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Rietveld Study of Cu Doped Gadolinium Orthoferrites

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Abstract: ***Polycrystalline $GdFeO_3$ and $GdCu_xFe_{1-x}O_3$ (x=0.2, 0.3) ferrites were synthesized through solid state reaction method. The prepared ferrites were characterized using x-ray diffraction (XRD) and a detailed structural study was analyzed by employing Rietveld refinement techniques with the help of the Maud Program. Phase transitions in copper-modified $GdFeO_3$, structural and micro structural changes of ferrite samples were estimated from the Rietveld analysis and the effect of Cu concentration in the crystalline phase and crystallite size were discussed in detail. Rietveld analysis revealed that octahedrally occupied Cu^{2+} ions modify the cationic distribution affecting the orthorhombic structure to shift into a partially inverse spinel structure in the Cu doped $GdFeO_3$ferrites. The results from Rietveld refinement were structurally illustrated using VESTA software.***

Keywords: $GdFe_3$, copper, X-ray diffraction, Rietveld analysis, Vesta.

I. INTRODUCTION

Multifunctional materials have been a subject of interest for researchers due to their technological applications such as magnetic field sensors, transducers and information storage. The structure type of perovskite is one of the most versatile structures for tailoring the properties of materials. The structure type of perovskite represents the parental structure for several complex atomic arrangements, which are controlled by intergrowths, oxygen deficiency or due to action ordering [1[1]]. Ferrites are promising eco-friendly materials to replace toxic lead-based perovskite relaxers, sensors, capacitors and optical storage devices [2].Rare earth orthoferrites with the chemical formula $RFeO_3$ (R is a rare-earth element) crystallizing in the perovskite structure, the R atom and the octahedrally coordinated six Fe^{3+} atoms are located at the A and B sites respectively[3, 4]. Rare earth orthoferrites are antiferromagnets with unique magnetic properties, such as spin reorientations and rare-earth moment orders at low temperatures. In ferrites the occupations at the A and B-sites may be substituted with distinct nonmagnetic cations. This may improve or add new properties[5, 6].In this present work, incorporation of Cu atoms in the $GdFeO_3$ lattice, induce further inter atomic Cu^{2+}–O–Gd^{3+} or Fe^{3+}–O–Cu^{2+} interactions. Here we are reporting that how the dopant induced cationic displacements promote phase transitions which further change the orthorhombic structure to inverse spinel.

II. EXPERIMENTAL STUDIES

$GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites were synthesized by standard solid-state reaction method. Gd_2O_3, Fe_2O_3, CuO chemicals were used as starting materials. All chemicals were of analytical grade and are used directly without further purification. Initially an appropriate amounts of Gd_2O_3 and Fe_2O_3have taken in stoichiometric ratio and well mixed in an agate mortar for 1h with an appropriate amount of acetone for homogenous mixing and then sintered at 1000°C for 5h in an electrical muffle furnace. Later 0.2 and 0.3 mol% Cu doped $GdFeO_3$ ferrites were weighed properly, grinded in an agate mortar and sintered at 1000°C for 5h. The final products were obtained and used for further characterizations.

III. ANALYTICAL PROCEDURES

X-ray diffraction patterns of the $GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites were collected using Philips diffract meter with Cu-K_α radiation. The crystal structures and microstructures were refined applying Rietveld profile refinements (MAUD 2.55 program) [7[7]]. This program has the capacity to perform simultaneously a refinement of both, the atomic arrangement (lattice parameters, atomic coordinates, occupancy factors, displacement parameters, quantitative abundances of individual phases) and the microstructure (crystallite sizes (D), and R.M.S. lattice microstrain). Due to the anisotropy of the crystallite sizes and microstrain values, the profiles of the Bragg reflections with distinct Miller indices exhibit different full widths of half maximum; this effect creates problems in Rietveld structure refinements frequently. To consider their influence in the profile shapes, the Popa anisotropic model incorporated in the MAUD program was applied. The process of successive considering the reflection profiles modulates the

different structural and micro structural parameters of the simulated pattern to fit the experimental diffraction pattern [8]. For illustrations of the structural changes in the undoped and Cu doped $GdFeO_3$ lattice, the VESTA software was used [9, 10].

