

**Solution combustion synthesis route for the formation of pure and mixed magnesium ferrites ( $Mg_{1-x}Zn_xFe_2O_4$ )**

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**Abstract**

Magnesium ferrite,  $Mg_{1-x}Zn_xFe_2O_4$ , (where  $x$  varies from 0-0.5 and having values  $x=0, 0.1, 0.3, 0.5$ ), has been synthesized through solution combustion route by using oxalic dihydrazide as a fuel for combustion process. Identities of these ferrite materials have been established by XRD (X-ray powder diffraction), FTIR (Fourier transform infrared spectroscopy), and Mössbauer spectroscopy. Single spinel phase ferrites have been synthesized by using solution combustion route. Synthesis of these ferrite materials is also achieved at low temperature and in shorter time. The crystallite size of these ferrite materials increases with Zn substitution. With increasing value of 'x' (Zn content), transition from the ferrimagnetic to the superparamagnetic nature is observed, which is evident from Mössbauer results.

**Keywords:** Ferrites, Solution combustion synthesis, X-ray diffraction, Mössbauer spectroscopy.

**Introduction**

Recently ferrite materials of the type  $AB_2O_4$ , are being investigated for having various applications, as ferrites are stable chemically as well as thermally [1-3] and show interesting magnetic and electric properties. Properties of nanoscale ferrite materials significantly different from their bulk form [4-9]. Now a days ferrite materials are also used as gas sensors [10, 11], in catalysis [12], dye adsorbent [13-15] and magnetic drug delivery [16]. Nanoscale magnesium ferrites find applications in refrigeration, ferrofluids, and magnetic resonance imaging [17]. Various synthetic routes have been used by different researchers for synthesis of nanoscale ferrite materials such as hydrothermal [18], sol-gel [19, 20], co-precipitation [21, 22] etc. Alkaline earth metal ferrites have also been synthesized by using metal ferricarboxylate precursors (formate malonate, maleate, citrate, ferrioxalate,) [23-27]. In this study, synthesis of magnesium ferrite has been carried out by using solution combustion method and synthesized powdered ferrites have been characterized by using FTIR, XRD and Mössbauer spectroscopy.

**Experimental**

Pure and mixed magnesium ferrites with composition  $Mg_{1-x}Zn_xFe_2O_4$  (x changes from 0 to 0.5 in steps of 0.1) have been synthesized by thoroughly mixing the stoichiometric solutions (aqueous) of magnesium chloride anhydrous ( $MgCl_2$ ), Zinc chloride ( $ZnCl_2$ ) and ferric nitrate [ $Fe(NO_3)_3 \cdot 9H_2O$ ]. Oxalic dihydrazide (ODH) paste was added to the mixture gradually. This mixture was heated and concentrated on a water bath for 3-4 hours. The concentrate was then subjected to heating in a muffle furnace up to  $650^{\circ}C$ . The temperature of muffle furnace was gradually increased in steps and sample was kept at  $650^{\circ}C$  for 3 hours. After that temperature of furnace was gradually decreased in steps. As synthesized ferrite powder was then characterized by using various physico-chemical techniques. IR studies were performed with Shimadzu spectrometer FTIR-8400S. PANALYTICAL diffractometer, PW3064, having Cu  $K\alpha$  source ( $\lambda=1.54\text{\AA}$ ) was used for X-ray diffraction studies. Mössbauer spectra of the ferrite powders were recorded with Mössbauer spectrometer MB-500 having  $^{57}Co$   $\lambda$ -ray source embedded in the Rhodium matrix and data was fitted with software WinNormos.

**Results and Discussion**

The FTIR studies of as synthesized ferrite powders (*Fig. 1-4*), with varying composition of Zn, reveal two absorption bands ( $600\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ ). The absorption peaks confirm the presence of A (tetrahedral, higher frequency) and B (octahedral, lower frequency) sites in ferrite samples [28-30].

