



IR Analysis of Zinc Doped Nickel and Copper Ferrite Nanoparticles

* T. Anjaneyulu ** A. T. Raghavender *** K. Vijaya Kumar **** P. Narayana Murthy ***** K. Narendra

* Department of Physics, Narasaraopet Engineering College, Narasaraopet - 522 601, A. P., India.

** Department of Electronics and Communication Engineering, Nishitha College of Engineering and Technology, Lemoor (V), Kandukur (M), R. R. District – 501 359, A. P., India

*** Department of Physics, Jawaharlal Nehru Technological University Hyderabad, College of Engineering, Nachupally (Kondagattu), Karimnagar - 505 501, A.P., India.

**** Department of Physics, Acharya Nagarjuna University, Guntur – 522 510, A. P., India.

***** Department of Physics, V.R. Siddhartha Engineering College, Vijayawada - 520 007, A. P.

ABSTRACT

Nanocrystalline Ni-Zn and Cu-Zn ferrites have been synthesized by oxalic acid based precursor method. The IR measurements showed the prominent bands due to the vibrations of metal ions and as a feature of spinel ferrite phase formation. The band positions were observed to be very sensitive to doping conditions. The IR bands were observed to shift their positions due to the doping concentration and as a result the structural changes were observed.

Keywords : Nanoferrites, IR analysis; Ni-Zn and Cu-Zn ferrite.

1. Introduction

Synthesis of nanoparticulated spinel ferrite exhibits unpredictable physical and chemical properties, which are entirely different from those of usual bulk materials, because of extremely small grain size or large specific surface area. Therefore synthesis and characterization of the nanocrystalline spinel ferrite powders have attracted increasing attention recently [1, 2]. Ni-Zn ferrite is a well-known spinel magnetic material. In the inverse spinel structure of NiFe_2O_4 , the tetrahedral sites are occupied by Fe ions and octahedral by ferric and nickel ions and Zn ions being occupied only in tetrahedral site. Ni-Zn ferrites are ferrimagnetic materials with a large number of technological applications in telecommunications and entertainment electronics. Ni-Zn ferrites are among the most widely used soft magnetic materials because of high frequency applications as they possess high electrical resistivity and low eddy current losses [3-5]. In CuFe_2O_4 the Fe ions occupy the tetrahedral sites and half of the octahedral sites, Cu ions generally occupy the octahedral sites and Zn ions completely occupy the tetrahedral sites [6, 7]. Nanocrystalline Cu-Zn ferrite have been extensively investigated due to their potential applications in non-resonant device, radio frequency circuits, rod antennas, high quality filters, transformer cores, read/write heads for high speed digital tapes and operating devices [8, 9].

In this work, we present the IR analysis of the systematic doping of non-magnetic Zn content on the nanocrystalline Ni and Cu ferrite synthesized by oxalic acid based precursor method.

2. Experimental

Nanocrystalline $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ and $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 0.8$) were prepared by oxalic acid based precursor method [10]. All of the chemicals were analytical grade from Sigma-Aldrich with purity $\geq 99\%$ and were used without any

further purification. In a typical procedure, the nickel nitrate hydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, copper hydrate $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, zinc nitrate hydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ferric nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as starting materials. Stoichiometric amounts of metal nitrates were dissolved in deionized water to get clear solution. The obtained aqueous solution of metal nitrates was mixed with oxalic acid in a molar ratio ranging from 1:3 to 1:0.15. The mixture solution were moved on to magnetic stirrer and stirred for 2 h at room temperature. The reaction mixtures turned turbid by varying molar ratios 1:3 and 1:2. When the molar ratio was further lowered to 1:1, precursor solution showed different colour shades. The resultant mixtures were evaporated on a hot plate at 150°C for 2 h. The obtained raw powders were thermally heat treated at 300°C for 4 h to get the single phase nanocrystalline spinel structure. The structural changes are observed by ABB Bomem MB 102 infrared spectrometer equipped with CsI optics and DTGS detector. The samples were mixed with KBr and made in the form of pellets for IR transmission measurements.

3. Results and discussions

3 (a) Ni-Zn ferrite analysis

Infrared analysis is one of the important techniques to investigate the spinel ferrite phase formation apart from the XRD analysis. In the Ni-Zn ferrite, ZnFe_2O_4 is considered to be normal spinel ferrite [11], represented by the formula $(\text{Zn}^{2+}\text{O}) [\text{Fe}^{3+}_2\text{O}_4]$, while NiFe_2O_4 is represented by the formula $(\text{Fe}^{3+}\text{O}) [\text{Ni}^{2+}\text{Fe}^{3+}_2\text{O}_4]$, where the square brackets enclose the ions in the octahedral sites, and the small brackets represent the tetrahedral sites. During the synthesis process of samples $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ from $x = 0.0$ to 0.8, one is expected to induce the structural changes both in the octahedral and tetrahedral sites of the samples.