IV. RESULTS AND DISCUSSION

A. XRD

Fig.s 2(a), 2(b) and 2(c) show the Rietveld refined XRD patterns of $GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites respectively. From XRD pattern it is clear that all ferrites are well crystalline in nature. Gd is at Wyckoff position (4c) (x y 1/4), Fe is at 4b (1/2 0 0) and O is at 8d (x y z) in $GdFeO_3$ structure[2, 6].

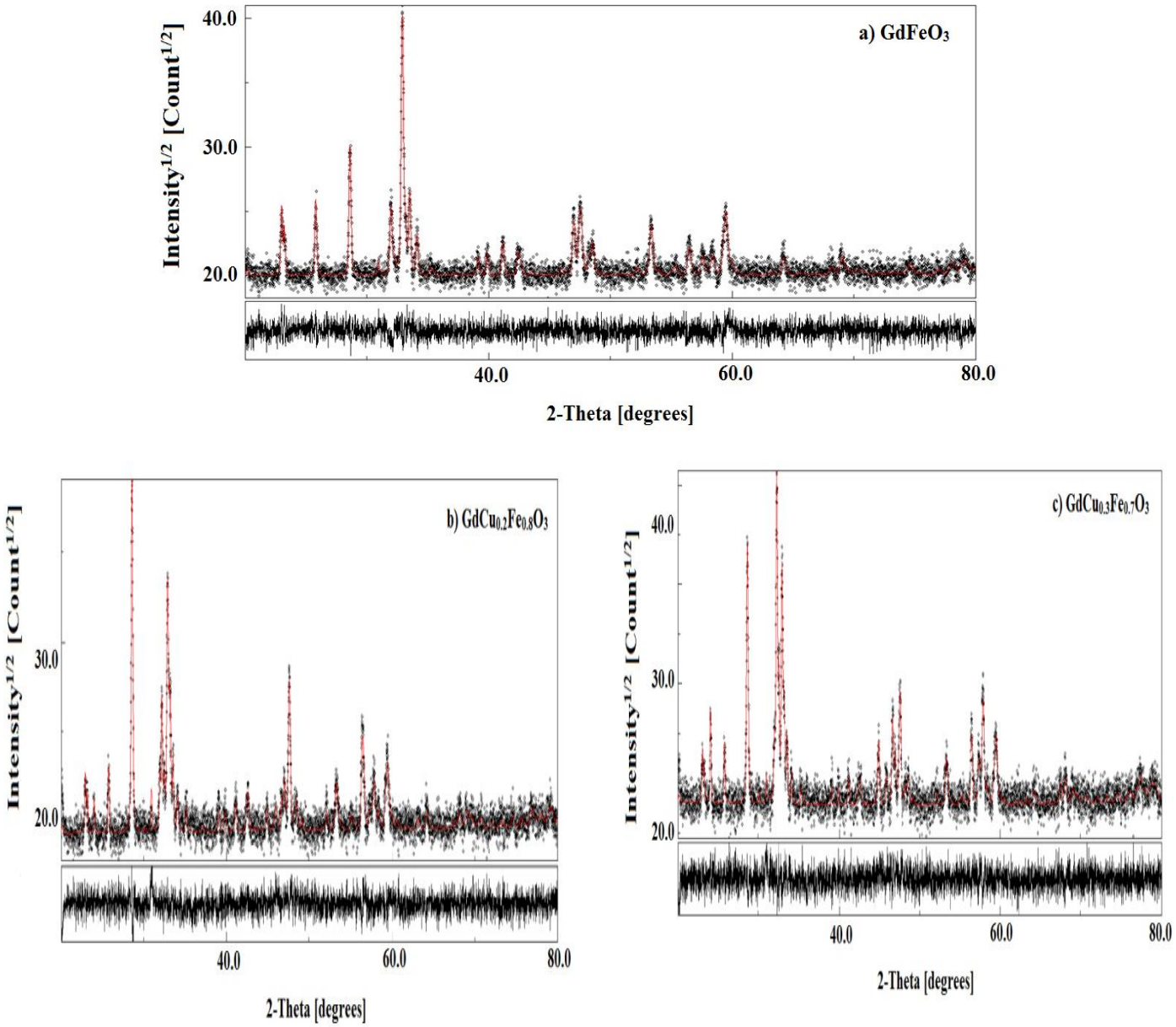


Fig2(a, b, c): Rietveld refined XRD patterns of $GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites respectively

