hardening. Oxalates in precursor act like a combustion agent which helps in lowering the calcinations temperature. Therefore the solid state reaction to obtain the ferrites was carried out in muffle furnace at optimized temperature of 600^oC for 6 Hrs for all samples irrespective of the oxalate reaction temperature.

X-ray diffractgrams of all the samples were recorded with Philips make PW 1710 powder diffractometer by continuous scanning in the range of $2\theta^0$ to $85\theta^0$ using CuKα radiation. The x-ray tube was excited at 40kV and 40mA. IR spectrographs were taken using SHIMATZU (FTIR-8400S) spectrometer by using IR spectrometer in the range of 200 cm-1 to 800 cm^{-1}. The spectrum, transmittance (%) against wavenumber (cm^{-1}) is used for interpretation of the results.

III. RESULT AND DISCUSSION:

The X-Ray diffraction patterns obtained for the samples $Mg_xZn_{1-x}Fe_2O_4$ using Cu Kα radiation (λ = 1.5418 AU) are shown in Fig 1 to 4. The (h,k,l) values which diffracts in X-ray spinels are (220), (311), (400), (422), (333) and (400) . All the planes are the allowed planes, which indicate the formation of single-phase cubic spinel structure [13].The lattice parameter were calculated using the

standard relation [14] for the cubic system and presented against composition and temperature of synthesis shown in fig. 5 and 6.