In the case of spinel ferrites the most interesting part of the IR spectra, is in the range $800 - 250 \text{ cm}^{-1}$. This range is as-

signed to the vibrations of ions in the crystal lattice [12 - 13]. In this range, ferrites give rise to two most prominent absorption envelopes as shown in Fig. 1. Between 800 and 500 cm^{-1} ν_1 band is found, which is assigned to Fe^{3+} -O and Zn^{2+} -O stretching vibrations inside the tetrahedral sites. Absorption band ν_2 is present between 450 and 300 cm^{-1} . This band is assigned to Fe^{3+} -O and Ni^{2+} -O stretching vibrations in the octahedral sites. A well resolved absorption peak at 330 cm^{-1} for $x \geq 0.4$ samples is observed and is assigned to be ν_3 . This band is attributed to the oscillations of zinc atoms in the tetrahedral environment [9].

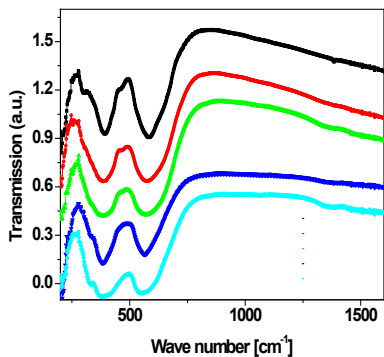


Fig. 1: IR spectra of Ni_{1-x}Zn_xFe₂O₄ (0.0 ≤ x ≤ 0.8) nanoparticles.

The variation of band positions ν_1 and ν_2 of Ni_{1-x}Zn_xFe₂O₄ with x is shown in Table 1 and Fig. 2. Variation of ν_1 peak position for samples of different x indicates structural changes in tetrahedral sites are taking place with the change in composition. The band position and its shape is largely affected not only by chemical composition of the sample, but also by a number of uncontrollable parameters, such as synthesis conditions, annealing temperature etc., it is observed that ν_1 band shifts towards the lower wave numbers with x over the whole composition range. This indicates the weakening of the metal-oxygen bonds in the tetrahedral sites due to the transition between inverse to normal spinel structure also Zn^{2+} possesses much larger preference to tetrahedral geometry than Fe^{3+} ions [13]. The formation of normal spinel structure due to the exchange of the positions of Fe^{3+} with Zn^{2+} ions causes weakening of the metal-oxygen bonding in tetrahedral sites.

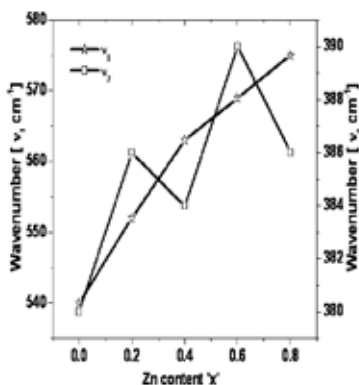


Fig. 2: Variation of IR peak position ν_1 and ν_2 (cm⁻¹) for Ni_{1-x}Zn_xFe₂O₄ (0.0 ≤ x ≤ 0.8) nanoparticles.

3 (b) Cu-Zn ferrite analysis

The IR spectra of Cu_{1-x}Zn_xFe₂O₄ (0.0 ≤ x ≤ 0.8) is shown in Fig. 3. According to Waldron and Hafner [13, 14], the bands around 600 cm^{-1} (ν_1) are attributed to the stretching vibration of Fe^{3+} -O²⁻ in the tetrahedral phases and the bands around 400 cm^{-1} (ν_2) to that of Cu^{2+} -O²⁻ in the octahedral complexes.

The IR spectra Fig.3 indicate the presence of two absorption bands ν_1 at 573 to 584 cm^{-1} and ν_2 at 414 - 408 cm^{-1} . The positions of these bands confirm the existence of Cu^{2+} ions in the octahedral sites and the Fe^{3+} ions in tetrahedral ones [15]. It is evident from Table.1 and Fig.4 that the bands ν_1 and ν_2 are sensitive with respect to doping concentration. These bands shift its position with increasing Zn content x. This suggests that increase of doping Zn content x increases magnetic moment of the particles. This is further supported by the fact that in ferrites the magnetization is positively correlated with particle size, because the increase of the particle size may lead to a decrease of non-magnetic fraction on the surface of the particle [16]. So it can be concluded that change of the size of the nanoparticles causes the variation of positions ν_1 and ν_2 infrared bands [17].