Each XRD profile was fitted with a pseudo-voigt type function in MAUD software. Rietveld refinement results infer that in undoped $GdFeO_3$consists of orthorhombic phase and cubic phases. This coexistence is due to the presence of small amounts of secondary phase $Gd_3Fe_5O_{12}$ (garnet) along with $GdFeO_3$ structure. Significant change in the phase concentrations of the lattice is also observed from the Rietveld analysis.[11, 12,13] The line width and variation in the intensities of different reflections are evident with increasing Cu content which is not in accordance with the structure and may have arisen due to structural changes

occurred at higher concentration of Cu ions. Fig. 3 shows that with an increase in Cu concentration the diffraction peak at (0 2 0) slightly shifts towards the higher 2θ valuesi.e. from 31.969^0 to 32.255^0. The shift in diffraction peaks towards higher 2θ value, indicates that co-substitution generates compressive lattice distortion in the host lattice which results in decrement of crystallite size [14].

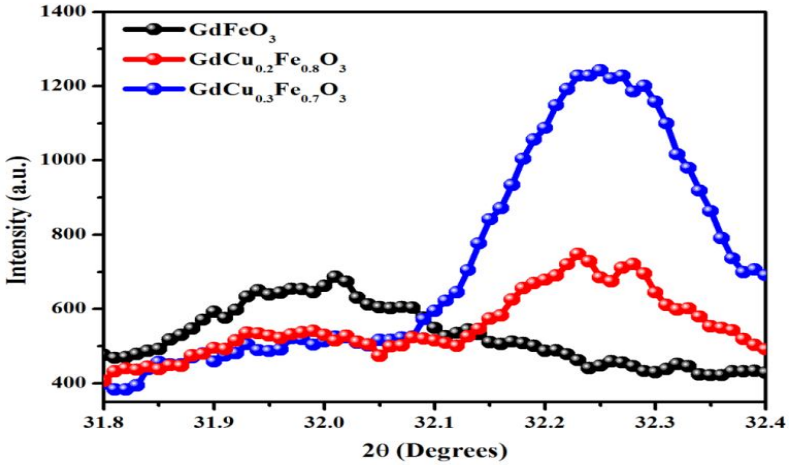


Fig. 3:Enlarged diagram of (0 2 0) XRD peak indicating a shift towards higher angles in $GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites

Considering the integrated intensity of the peaks as a function of structural parameters only, the Marquardt least squares procedures were adopted for minimization the difference between the observed and simulated powder diffraction patterns and the minimization was carried out by using the reliability index parameter, R_{wp} (weighted residual error), R_B (Bragg factor) and R_{exp} (expected error) [11-14]. The accuracy of the profile fitting was judged by the reliability parameters R_{wp}(equation i), R_{exp}(equation ii), R_B (equation iii)and the goodness of fit (GOF) (equation iv)as given below

$$R_{wp} = \left[\frac{\sum w_i(I_o - I_c)^2}{\sum w_i I_o^2}\right]^{1/2} \quad \text{.....(i)} \qquad R_{exp} = \left|\frac{N-P}{\sum w_i I_0^2}\right|^{1/2} \quad \text{.....(ii)}$$

$$R_b = \frac{\sum|I_o - I_c|}{\sum I_o} \quad \text{.....(iii)} \qquad GOF = \frac{R_w}{R_{exp}} \quad \text{.....(iv)}$$

where I_0 and I_c are the experimental and calculated intensities respectively, $w_i(1/I_0)$ and N are the weight and number of experimental observations, respectively, and P is the number of fitting parameters. The refinement of the structural parameters is continued till convergence is optimized to a goodness of fit (GOF) between 1.0 and 1.2[15, 16, 17]. The Rietveld refined parameters are tabulated in table 1.