X = 0.3

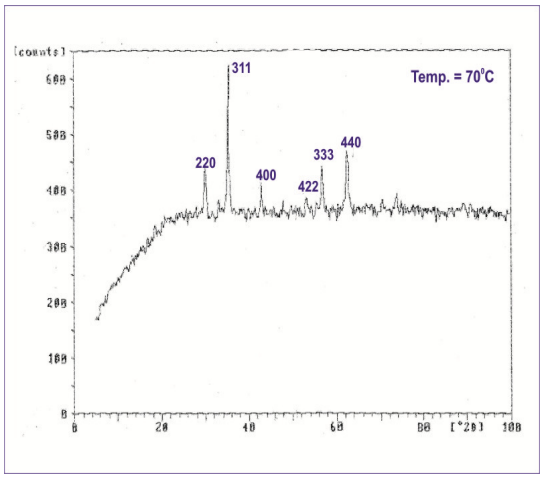


Figure 1-Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.3

X= 0.4

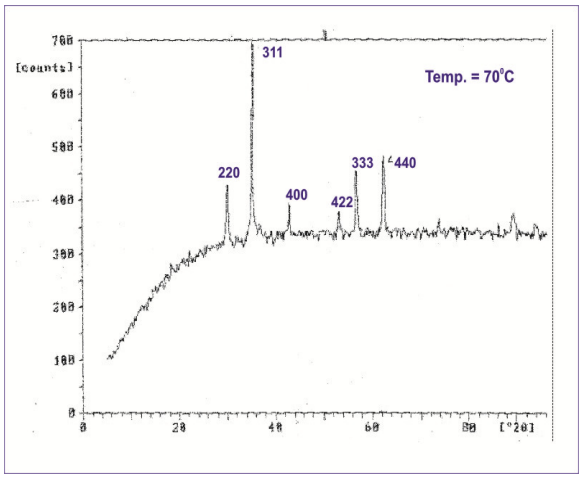
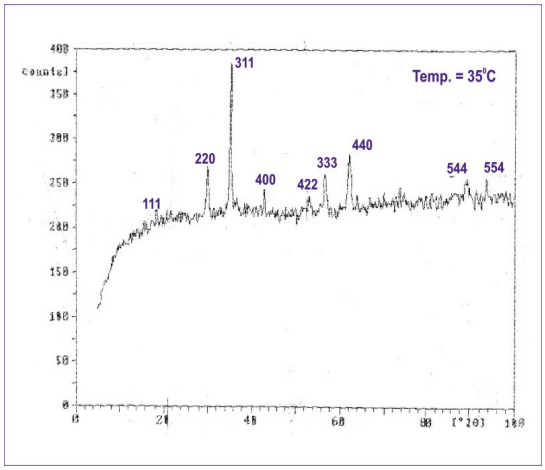
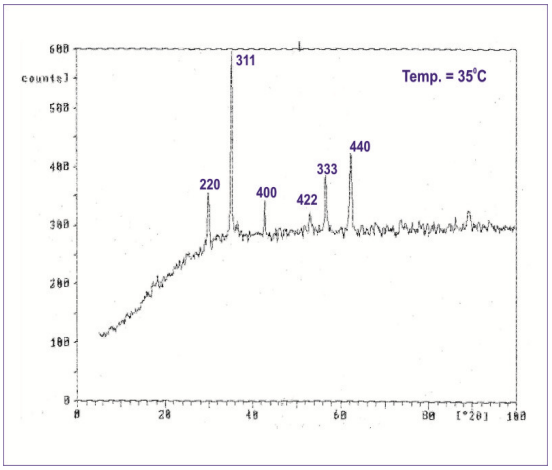
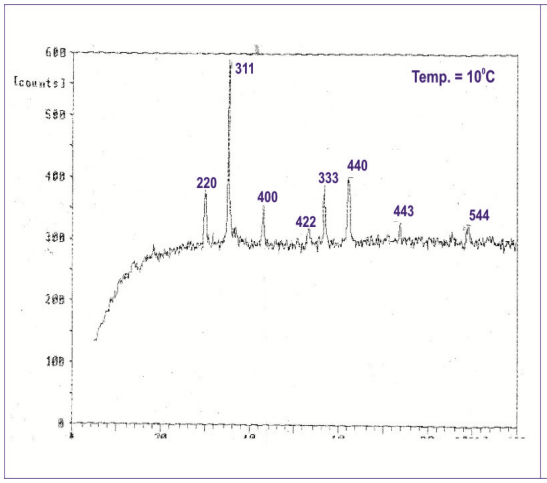
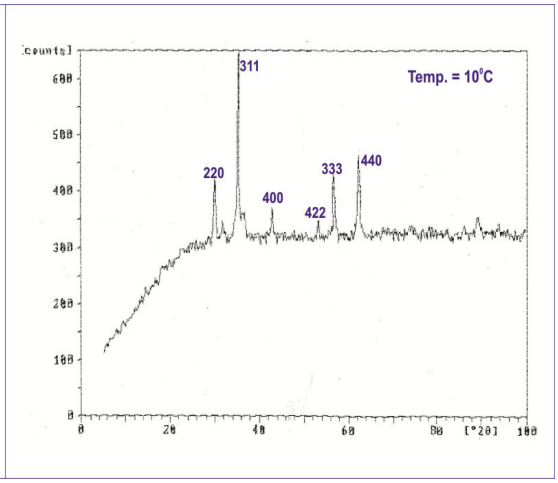


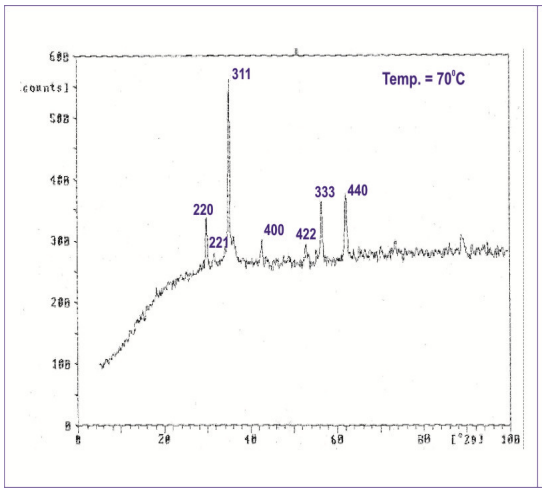
Figure 2 -Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.4

