



EFFECT OF ANNEALING TEMPERATURE ON THE XRD AND IR PROPERTIES OF GD DOPED NICKEL FERRITES NANOPARTICLES

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Article History: Received: 03.12.2022

Revised: 15.01.2023

Accepted: 20.02.2023.

Abstract: Gd doped nickel ferrite samples, $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) were synthesized with sol-gel method and calcinated at temperatures 700°C, 950°C and 1200°C. With the increase in temperature, we observed the structural changes in the XRD and Fourier Transform IR data. With doping Gd content we observed secondary phases in the XRD analysis which has been confirmed with IR analysis. From the XRD and Fourier Transform IR experimental observations, we confirmed that the secondary phases might be due to larger ionic radii of Gd compared to Ni ions. The secondary phases observed in all the samples were not able to disappear even with the higher annealing temperatures.

Keywords: Gd doped Ni Ferrites; XRD; FTIR; Structural Properties

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DOI:

10.31838/ecb/2023.12.si4.0572023.22/04/202

INTRODUCTION

Nanoscale magnetic materials received tremendous attention, owing to fundamental interest in different properties compared to their bulk counterparts because of its promising applications like in the high-density magnetic storage [1-4]. Nickel ferrite is considered to be one of the soft magnetic materials which has different types of applications in high frequency devices magnetic semiconductors and in power Transformers etc. Nickel ferrite is a soft magnetic material because of its interesting ferromagnetic properties at low temperature. They have low conductivity, low Eddy current losses, high electrochemically stable, excellent catalytic behaviour etc.

Nickel ferrite is a cubic ferromagnetic oxide with an inverse structure where the divergent Ni^{2+} ions occupy the octahedral [B] sites and the trivalent (A) ions Fe^{3+} occupies both the (A) and [B] sites. To enhance the magnetic properties of soft magnetic materials like nickel ferrite doping of trivalent and divalent elements can be used. Several researchers have used different techniques to examine their properties to see the effect of synthesis techniques as well as doping element on the structural, electrical, optical and magnetic properties. Substitution of rare earth ion (RE) into the spinel ferrites gives interesting properties compared to other substituted ferrites [5]. Several researchers have reported that, rare earth doping in ferrites causes the structural distortion, thereby significantly changing the properties [6, 7]. The fact is that, RE ions has the un-paired (4f) electrons and the strong spin-orbit coupling. It is observed that in ferrites, Fe – Fe exchanges are due to the spin coupling of (3d) electrons, influence the structural, electrical, optical and magnetic properties. When RE ions occupy the ferrite lattice sites, the RE-Fe interactions i.e., 3d – 4f coupling leads to the enhanced magnetic and electrical properties. And, also helps in determining the magnetocrystalline anisotropy among spinel ferrites. Rare earth substituted ferrite materials are effective materials in enhancing the electromagnetic properties [8-12]. Based on the above discussions, in recent years the RE doped ferrites showed unusual optical, electrical and magnetic properties due to which several researchers got attracted and investigated their properties extensively.

In this present work doped Gd in nickel ferrite which were synthesized using sol gel technique to understand the structural changes taking place with doping and the calcination temperature.

EXPERIMENTAL

$\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples were prepared using sol-gel method [13, 14]. Nickel nitrate, ferric nitrate, Gadolinium oxide, ammonia and citric acid was used as starting materials. The starting chemicals with stoichiometric ratio were mixed with deionized water to obtain a clear solution. The molar ratio of between citric acid and nitrate solution was 1:3 ratio. Ammonia was added to maintain the $\text{pH} = 7$. The chemical liquid was initially heated at temperature 100°C using a hot plate with stirrer. After couple of hours a viscous gel was observed. With further increase in temperature to 200°C , after few minutes a self-propagating combustion reaction started occurring. When the gel is completely burnt, a loose powder was obtained [13, 14]. The as-prepared powder was calcinated at temperatures 700°C , 950°C and 1200°C for 8h.

The XRD analysis for $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) synthesized samples were measured with Phillips expert X-ray diffractometer. Fourier Transform IR data was recorded using Shimadzu FTIR spectrometer.

RESULTS AND DISCUSSIONS

Fig's 1 to 3 shows the XRD patterns of $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) annealed at three different temperatures 700°C , 950°C and 1200°C for 8 hours. The XRD data confirms the cubic structure in all the synthesized samples. A close observation from the XRD data revealed that the diffraction peaks become broader with the increase of Gd concentration as a result of nanocrystalline nature of the samples. With the increase of Gd doping content 'x' there is a slight change in the peak position, which signifies the change in the structural properties.