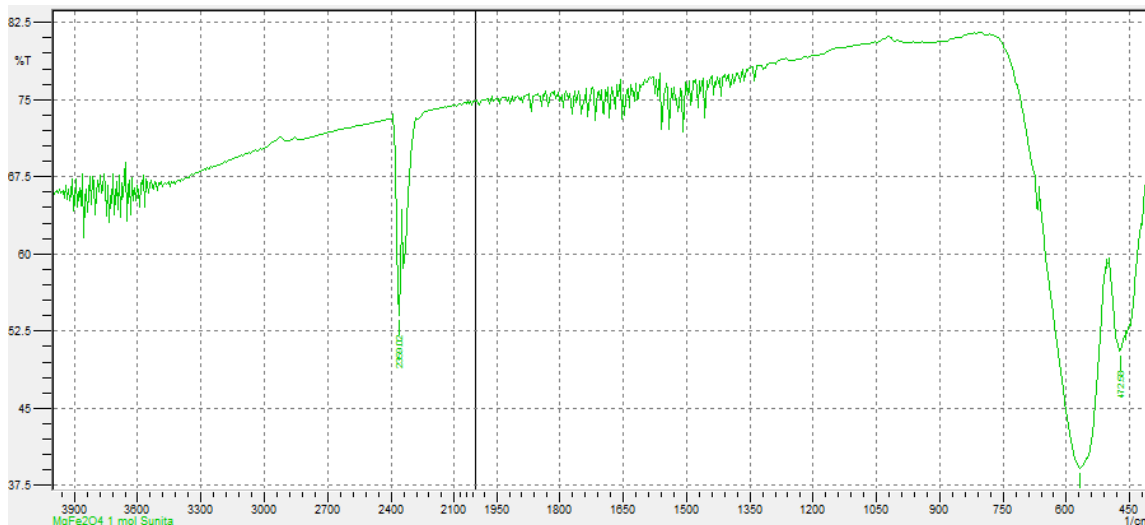


Figure 1: FTIR spectrum, Mg<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x=0)

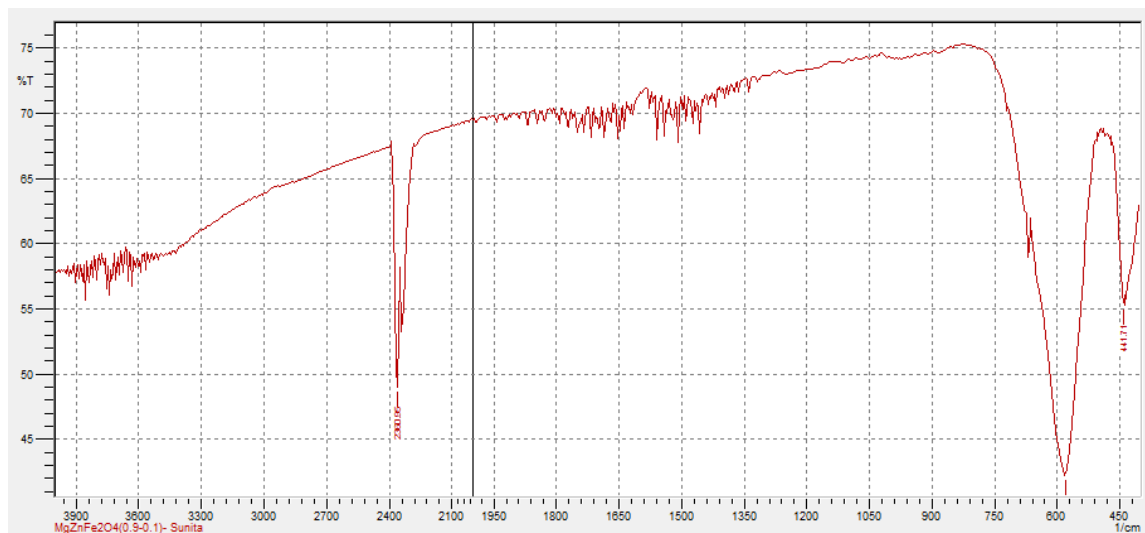


Figure 2: FTIR spectrum, Mg<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x=0.1)