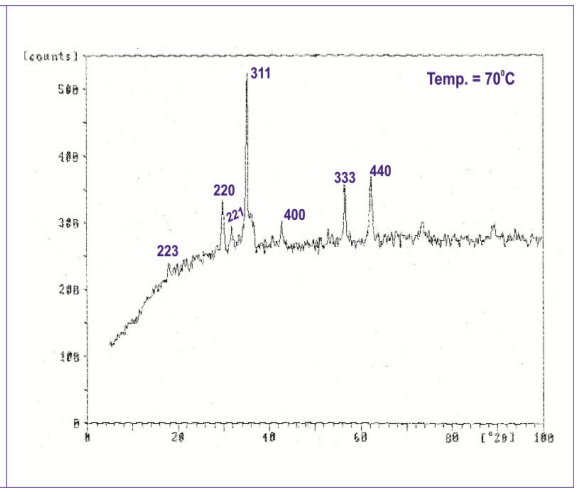


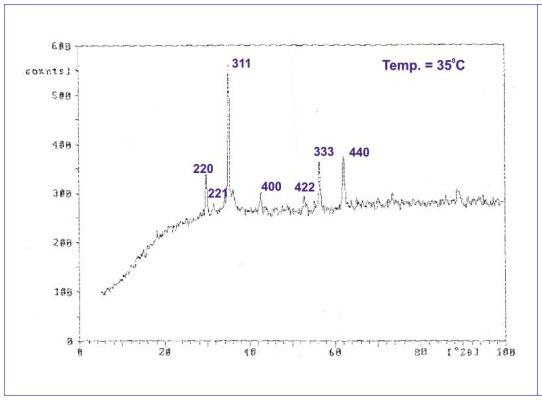


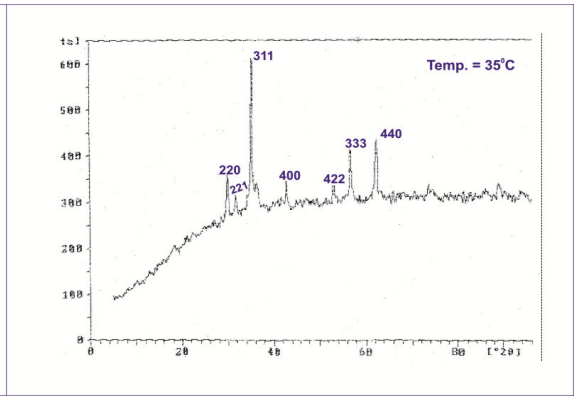


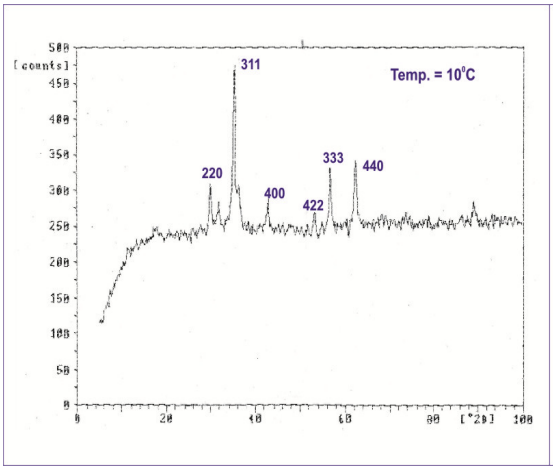












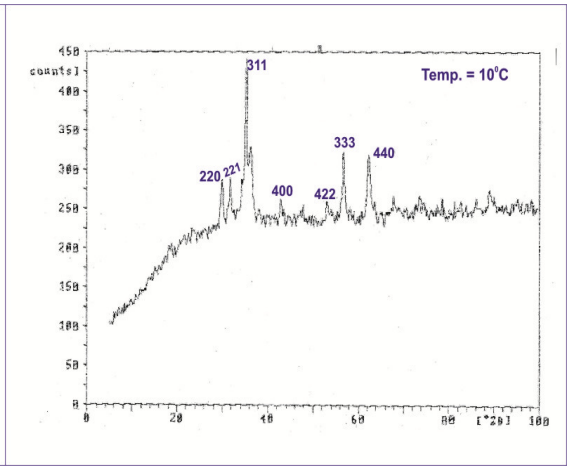


Figure 3 -Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.5

Figure 4 -Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.6

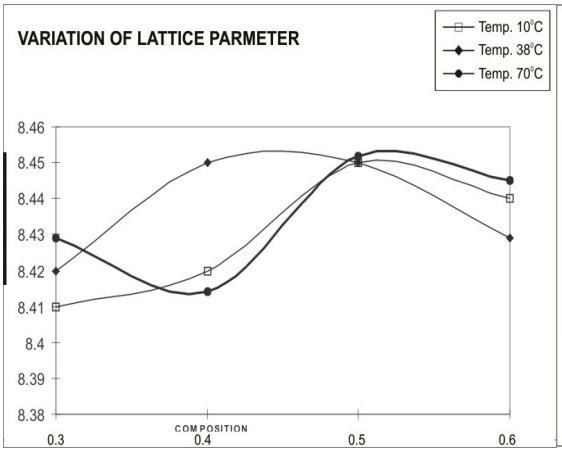


Figure 5- Variation of lattice parameter with composition

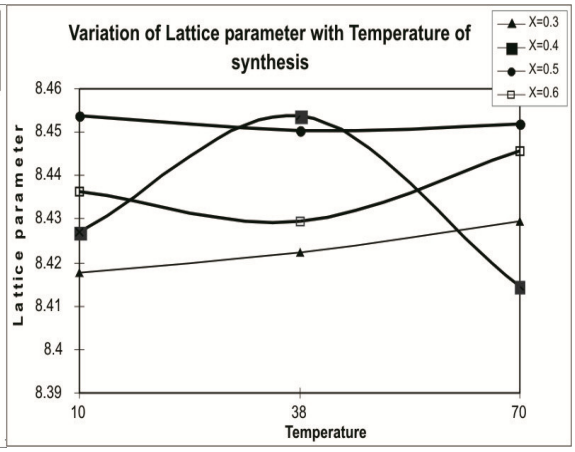


Figure 6- Variation of lattice parameter with temperature of synthesis.

The lattice parameter obtained using the XRD data is found to be in the range 8.42A° to 8.45 A°. The variation may be attributed to the ionic size difference between Mg^{2+}(0.06 nm) and Zn^{2+} ion (0.074 nm) where Zn^{2+} ion replaces Mg^{2+} ion on B site. For high concentration of Zinc (X=0.6), the lattice parameter is found to decrease, which may be attributed to shifting on some Fe^{3+} ions from A site to B site for higher composition [13]. The Temperature of synthesis does not seem to show variation in lattice parameter indicating that the range of temperature chosen for synthesis does not appreciably affect the lattice parameter. From Fig. 5 it can be seen that the samples synthesized at room temperature shows largest values for lattice parameter.

Infrared absorption spectra for the sample $Mg_{1-x}Zn_XFe_2O_4$ under investigation obtained using IR spectrophotometer and the variation of ν_1 and ν_2 bands with composition at different reaction temperatures is shown in Figure 7.These spectra show