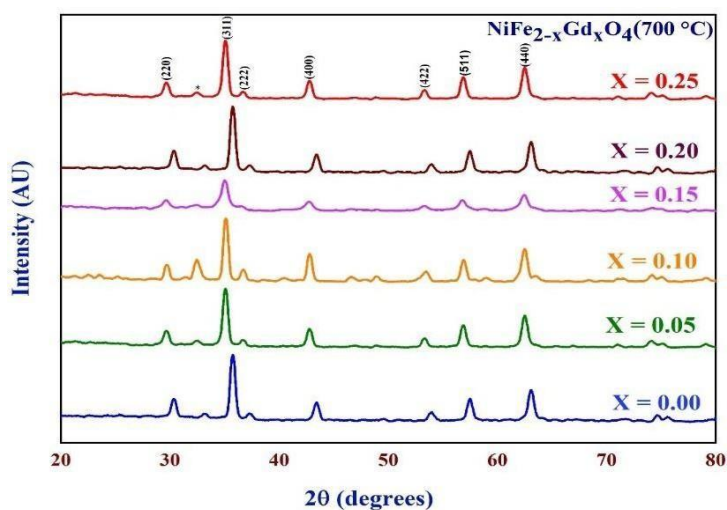


Figure 1: XRD pattern of $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples calcinated at 700°C

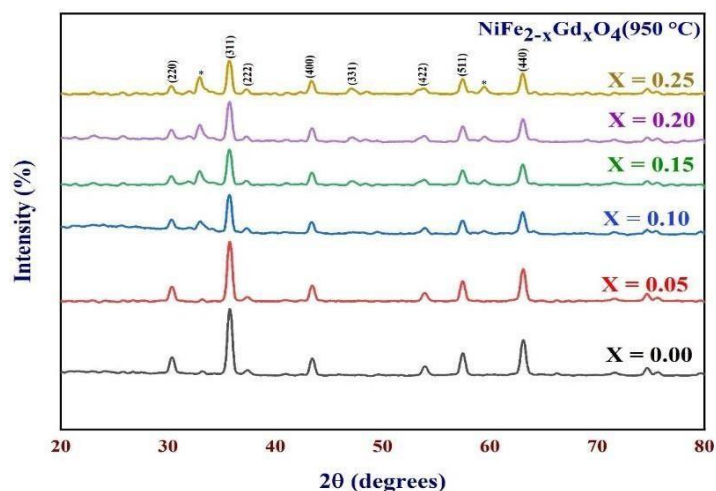


Figure 2: XRD pattern of $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples calcinated at 950°C

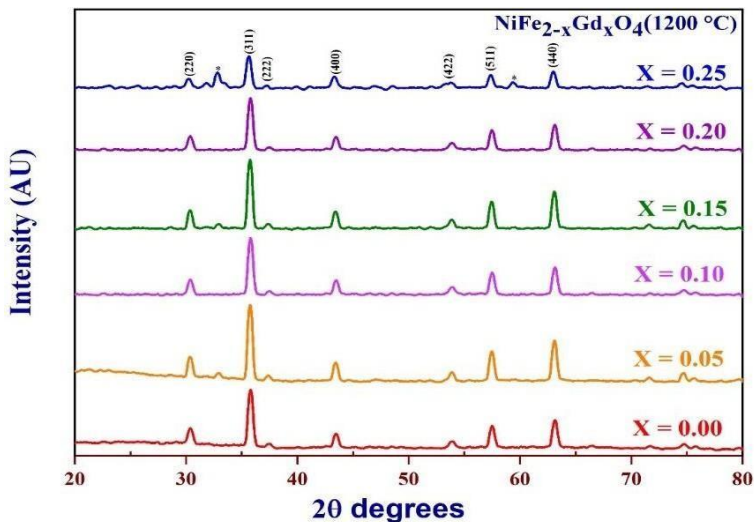


Figure 3: XRD pattern of $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples calcinated at 1200°C

The grain size was observed to increase with Gd doping concentration and the lattice constant also showed the increasing behaviour as shown in Fig's 4 and 5. The observed linear increase in the grain size and the lattice constant with Gd

doping in nickel ferrite was due based on the difference of ionic radii between Ni and Gd. The smaller ionic radius of Ni 0.74 \AA has been replaced by the larger ionic radius of Gd 0.94 \AA .