Refined Parameters	$GdFeO_3$	$GdCu_{0.2}Fe_{0.8}O_3$	$GdCu_{0.3}Fe_{0.7}O_3$
Crystallite size (nm)	120.23	113.25	105.09
R.M.S. Microstrain (ε) $x10^{-3}$	1.1	1.6	2.8
R_w(%)	5.23	5.41	5.41
R_b(%)	4.16	4.54	4.37
R_{exp}(%)	4.83	5.07	5.06
GOF	1.08	1.06	1.08

Table 1: Rietveld refined results of $GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites

B. Phase Transitions

Rietveld results had shown that doping of Cu^{2+} ions into the $GdFeO_3$ lattice has induced formation of new structural phases in the $GdFeO_3$ lattice structure because of the difference in valency, ionic sizes of the dopant and host lattice ions [18, 19]. The relative percentages of phases obtained from Rietveld analysis are listed in table 2 and are plotted against Cu Concentration in Fig. 4.

Sample	Relative phase percentages		
	Orthorhombic $GdFeO_3$	Cubic $Gd_3Fe_5O_{12}$	Tetragonal $CuGd_2O_4$
$GdFeO_3$	80	20	0
$GdCu_{0.2}Fe_{0.8}O_3$	47	44	9
$GdCu_{0.3}Fe_{0.7}O_3$	38	36	26

Table 2: Phase percentages of the $GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites obtained from the Rietveld refinement of the XRD patterns

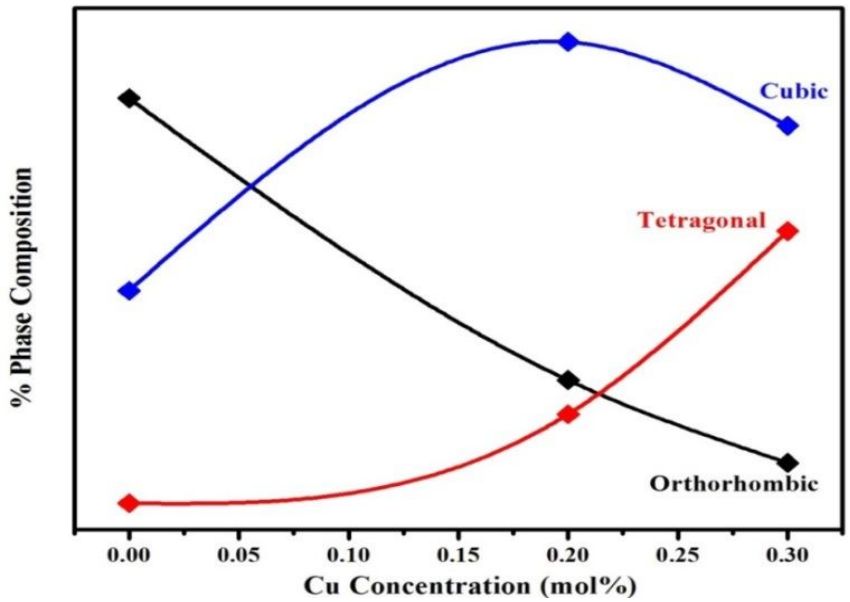


Fig. 4: Relative percentage of phases observed in undoped and $GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites

From Fig.4 it is clear that the percentage of the tetragonal phase seems to increase at the expense of orthorhombic and cubic phases with an increase in Cu concentration [20]. Based on the results of Rietveld analysis, tetragonal phase formation can be explained as follows