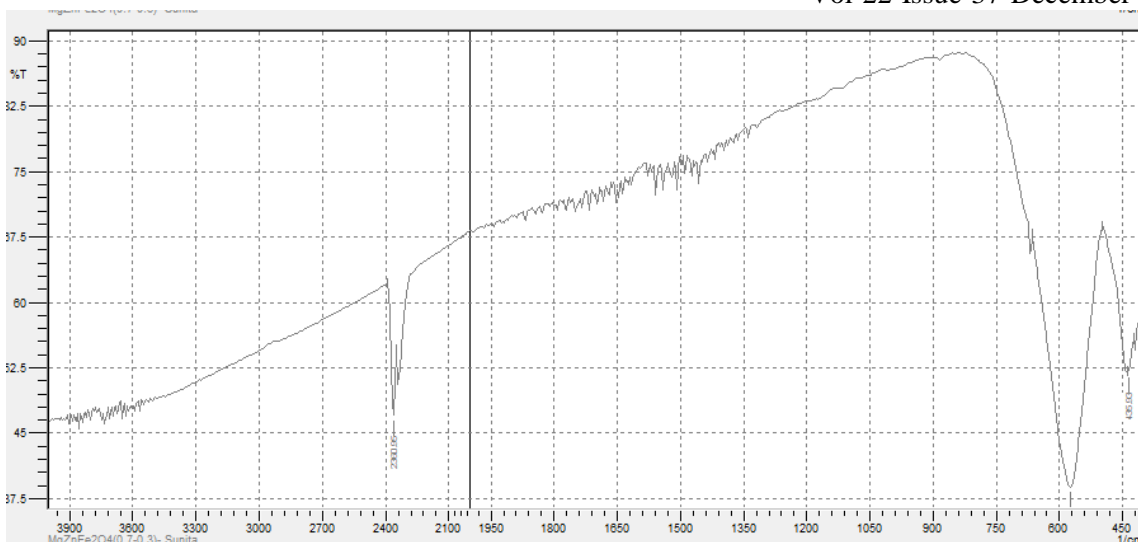


Figure 3: FTIR spectrum,  $Mg_{1-x}Zn_xFe_2O_4$  ( $x=0.3$ )

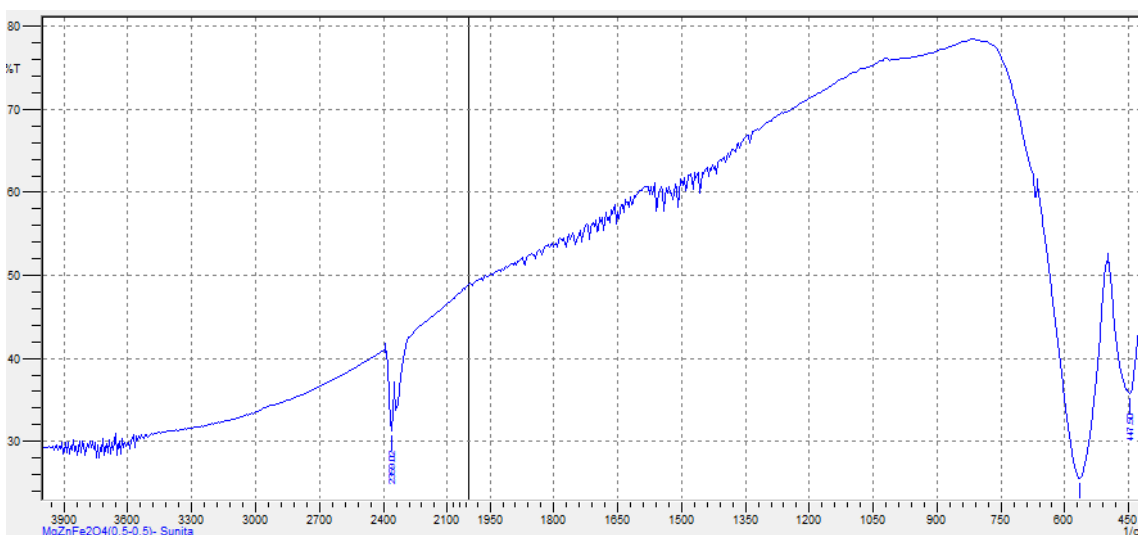


Figure 4: FTIR spectrum,  $Mg_{1-x}Zn_xFe_2O_4$  ( $x=0.5$ )

XRD studies for as synthesized ferrite powders (Fig. 5, 6) show the presence of single-phase cubic spinel structure [31]. With increase in Zn substitution, lattice parameter of these ferrite samples increases, as revealed from XRD. With increase in the value of ‘x’  $Mg^{2+}$  ions get replaced with  $Zn^{2+}$  ions and change in lattice parameter is attributed to larger size of  $Zn^{2+}$  ions [31]. The crystallite size of these samples (as per Scherrer’s equation) [31] increases with increasing Zn content.