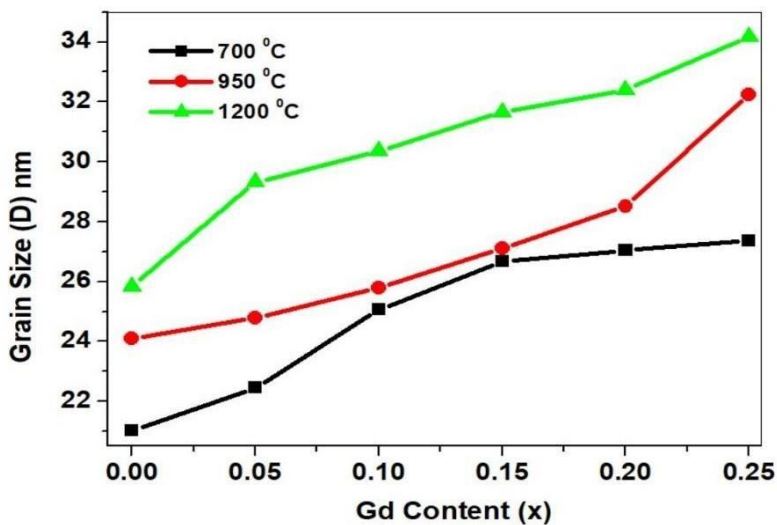


Figure 4: Variation of particle size with different annealing temperatures and Gd content x for $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples

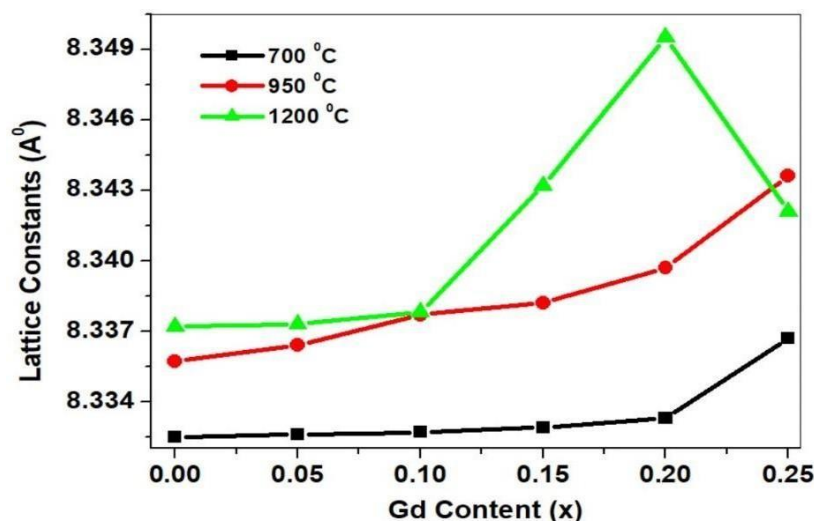


Figure 5: Variation of lattice constant with different annealing temperatures and Gd content x for $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples

In the Gd doped nickel ferrite samples the calcination temperatures showed substantial impact on the structural behaviour of these samples which is further examined by IR analysis. Generally, the as-prepared samples contain vibrational bands with respect to starting chemicals. The main vibrational bands corresponding to ferrites occurs 400 to 1000 cm^{-1} range. The absorption bands near 3150 and 3450 cm^{-1} are due to O-H bonding groups, the bands near 1600 cm^{-1} are due to COO^- groups and the bands near 1350 cm^{-1} are assigned to NO_3^- absorption bands. These bands occur in the as-prepared samples due to the initial chemicals used such as metal nitrates, citric acid, ammonia and deionized water used during the preparation of samples. All the above bonds are supposed to disappear completely when annealed at temperatures above the 420 $^\circ\text{C}$ [14].

The important feature in Fourier Transform IR for Gd doped nickel ferrite samples lies in the range of 1000 - 250 cm^{-1} range [14]. Fig's 6 - 8 shows the Fourier Transform IR Spectra of the Gd doped nickel ferrite samples annealed at 700, 950 and 1200 $^\circ\text{C}$ for 8h. Waldron [15] reported that the absorption band at $\approx 600\text{cm}^{-1}$ corresponds to the intrinsic stretching vibrations of the tetrahedral sites and the absorption band at $\approx 450\text{cm}^{-1}$ is attributed to the vibrations of the octahedral sites. The first two absorption bands at 450 and 650 cm^{-1} correspond to the metal-oxygen intrinsic stretching vibrations at the octahedral site, $\text{M}_{\text{octa}} \leftrightarrow \text{O}$ and tetrahedral metal-oxygen stretching, $\text{M}_{\text{tetra}} \leftrightarrow \text{O}$ [14, 16, 17]. The absorption band at 1390 cm^{-1} are due to N-O in nitrate ion [15, 17] in the synthesized samples.