In $GdFeO_3$ (ABO_3) structure, B ions were octahedrally coordinated by six oxygen ions (BO_6 as shown in Fig. 5). The site symmetries of the A and B atoms in the parental perovskite-structure type are $m\bar{3}m$. On doping with Cu ion the point symmetry of the Fe ion is reduced because Cu^{2+} ion with d^9 configuration prefers to have octahedral geometry as it attains more crystal field stabilization energy (CFSE) in octahedral coordination rather than in tetrahedral coordination. This substitution of Cu^{2+} causes a change in cationic environment which in turn causes a lattice distortion with the elongation of the out-of-phase B-O bonding lengths and the shortening of the in-plane B-O bond (as shown in Fig. 5) [21,22,23]. This co-substitution stimulates the formation of $CuGd_2O_4$, a partially inverse spinel with B site having Gd^{3+} ions. Gd^{3+} ions tend to have tetrahedral coordination for charge compensation and to maximize the lattice stabilization energy. As the incoming flux of dopant increases, Fe atoms are replaced by more number of Gd^{3+} ions and they appear in tetrahedral coordination because of their high spin state than Fe^{3+} ions. These interpretations can be confirmed from the Rietveld analysis of Cu doped $GdFeO_3$ferrites. The cooperative nature of the crystal distortions in these compounds can be rationalized in terms of elastic interactions between the locally distorted polyhedra. Each polyhedron possesses its own local distortion, ground state splitting, and stabilization energies, which persist in the low-symmetry phase. The distortions in spinels demonstrate that tetragonal structures result from parallel alignments of tetragonally distorted polyhedra. The tetragonal distortion with c/a>1.0 are found at tetrahedral B-site Gd^{3+} ions. In atoms having outer electron configuration d^4 or d^9,there is a strong elastic anisotropy that favours tetragonal (c/a>1.0) distortion of the octahedrally coordinated atoms. This is a unique feature of Jahn-Teller effect found in octahedrally coordinated atoms having high spin state. The structural phase changes appear as a consequence of coupling of local electronic states to bulk deformations and optical phonons of the lattice. The relation between the structure types of distorted perovskite ($GdFeO_3$) and inverse spinel (Gd_2CuO_4 resulting from Cu doping of $GdFeO_3$) can be predicted as shown in Fig.5.

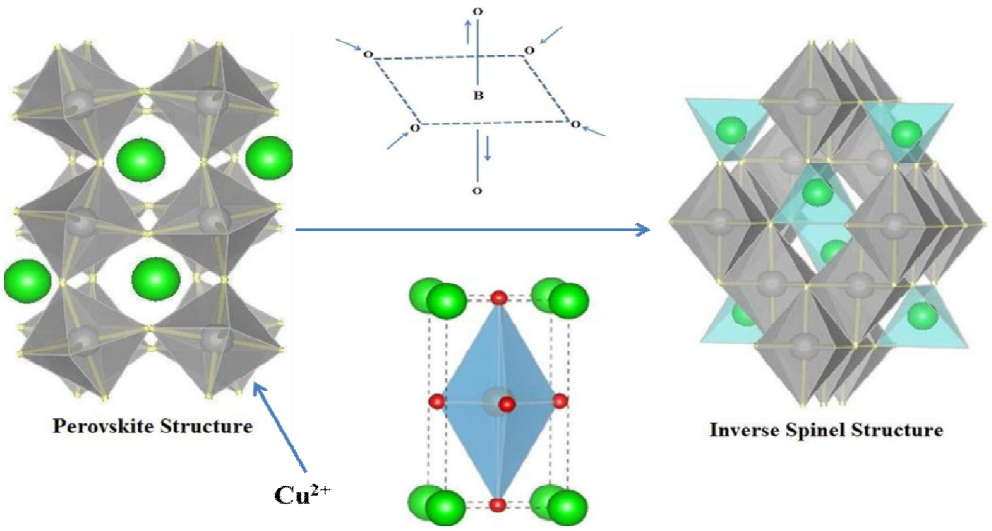


Fig.5: Schematic representation of Phase transition from Orthorhombic to tetragonal in Cu doped $GdFeO_3$ structure

