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Infrared absorption spectroscopic study of Cu^{2+} substituted NiZn ferrites

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ABSTRACT

Ni-Cu-Zn ferrites with general formula $Ni_{0.52}Cu_{x/2}Zn_{0.5-x/2}Fe_2O_4$ (with x = 0.3, 0.4, 0.5 and 0.6) have been synthesized using oxalate precursor method with different precursor reaction temperatures in the range 10^oC to 70^oC. The structural analysis has been carried out using X-ray diffraction and IR absorption studies which reveal the formation of ferrite structure. Far infrared absorption spectra show two significant absorption bands, first at about $550cm^{-1}$ and second at about $415 cm^{-1}$, which were respectively attributed to tetrahedral (A) and octahedral (B) sites of the spinel. The position of bands, are found to be composition dependent. The force constants K_t and K_o, were calculated as a function of Zn^{2+} concentration. Compositional dependence of force constants is explained on the basis of cation distribution and magnetic moment.

Keywords: Oxalate precursor; Tetrahedral; Octahedral; Cation distribution; Magnetic moment.

INTRODUCTION

NiZn ferrites have been used in the high frequency applications and also multilayer chip conductor with silver as a suitable material for inner conductor, however cofiring silver with the NiZn ferrites at temperatures higher than 1250^oC is unsuitable as the melting point of silver is 961^oC [1,2]. Cu^{2+} can be introduced to reduce the sintering temperature and at the same time enhance sintering process [3, 4]. Ni-Cu-Zn Ferrites having oxygen deficiency have been reported to be useful materials in CO_2 decomposition in reducing green house effect with 100% efficiency [5]. 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 [6]. A combination of lower reaction temperature followed by calcination

at suitable elevated temperature for the solid state reaction could be useful for synthesizing the ferrites with required parameters.

Various preparation techniques such as sol gel auto combustion [7], microwave assisted combustion synthesis[8,9], soft chemical method [10-14], combustion synthesis [15] have been used to synthesize ferrites. In the present communication, efforts have been made to synthesize Ni-Cu-Zn ferrites in two steps, involving oxalate co-precipitation at three different reaction temperatures [16], followed by calcination at 600^oC for the completion of the solid state reaction. The choice of calcination temperature has been based on the fact that ferrous oxalate gets converted into ferrous oxide at 400^oC [17] while the ferrite formation is reported to take place at around 600^oC [18-20]. It has also been reported that there is exothermic peak around 620^oC due to crystallization [21, 22].

MATERIALS AND METHODS

Experimental:
Ni-Cu-Zn ferrites with general formula $Ni_{0.5} Cu_{x/2}Zn_{0.5-x/2}Fe_2O_4$ (with x = 0.3, 0.4, 0.5 and 0.6) have been synthesized using AR grade metal sulphates as starting material. The stoichiometric proportions of metal sulphates were added to 200 ml distilled water. The temperature of chemical reaction was maintained at three different values i.e. 10^oC, 35^oC and 70^oC, using thermally controlled water bath. The chemicals were also maintained at the three temperatures before the chemical reaction was carried out. The reaction temperatures were chosen considering the room temperature of the work place during summer. The summer room temperature is in the range of 35^oC which could be easily maintained. The other two temperatures were chosen which have the variation of more than 25^oC on either side of the room temperature.

Ammonium oxalate was added drop by drop in the flask containing the metal sulphates up to the completion of the chemical reaction. Barium chloride test was used to confirm the completion of chemical reaction. The filtrate was washed with distilled water and dried using electric lamp. Oxalates in precursor act like a combustion agent which helps in lowering the calcination 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 diffractograms were recorded using Philips PW 1710 powder diffractometer by scanning in the range 20^oC to 80^oC. IR spectrographs were taken using SHIMATZU (FTIR-8400S) spectrometer.