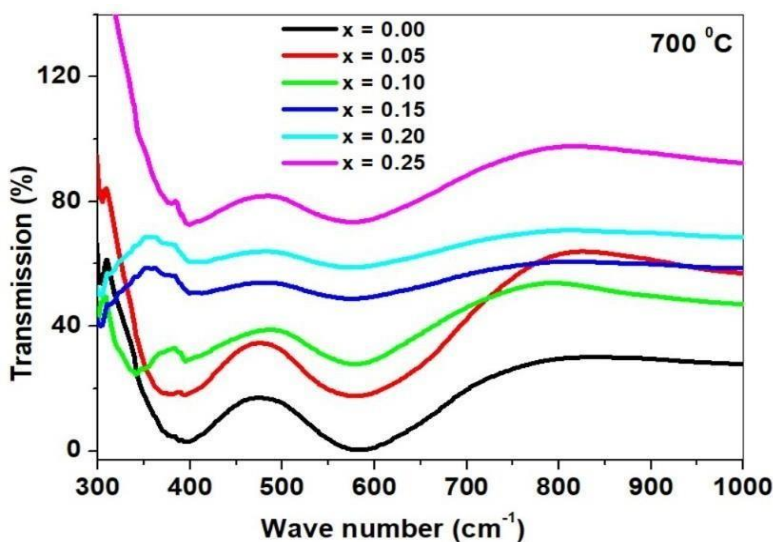


Figure 6: FTIR spectra $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples calcinated at 700 $^\circ\text{C}$

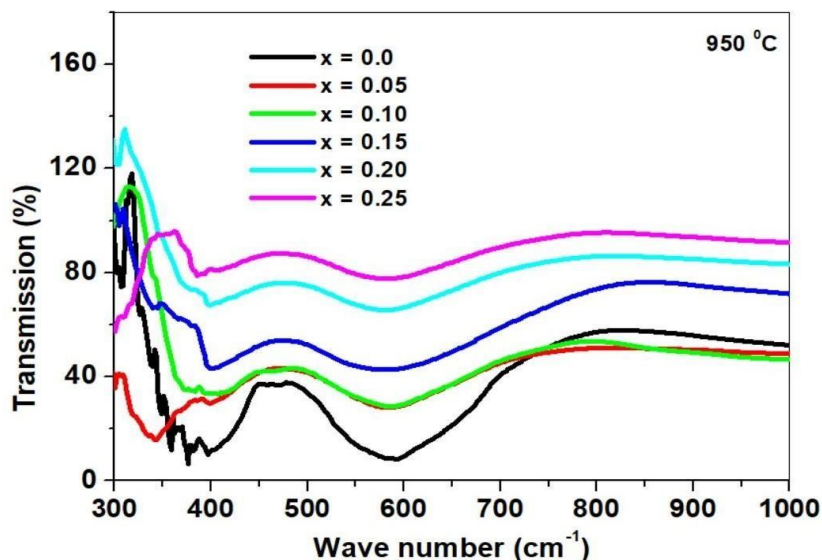


Figure 7: FTIR spectra of $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples calcinated at 950°C

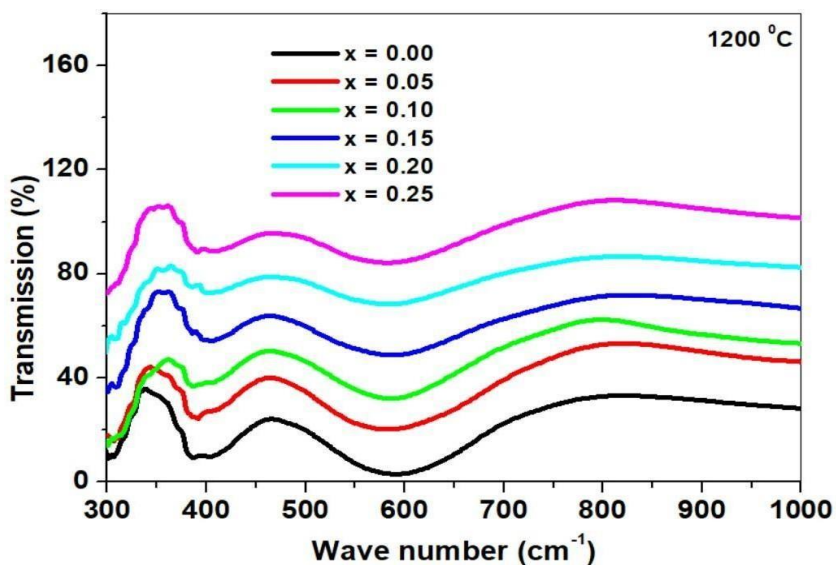


Figure 8: FTIR spectra of $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples calcinated at 1200°C