two strong absorption bands at the frequency about (600 cm^{-1} and 400 cm^{-1}) for all the compositions. The absorption bands observed within these specific frequency limits reveal the formation of single-phase spinel structure having two sublattices, tetrahedral (A) site and octahedral (B) site [9].

The absorption band, ν_1 observed at about is 600 cm^{-1} is attributed to the tetrahedral site whereas that of ν_2 observed at about 420 cm^{-1} is assigned to octahedral group complexes. The position of absorptions bands and wave numbers are presented in the fig. 7, 8 ,9 , it is found that the positions of bands are composition dependent. The wave number of band ν_1 shifts towards higher values with increasing zinc concentration (x). This variation in the band positions may be due to variations in the cation-oxygen bond length (A-0) [9]. Zinc ion, which when substituted, resides on tetrahedral (A) site, displacing proportional amount of Fe^{2+} ion from A to B site [14]. This leads to increase in the cation oxygen bond length of tetrahedral lattice site (A) of Spinel [14].The position of ν_2 band is seen to be independent of composition, which suggests the occupancy of cations of different characters on the same site [15].

The force constants for tetrahedral (k_t) and Octahedral site (K_o) , have been calculated by using the method suggested by Woldron [5]. The values of force constants as a function of Zn concentration have been estimated using the cation distribution depicted in table 1,in accordance with the observed values of magnetic moment are given in table1.