In further detail, it has been shown that if there is a degenerate orbital state associated with localized d electrons at the transition metal cation in polar crystal, the structure is unstable to a distortion that provides enough asymmetry to lift the degeneracy [24, 25]. The calculated crystallite size and R.M.S micro strain were summarized in table 1. The changes in lattice parameters of $GdFeO_3$ were determined from the refinement program and are shown as a function of Cu content in Fig. 6. From the Fig.*a* and*c* decreases with an increase in Cu content while the lattice parameter b increases with Cu content. From that Fig. it is clear that within the doping range x = 0.2 & 0.3 the lattice parameter $c\sqrt{2}/2>a$. With increasing Cu, the lattice parameters *a* and$c\sqrt{2}/2$ decrease but the change in former is less than the latter. The cooperative Jahn- Teller effect, arising from the octahedral Cu^{2+} ions affects the shape of the octahedron so that the lattice gets distorted, c/a>1[2].

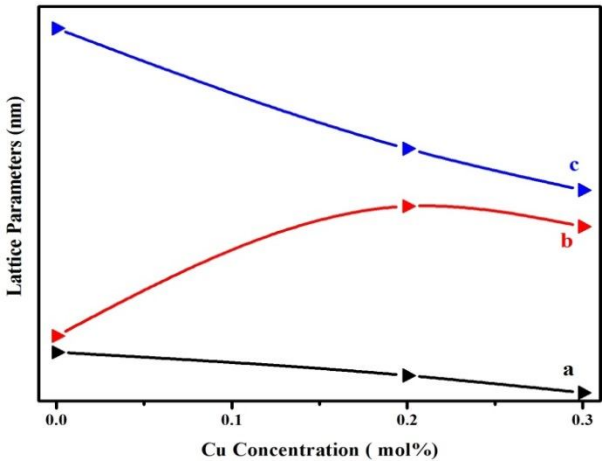


Fig. 6: Variation of lattice Parameters a,b,c in $GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites

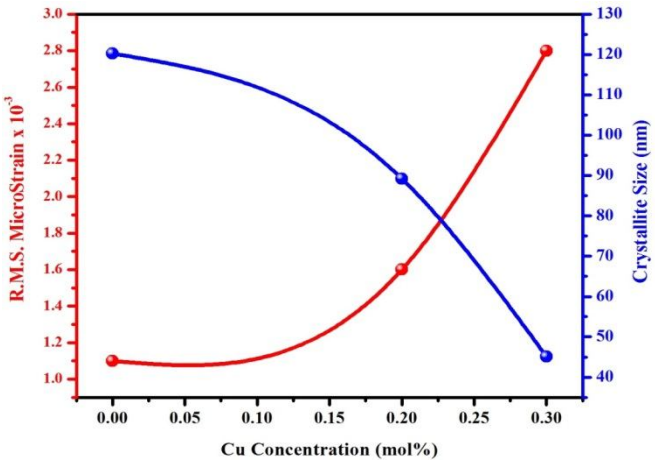


Fig. 7: Effect of Cu concentration on Crystallite size and R.M.S Microstrain of $GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ ferrites