RESULTS AND DISCUSSION

The XRD patterns indicate the single phase cubic structure for all the samples. The variation of lattice parameters with reaction temperatures for different compositions is shown in Figure 1. The lattice parameters obtained using the most intense 311 peak are found to be in the range 8.37 to 8.42Å for all the samples, which are in the range of the reported values for the NiCuZn ferrites [15]. The effects of reaction temperatures on the position of most intense (311) peak in the diffraction pattern are shown in Figures 2, 3, 4 and 5. The peak is found to shift towards smaller angle for reaction temperature 35^oC for all the compositions, while the peak intensities are found to be maximum for reaction temperature of 70^oC for x = 0.3 and 0.4, while for x = 0.5 and 0.6 the maximum intensity is observed at reaction temperature of 10^oC. The reaction temperatures show their effects in position as well as the intensity of the (311) peak. The variation in, peak intensities and sharpness with reaction temperature has been reported by Qu et.al [23]. They have also reported the increase of particle size, lattice constant and Ms with reaction temperature.
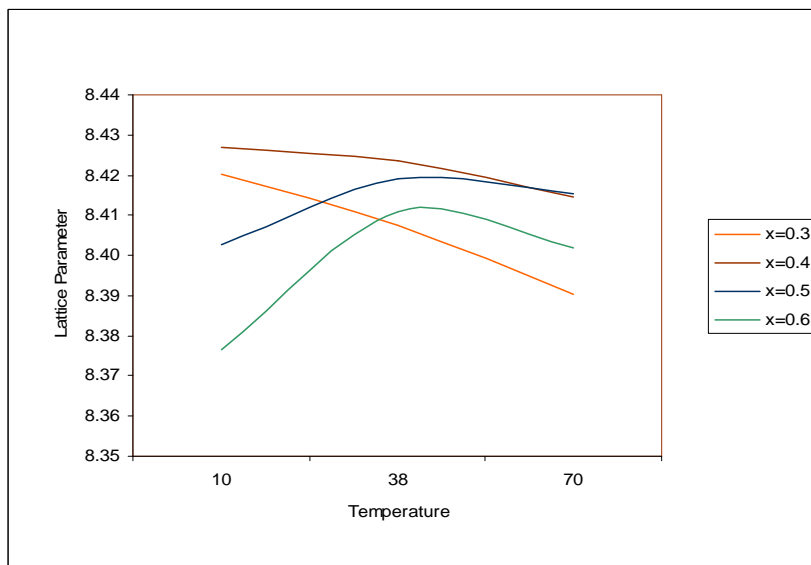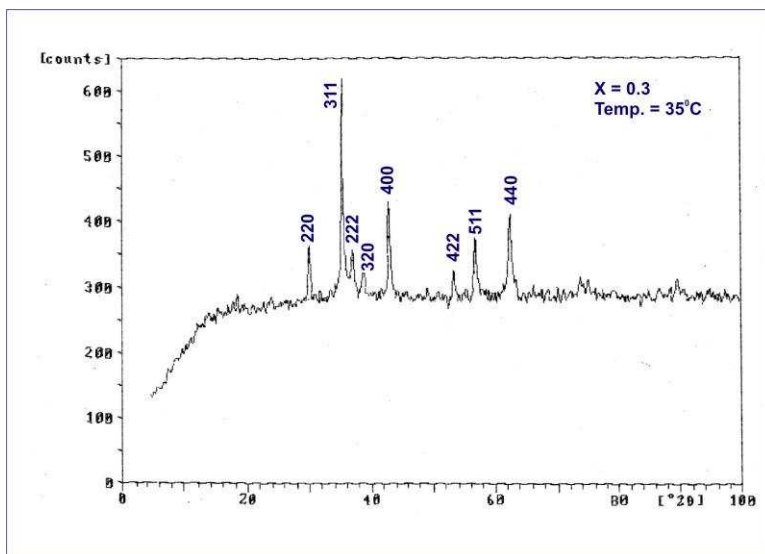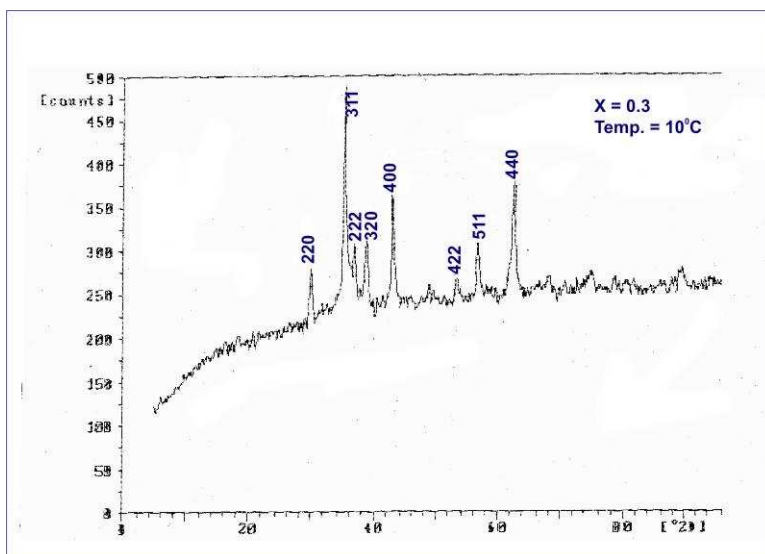
Figure 1-Variation of lattice parameter with temperature of chemical reaction for the compositions x = 0.3,x = 0.4,x = 0.5 and x = 0.6