Table 1 Magnetic moment, cation distribution

Sr. No	Conc. Zn	Cation distribution		μB (Observed)	μB (Calculated)
1	0.3	$[Zn_{0.01}Fe_{0.99}]^A$	$[Mg_{0.7}Zn_{0.29}Fe_{1.01}]^B$	0.15	0.11
2	0.4	$[Zn_{0.013}Fe_{0.987}]^A$	$[Mg_{0.6}Zn_{0.387}Fe_{1.013}]^B$	0.27	0.23
3	0.5	$[Zn_{0.016}Fe_{0.984}]^A$	$[Mg_{0.5}Zn_{0.484}Fe_{1.016}]^B$	0.14	0.19
4	0.6	$[Zn_{0.02}Fe_{0.98}]^A$	$[Mg_{0.4}Zn_{0.58}Fe_{1.02}]^B$	0.12	0.12

On inspection of figure 8,9**.** It is seen that the force constant of tetrahedral site (k_t) decreases with increasing zinc concentration. This behavior can be attributed to the variation in cation oxygen bond lengths. The octahedral force constant (K_o) is found to increase up to X=0.4 and then it becomes constant on Zn^{2+} substitution, which supports Zn^{2+}on B site [16]. The increase in force constant is associated with increase in lattice parameter. The value of magnetic moment is greater for X=0.4 compositions and then it decreases due to the canted spin [17].The Temperature of synthesis does not seem to show variation in force constant indicating that the range of temperature chosen for synthesis does not appreciably affect the force constant.

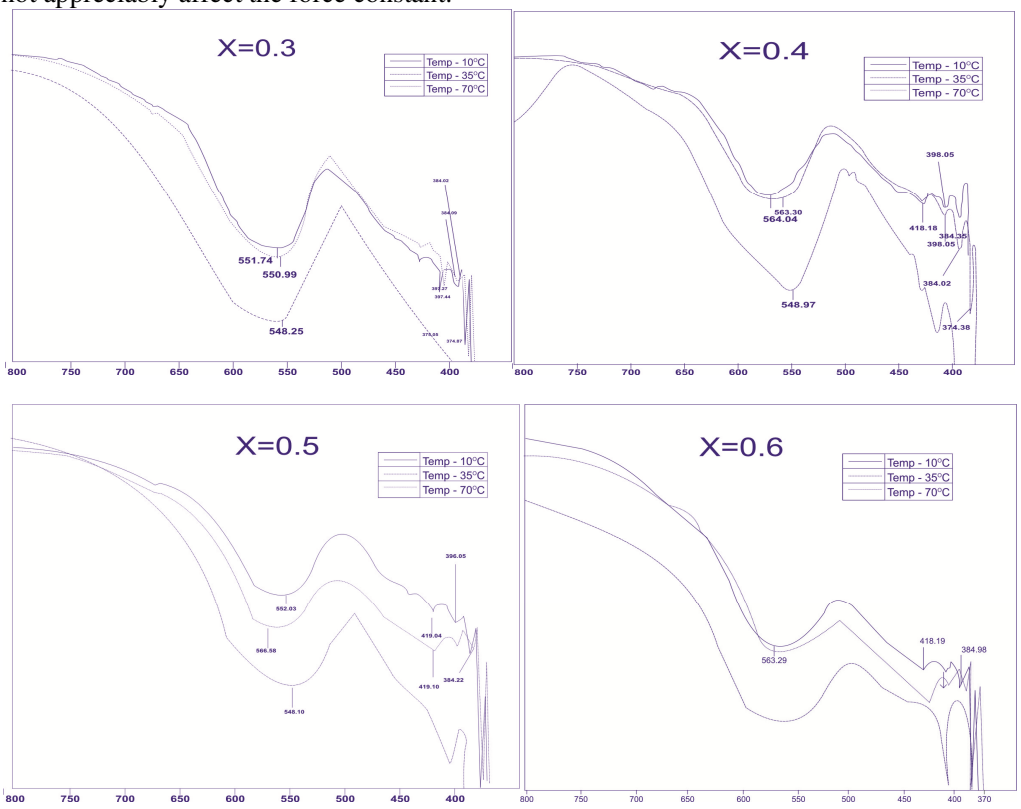
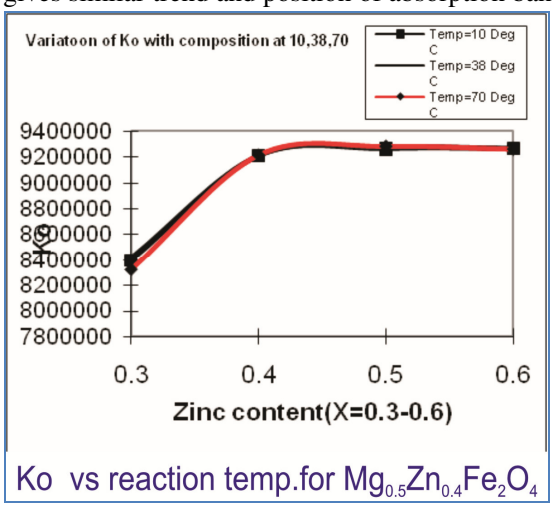