The other spectral structures observed in the synthesized sample are the presence of $\alpha\text{-Fe}_2\text{O}_3$. They have been identified by comparing with $\alpha\text{-Fe}_2\text{O}_3$ as reported for Zn doped nickel ferrites [15]. The $\alpha\text{-Fe}_2\text{O}_3$ peaks in the IR spectra for all the synthesized samples appears as a small shoulder. Based on the above discussions, we confirm the traces of $\alpha\text{-Fe}_2\text{O}_3$ in the synthesized samples. These extra peaks due to $\alpha\text{-Fe}_2\text{O}_3$ did not disappear even with higher annealing temperatures of 1200°C . The variation of ν_1 and ν_2 of $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples with x and annealing temperatures are shown in Fig's 9 and 10. The variation of ν_1 and ν_2 peak position for all the

samples x and corresponding annealing temperatures is clearly evident from Fig's 9 and 10. Shift in the band positions indicates the changes taking place in the (A) sites with Gd doping. The shape and the band positions of the samples are not only influenced with the chemical composition but also due to uncontrollable parameters like temperature, doping, conditions during the synthesis, atmosphere etc. A general tendency observed in the samples is that ν_1 band positions shifts in the direction of lower frequencies throughout the samples.

Simultaneously the changes in the [B] sites also observed for ν_2 band. Similar arguments mentioned ν_1 also valid for ν_2 band position changes with Gd doping. All the above results are in

good agreement with our previous data of Zn doped NiFe_2O_4 samples [14].

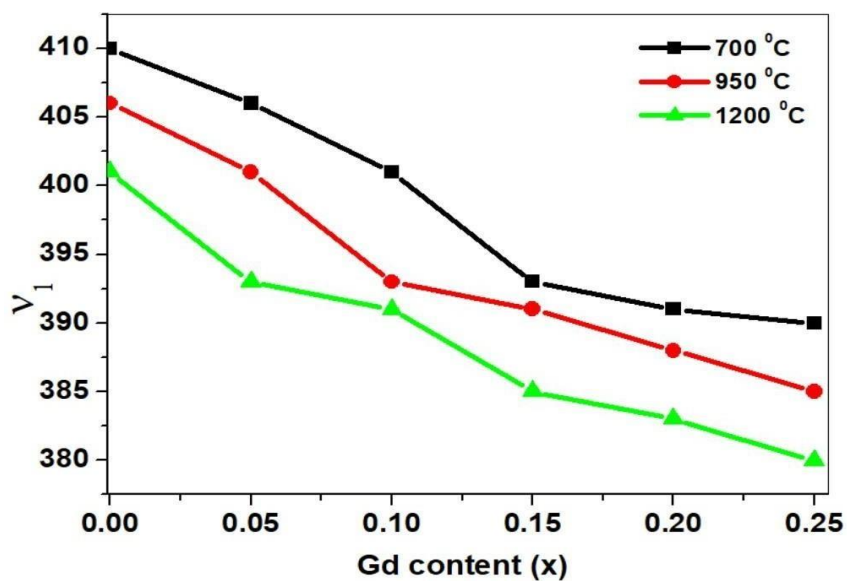


Figure 9: Variation of peak positions for ν_1 of $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples with different annealing temperatures and Gd content x