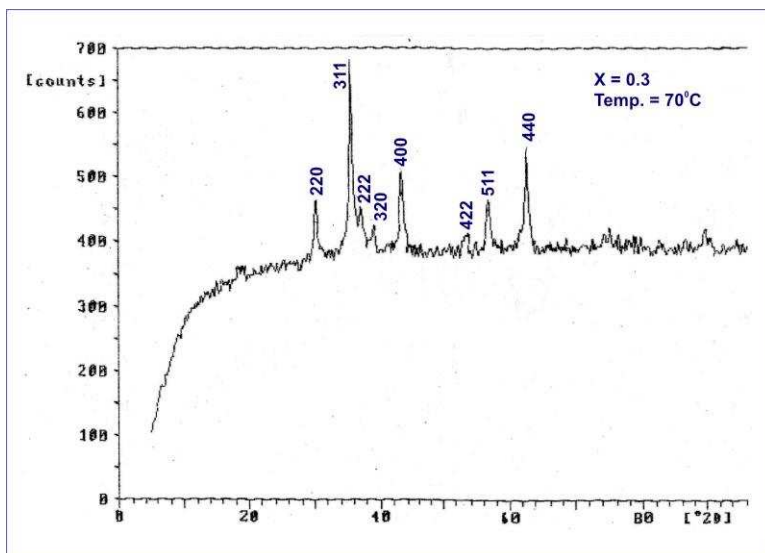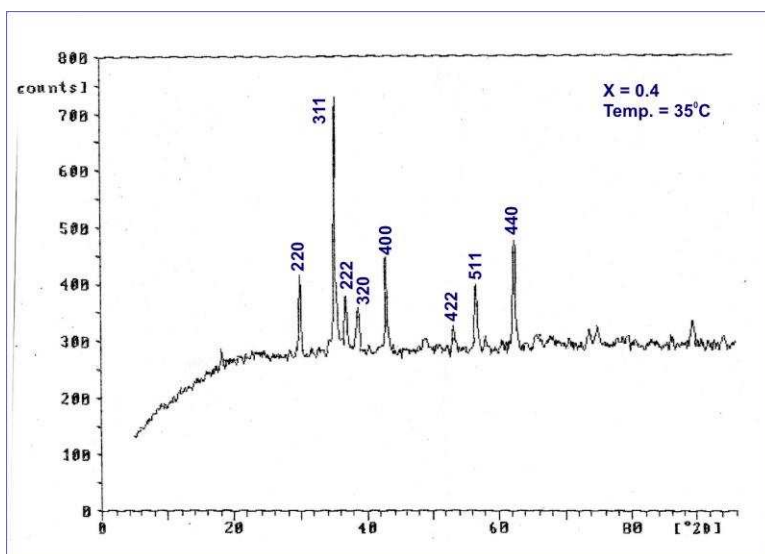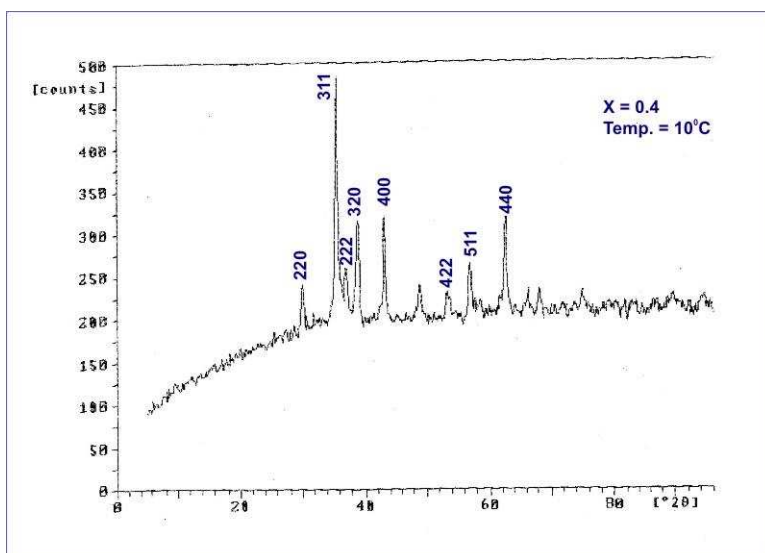
Figure 2-Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.3
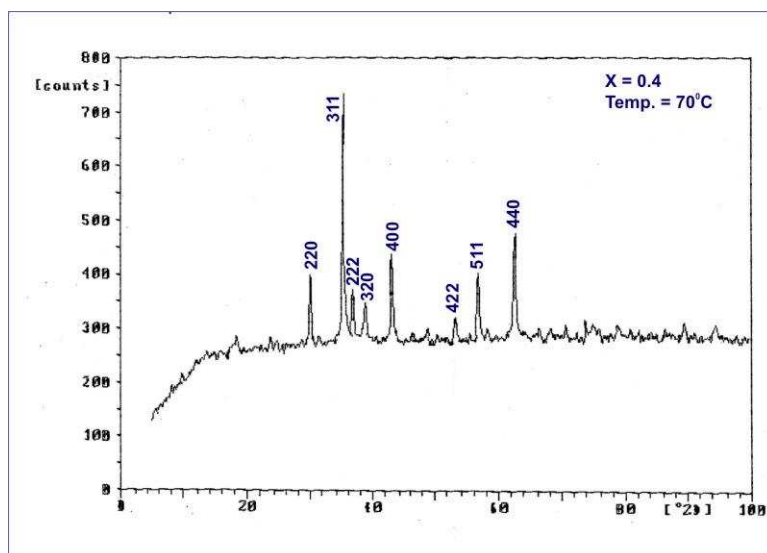
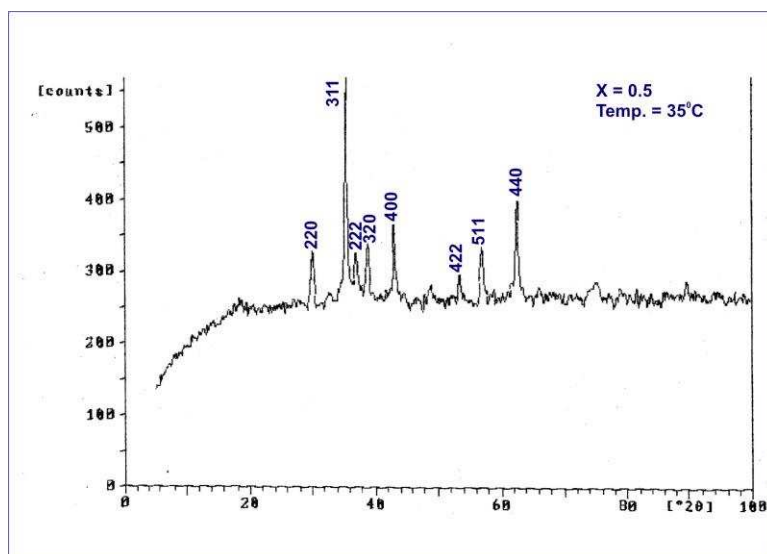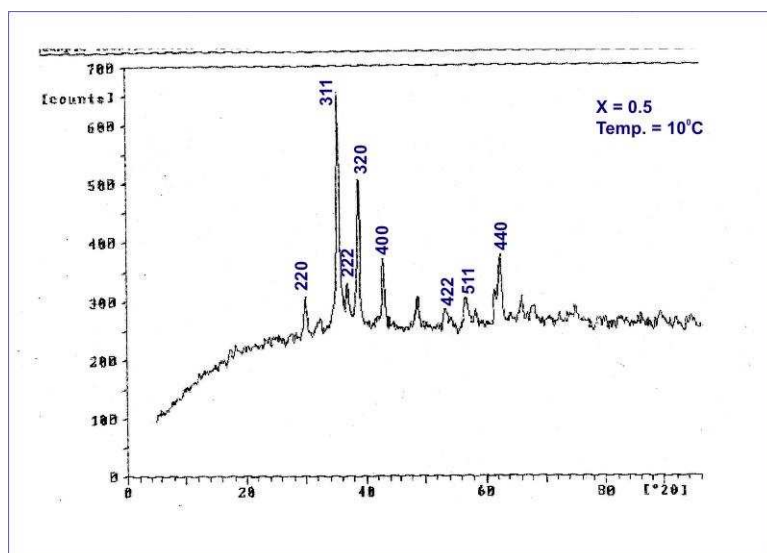**Figure 3-Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.4**
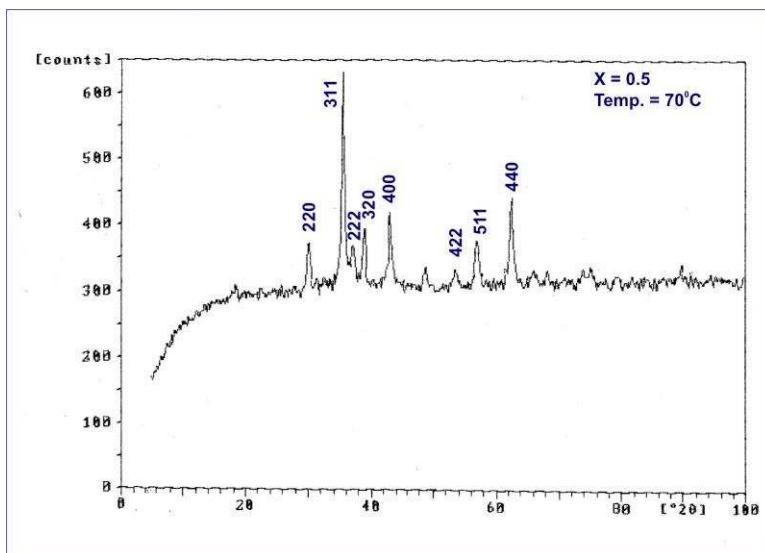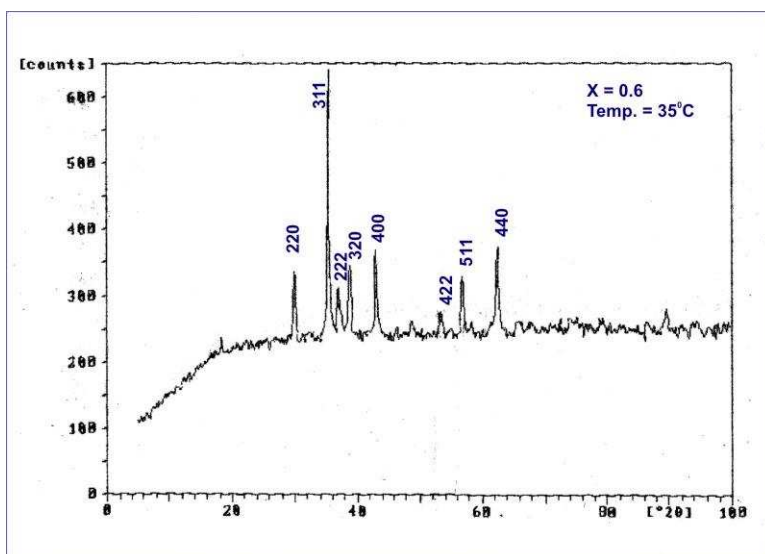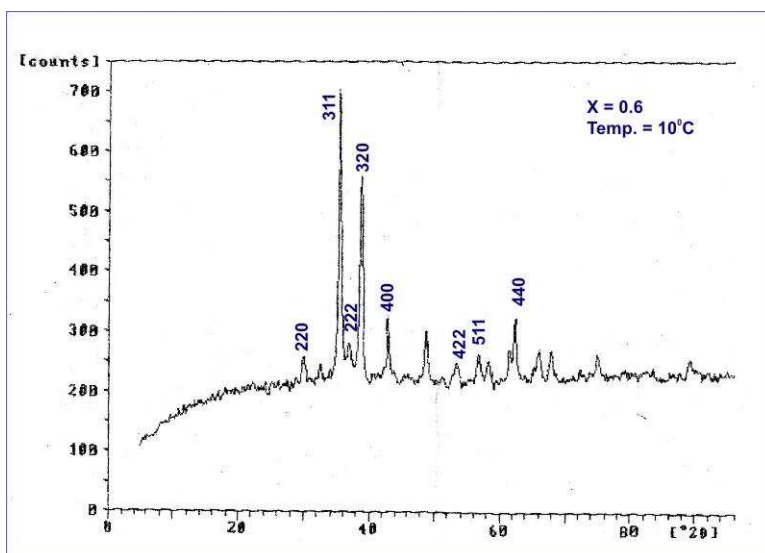