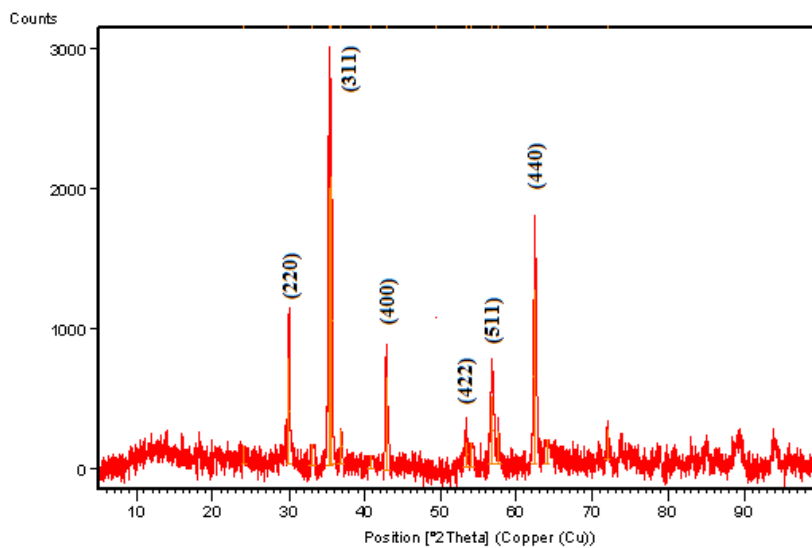


Figure 5: X-ray powder diffraction,  $Mg_{1-x}Zn_xFe_2O_4$  ( $x=0$ )