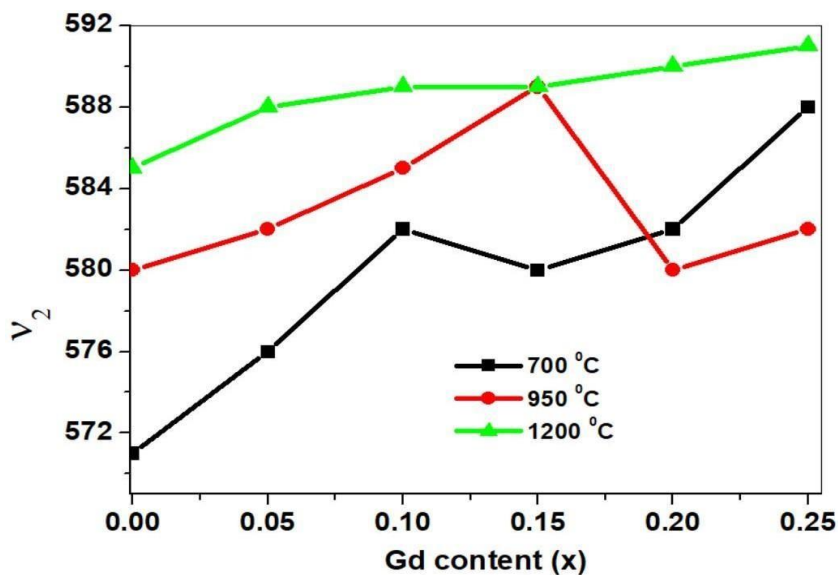


Figure 10: Variation of peak positions for ν_2 of $\text{NiFe}_{2-x}\text{Gd}_x\text{O}_4$ ($0.00 \leq x \leq 0.25$) samples with different annealing temperatures and Gd content x

CONCLUSIONS

Nanocrystalline NiFe_{2-x}Gd_xO₄ (0.00 ≤ x ≤ 0.25) ferrites samples were synthesized using sol-gel method and annealed at three different temperatures 700 °C, 950 °C and 1200 °C for 8 hours. The grain size was observed to increase with the increase in Gd content. The increase in lattice values with increasing Gd content was based on the difference between ionic radii of Gd

than Ni. In all the samples we observed that doping and annealing temperature showed the significant effect in observing the structural changes as observed from the systemic investigations carried using XRD and IR measurements.

ACKNOWLEDGEMENTS

The authors express their thankfulness to the Principal, Government Degree College Medak, the Principal, International School of Technology and Sciences for Women,

Rajamahendravaram, the Principal, JNTUH University College of Engineering Rajanna Sircilla and the Registrar, Gandhi Institute of Technology and Management, Hyderabad.

REFERENCES

- [1] H. Gleiter, Prog. Mater. Sci. 33 (1989) 223.
- [2] J.H. Fendler, Chem. Rev. 87 (1987) 877.
- [3] M.P. Pileni, Adv. Funct. Mater. 5 (2001) 323.
- [4] Q. Song, Z.J. Zhang, J. Am. Chem. Soc. 126 (2004) 6164.
- [5] A.K. Nikumbh, R.A. Pawar, D.V. Nighot, G.S. Gugale, M.D. Sangale, M.B. Khanvilkar, A.V. Nagawade, J. Magn. Magn. Mater. 355 (2014) 201–209.
- [6] G.L. Sun, J.B. Li, J.J. Sun, X.Z. Yang, J. Magn. Magn. Mater. 281(2004) s2–3.
- [7] N. Rezlescu, E. Rezlescu, C. Pasnicu, M.L. Craus, J. Phys. Condens. Matter. 6 (1994) 5707- 5716.
- [8] R. Hochschild, H. Fuess J. Mater. Chem. 10 (2000) 539–542.
- [9] M.L. Kahn, Z. Zhang, J. Appl. Phys. Lett. 78 (2001) 3651–3653.
- [10] J. Jiang, L.C. Li, F. Xu, Y.L. Xie, Mater. Sci. Eng. B 137 (2007)166–169.
- [11] J. Jiang, L.C. Li, F. Xu, J. Rare Earths 25 (2007)79–83.
- [12] J. Jiang, L.C. Li, F. Xu, Z.T. Li, J. Rare Earths 23 (Suppl.) (2005) 259–262.
- [13] A. T. Raghavender, Damir Pajic, Kreso Zadro, Tomislav Milekovic, P.Venkateshwar Rao, K.M.Jadhav, D.Ravinder, J. Magn. Magn. Mater. 316 (2007) 1-7.
- [14] A.T. Raghavender, N. Biliškov, Ž. Skoko, Mater. Lett. 65(2011) 677-680.
- [15] R.D. Waldron, Phys. Rev. 99 (1955) 1727.
- [16] K. Vijaya Kumar, Sara Durga Bhavani, Phase Transitions, 95 (2022) 770-785.
- [17] Yu, L., Ruan, H., Zheng, Y. and Li, D, Nanotechnology 24(37) (2013) 375601.
- [18] K. Vijaya Kumar, Sara Durga Bhavani, Science of Sintering, 54 (2022) 457-468.