Figure7- Infrared Absorption spectra for the system $Mg_{1-x}Zn_xFe_2O_4$ for X= 0.3 -0.6

Ladgaonkar et.al [16] have synthesized the sample at temperature above 1000ºC and obtained the values ν_1 ,ν_2 in the range 585cm^{-1} to 555 cm^{-1} and force constant in the range 2.5X10^5 dyne/cm -- 2.4X10^5 dyne/cm. Mazen et.al[13] have synthesized the sample at temperature above 1000 ºC and obtained the lattice parameter 8.41°A,also Pradeep et.al[18], Joshi et.al[19], A.Vital et.al [20], Bhosale et.al [21], have observed similar trend of results and they have synthesized the sample at higher temperature. Whereas in the present case the samples have been synthesized below 100ºC but

the force constant showing similar trend. Hence it can be concluded that room temperature synthesis gives similar trend and position of absorption band to other reported value.



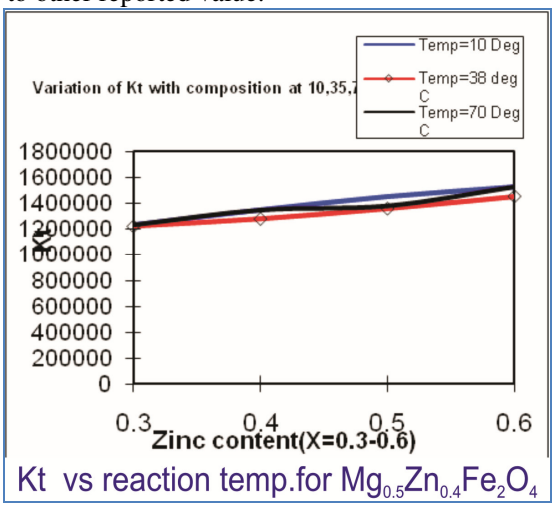


Figure 8- Variation of Kt and Ko verses reaction temperature $Mg_{1-x}Zn_xFe_2O_4$ for X= 0.3 -0.6

IV. CONCLUSION

Infrared absorption spectra of the compositions under investigation reveal formation of single phase cubic spinel, showing two significant absorption bands. The position of absorption bands are compositional dependent, whose dependence could be attributed to the variation in cation oxygen bond distances. Variations in the force constants of tetrahedral and octahedral sites support predicted cation distribution, wherein Zn^{2+} ion gets preferentially distributed among A and B sites and Mg occupies B site.

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Watawe Shrikant Chintamani is working as Associate Professor at Gogate Jogalekar College, Ratnagiri. He has completed M.Sc. M.Phil. Ph.D.(Materials Science). He has published 16 papers in reputed International journals , 03 papers in Indian Journals , 03Books Published/to be published, 22 Papers presented in International Conferences, 23 Papers presented in National Conferences, 05 Research Projects Completed, 03 M Phil/PhD Guidance. He is life member of various societies such as: Materials Research Society of Singapore upto 2005, Indian Association of Physics Teachers, Materials Research Society of India, Magnetic Society of India, Instrument Society of India, Ratnagiri Education Society. His areas of research include- Soft magnetic materials, microwave ferrites, ferrite applications, Nanoscience and Technology.

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