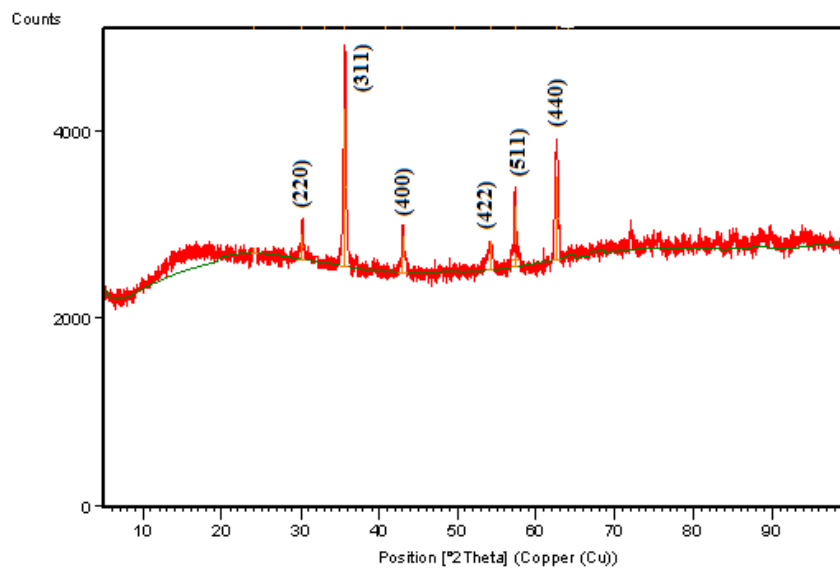
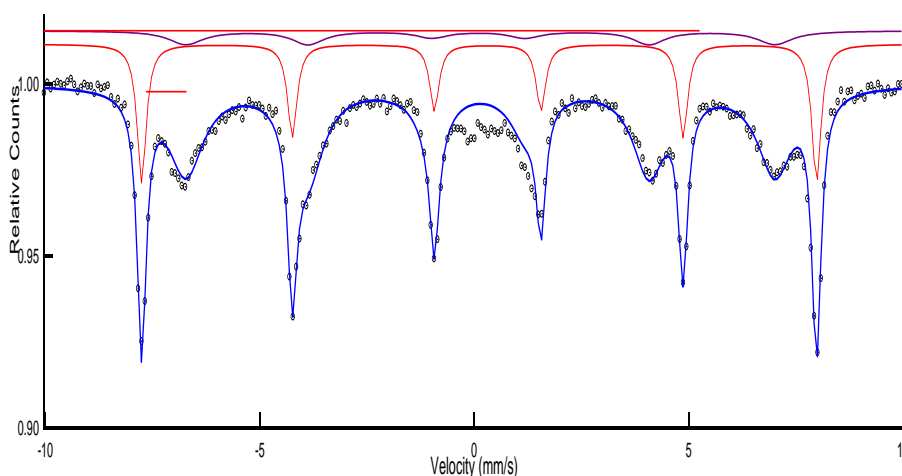
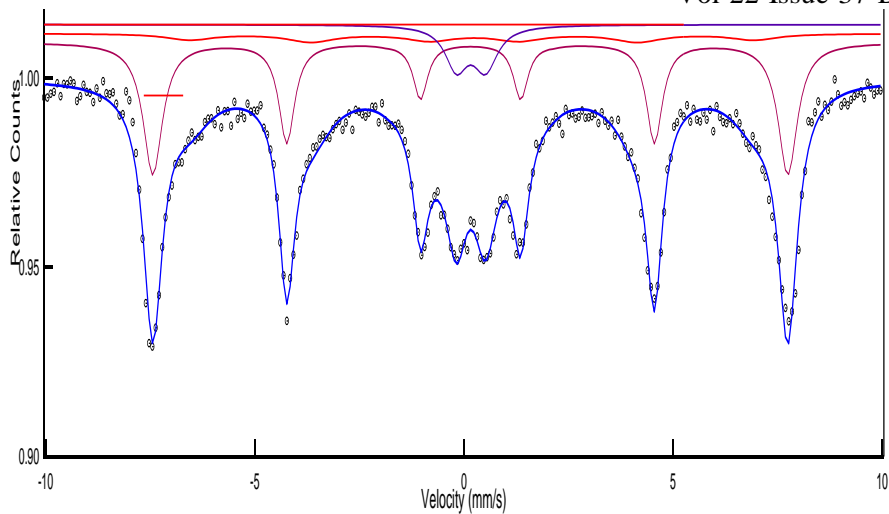


Figure 6: X-ray powder diffraction,  $Mg_{1-x}Zn_xFe_2O_4$  ( $x=0.1$ )

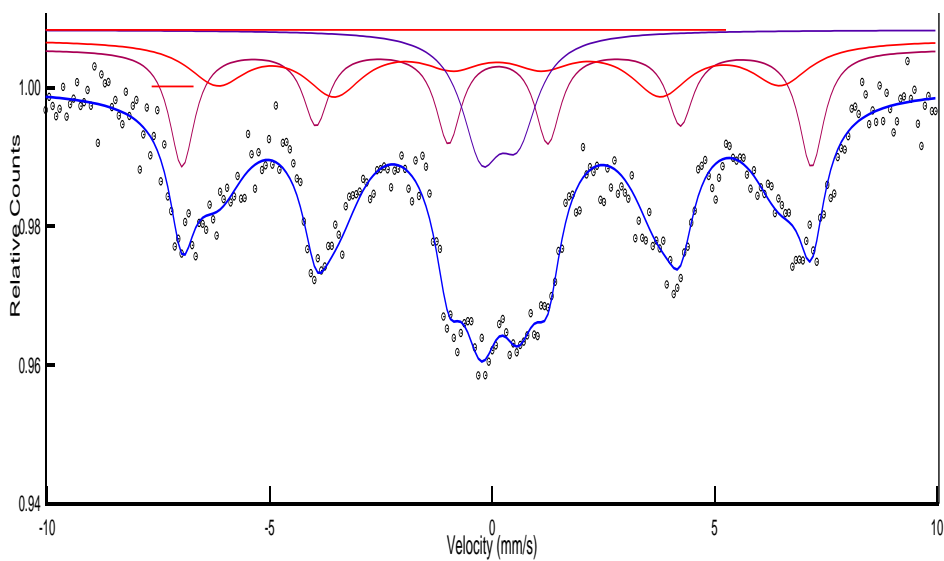
Figure 7-10 show room temperature Mössbauer spectra for ferrite powders. Mössbauer spectrum of  $Mg_{1-x}Zn_xFe_2O_4$  ( $x=0$ ) show two well resolved Zeeman hyperfine magnetic sextets which are assigned to ferrimagnetic character of the ferrite structure and the sextets appear due to the distribution of ferric ions ( $Fe^{3+}$ ) in both A and B sites. With increase in Zinc substitution ( $x=0.1$  to  $0.5$ ) super-paramagnetic doublet can also be seen along with two sextets. With increasing value of 'x', relative intensity of the doublet is also increasing. This central doublet along with sextets is due to presence of magnetically isolated ions ( $Fe^{3+}$ ) [32]. This could also be due to increase of the non magnetic zinc ions, which results in the magnetic coupling weakening. A transition in character (ferrimagnetic to super-paramagnetic) happens, as evident from spectra, with increasing Zn content.