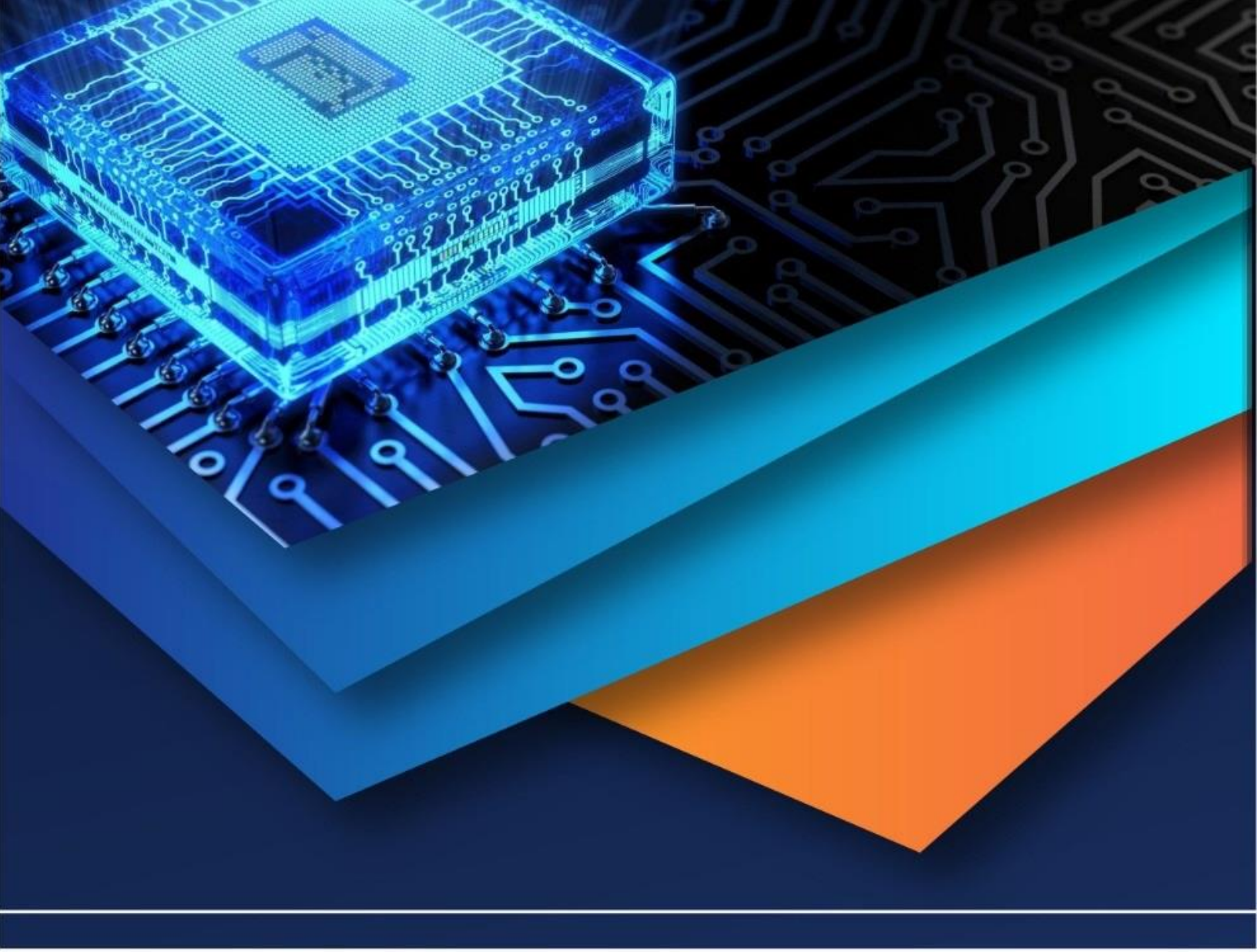
The increase of the value of b with the increase of Cu concentration indicates the decrease of cooperative JT distortion since the non-JT active Gd ion replaces the JT active Fe ion. With the increase of Cu content the orthorhombicity factor c/a decreases. Results showed that increasing the Cu content (x) decreases the crystallite size from120 nm to 105 nm, but increases the average maximum micro strain from 1.1 x 10^{-3} to 2.8 x 10^{-3} for x=0 and x=0.3 respectively. When cation of different radii and valence is introduced into a host lattice, the mismatch between ionic sizes of the host and dopant cations creates a strain in the lattice which usually affects the unit cell size and volume[5].Fig. 7 shows the change of crystallite size and micro strain with an increase in Cu concentration in $GdFeO_3$ferrites.

V. CONCLUSIONS

$GdFeO_3$, $GdCu_{0.2}Fe_{0.8}O_3$ and $GdCu_{0.3}Fe_{0.7}O_3$ orthoferrites were synthesized through solid state reaction method. Structural and compositional analysis of Cu doped $GdFeO_3$ ferrites were studied using XRD. Structural changes occurred on successful incorporation of Cu into the $GdFeO_3$ lattice were determined using Rietveld refinement technique. Rietveld analysis of XRD data revealed the existence of multiple phases and stabilization of Cu doped $GdFeO_3$ in tetragonal phase forming an inverse spinel at higher concentrations of Cu. Based on these results structural illustrations were crafted using VESTA software. The formation of new phases is also confirmed by variations in lattice parameters, decrease in crystallite size and increase in micros train.