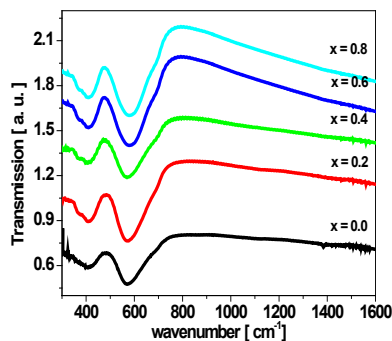


Fig. 3: IR spectra of Cu_{1-x}Zn_xFe₂O₄ (0.0 ≤ x ≤ 0.8) nanoparticles

Table 1

Ni _{1-x} Zn _x Fe ₂ O ₄		Cu _{1-x} Zn _x Fe ₂ O ₄		
x	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)
0.0	541	382	562	406
0.2	553	385	569	403
0.4	562	385	571	399
0.6	571	391	580	395
0.8	578	387	584	392

Table 1: Variation of band position ν_1 and ν_2 (cm-1) for Ni_{1-x}Zn_xFe₂O₄ and Cu_{1-x}Zn_xFe₂O₄ (0.0 ≤ x ≤ 0.8) nanoparticles.

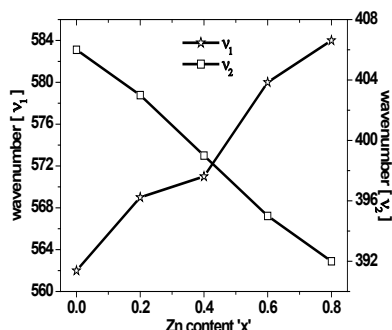


Fig. 4: Variation of IR peak position ν_1 and ν_2 (cm-1) for Cu_{1-x}Zn_xFe₂O₄ (0.0 ≤ x ≤ 0.8) nanoparticles.

4. Conclusions

Ni-Zn and Cu-Zn ferrites nanoparticles were synthesized by oxalic acid based precursor method. IR was as a tool for characterizing spinel ferrite phase formation. The IR analysis showed the prominent bands due to the vibrations of metal ions. The band positions were observed to be very sensitive to doping conditions. The structural changes were confirmed due to the shift in the band positions due to Zn doping.

REFERENCES

- [1] Z. Zhong, Q. Li, Y. Zhang, H. Zhong, M. Cheng, Y. Zhang, Powder Technology, 155 (2005) 193-195. | [2] Z. Yue, J. Zhou, L. Li, H. Zhang, Z. Gui, J. Magn. Mater. 208 (2000) 55-60. | [3] X. He, G. Song, J. Zhu, Materials Letters, 59 (2005) 1941-1944. | [4] Y. Matsuo, M. Inagaki, T. Tomozawa, F. Nakao, IEEE Trans. Magn. 37 (2001) 2359-2361. | [5] P.S. Anil Kumar, J.J. Shrotri, S.D. Kulkarni, C.E. Deshpande, S.K.Date, Mater. Lett. 27 (1996) 293-296. | [6] G.F.Goya, H.R.Rechenberg, J. Appl. Phys. 84 (1998) 1101. | [7] D. Pajic, K. Zadro, R. E. Vanderberghe, I. Nedkov, J. Magn. Mater. 281 (2004) 353. | [8] S. K. Pradhan, S. Bid, M. Gateshki and V. Petkov, Mater. Chem. Phys. 93 (2008) 224. | [9] A. R. Lamani, H. S. Jayanna, P. Parameshwara and R. Somasekhar, Ind. J. Pure and App. Phys. 47 (2009) 715. | [10] A. T. Raghavender, Sagar E. Shirsath, K. Vijaya Kumar, J. Alloys Comp. 509 (2011) 7004. | [11] F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th edition, John Wiley and Sons, New York, 1988, page 9. | [12] A. T. Raghavender, N. Biliskov, Z. Skoko, Mater. Lett. 65 (2011) 677. | [13] R.D. Waldron, Phys. Rev. 99 (1955) 1727-1735. | [14] S.T. Hafner, J.Kristallogr. 115 (1961) 331. | [15] W.Z. Lv, B. Liu, Z. K. Luo, X.Z. Ren, P.X. Zhang, J.Alloys.Comp. 465 (2008) 261. | [16] M. Andrés – Vergés, C. de Julián, J. M. González, C. J. Serna, J. Mater. Sci. 28 (1993) 2962. | [17] T. Suto, K. Haneda, T. Iijima, M. Seki, J. Appl. Phys. A 50 (1990) 13. |