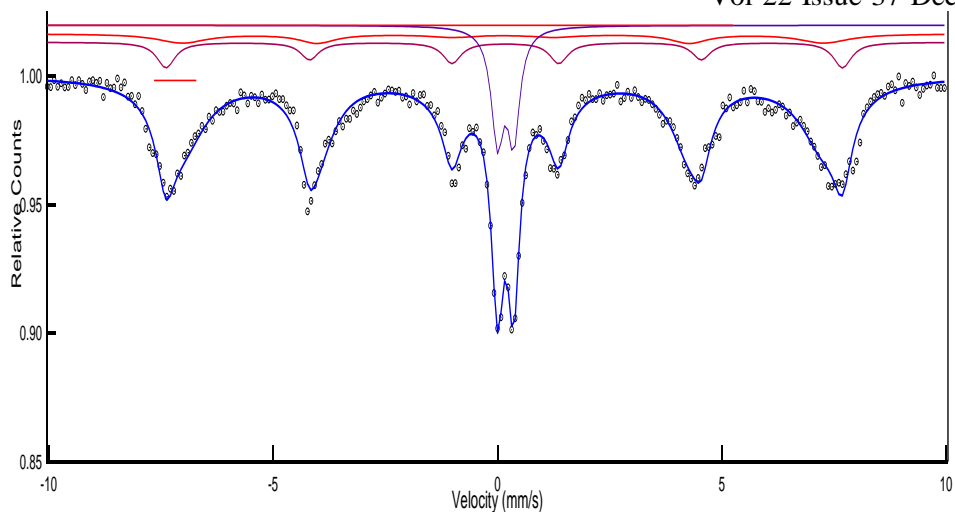
**Figure 7: Mössbauer spectrum for  $Mg_{1-x}Zn_xFe_2O_4$ , ( $x=0$ )**



**Figure 8: Mössbauer spectrum for  $Mg_{1-x}Zn_xFe_2O_4$ , ( $x=0.1$ )**



**Figure 9: Mössbauer spectrum for  $Mg_{1-x}Zn_xFe_2O_4$ , ( $x=0.3$ )**



**Figure 10: Mössbauer spectrum for  $Mg_{1-x}Zn_xFe_2O_4$ , ( $x=0.5$ )**

### Conclusion

Zn substituted magnesium ferrites,  $Mg_{1-x}Zn_xFe_2O_4$ , have been synthesized by solution combustion method. In this method, oxalic dihydrazide (ODH) acts as a fuel. This method has many advantages over other conventional methods. Due to atomic scale mixing of starting materials, single-phase and nano-scale particles are synthesized. The ferrite powders are synthesized at low temperature and in less time. FTIR and XRD studies confirm the presence of tetrahedral (A sites) and octahedral (B sites) sites in these ferrites and formation of single cubic phase respectively. Mössbauer analysis of as such synthesized ferrite powders revealed the transition in character (ferrimagnetic to super-paramagnetic) with increase in Zn substitution.

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