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Figure 4-Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.5
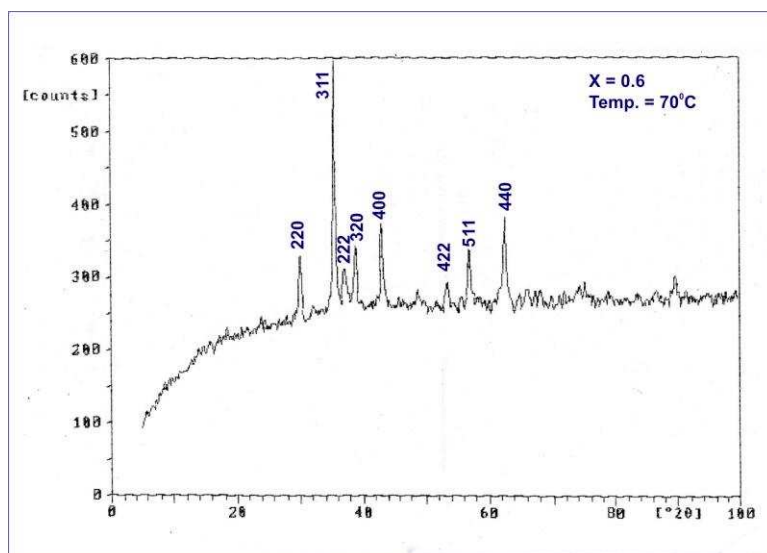
Figure 5-Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.6
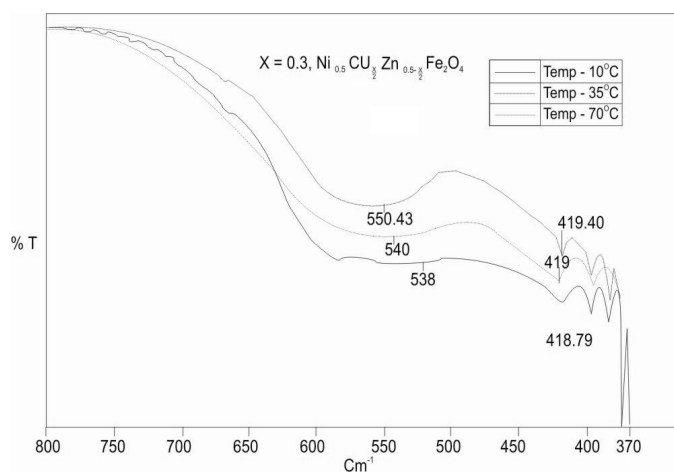

Figure 6-Variation of ν_1 and ν_2 bands with temperature of chemical reaction for the composition x = 0.3

Figure 7-Variation of ν_1 and ν_2 bands with temperature of chemical reaction for the composition x = 0.4

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Figure 8-Variation of ν_1 and ν_2 bands with temperature of chemical reaction for the composition x = 0.5

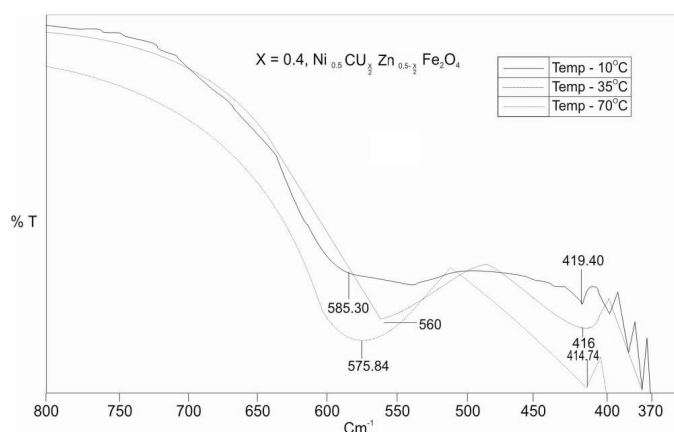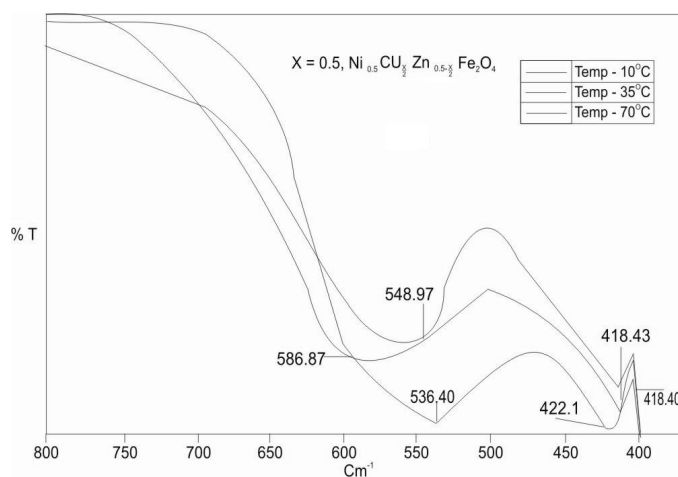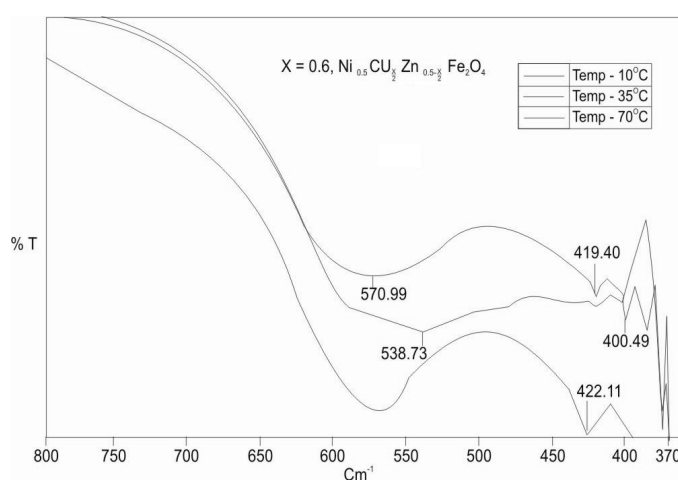**Figure 9-Variation of ν_1 and ν_2 bands with temperature of chemical reaction for the composition x = 0.6**

The infrared spectroscopy shows two characteristic peaks in the range 550 cm^{-1} and 415 cm^{-1} attributed to tetrahedral and octahedral site vibrations. The variation of ν_1 and ν_2 bands with composition at different reaction temperatures is shown in Figures 6, 7, 8 and 9. In the present communication Cu^{2+} ions have been substituted for Zn^{2+} ions having a strong preference for A site while Cu^{2+} has a preference for B site. Therefore Fe^{3+} ions from A site shifts to B site creating space for Cu^{2+} ions. The shift of Fe^{3+} ions depends upon the amount of Cu^{2+} ions substituted. Therefore for lower concentration of Cu^{2+} ions the ν_1 band shifts towards higher values as reported [24], but for higher concentration of Cu^{2+} ions the peaks shift towards lower values. This may be due to the variation in the bond length due to cationic arrangement of ions as the Cu-O-Fe linkage is weaker than Fe-O-Fe linkage. The variation of, ν_2 band is random due to variation in ionic concentration on A site. The variation with composition is as expected but there is also variation with temperature of chemical reaction.

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 Ni^{2+} occupies B site. Cu^{2+} occupies B site.

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