REFERENCES

[1] N. Sahu, S. Panigrahi, Rietveld analysis of La^{3+}/Al^{3+} modified $PbTiO_3$ ceramics, Ceram. Int. 38 (2012) 1085-1092
[2] K. Sultan, M. Ikram, K. Asokan, Structural, Optical and dielectric study of Mn doped $PrFeO_3$ ceramics, Vacuum 99 (2014) 251-258
[3] A.M. BolarinMiro, F. Sanchez-De Jesus, C.A. Cortes Escobedo , R.Valenzuela , S. Ammar,Structure and magnetic properties of $Gd_xY_{1-x}FeO_3$ obtained by mechanosynthesis, J. Alloys Compd. 586 (2014) S90-S94
[4] A. Wu, Z. Wang, B. Wang, X. Ban, L. Jiang, J. Xu, S. Yuan, S. Cao, Crystal growth and magnetic properties of $GdFeO_3$ crystals by floating zone, Solid State Commun. 185 (2014) 14-17
[5] Z.K. Heiba, N.Mostafa, O.AbdElkader,Structural and magnetic properties correlated with cation distribution of Mo-substituted cobalt ferrite nanoparticles,J. Magn. Magn. Mater. 368 (2014) 246-251
[6] A. Bashir, M. Ikram, R. Kumar, Structural, electronic Structure, transport and magnetic Studies of $NdFe_{1-x}Ni_xO_3$ (x = 0.4, 0.5), Mod. Phys. Lett. B 25 (2011) 2439-2450
[7] L. Lutterotti, Maud 2.55, http://nanoair.dii.unitn.it:8080/maud/
[8] Z. K. Heiba, N.G. Imam, M. B. Mohamed,Temperature dependent cation distribution correlated with optical and magnetic properties of nanocrystalline $NiFe_{1.8}Gd_{0.2}O_4$,J. Mol. Struct. 1095 (2015) 61-68
[9] K. Momma, F.Izumi,VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Crystallogr. 44 (2011) 1272-1276
[10] J.A. Cardona Vasquez, D.A. Landinez Tellez, J. Roa Rojas, Physical properties of the new multiferroic perovskite-like material $HoMn_{1-x}Fe_xO_3$, Physica B 455 (2014) 39-43
[11] S. Mohammadi, H. Shokrollahi, M.H. Basiri,Effects of Gd on the magnetic, electric and structural properties of $BiFeO_3$nanstructures synthesized by co-precipitation followed by microwave sintering, J. Magn. Magn. Mater. 375 (2015) 38-42
[12] V. Fuster, A.V. Druker, A. Baruj, J.Malarria, R. Bolmaro,Characterization of phases in an Fe–Mn–Si–Cr–Ni shape memory alloy processed by different thermomechanical methods, Mater. Charact. 109 (2015) 128-137
[13] M. Bhagwat, A.V. Ramaswamy, A.K. Tyagi, V. Ramaswamy,Rietveld refinement study of nanocrystalline copper doped zirconia, Mater. Res. Bull. 38 (2003) 1713-1724
[14] M.P. Singh, W. Prellier, L. Mechin, Ch. Simon, B. Raveau,Can multiferroics be synthesied by superlattice approach?, Thin Solid Films 515 (2007) 6526-6531
[15] S. Bandyopadhyay, H. Dutta, T. Kar, S.K. Pradhan, Room temperature mechanosynthesis and microstructure characterization of nanocrystalline $Si_{0.9}Al_{0.1}C$, Mater. Chem. Phys. 169 (2015) 1-6
[16] S.K. Manik, S.K. Pradhan, Microstructure characterization of ball milled prepared nanocrystallineperovskite $CaTiO_3$ by Rietveld method, Mater. Chem. Phys. 86 (2004) 284-292
[17] M.R. Panigrahi, S. Panigrahi,Rietveld analysis of single phase $Ba_{0.99}$ $Dy_{0.01}$ TiO_3 ceramic, Physica B 405 (2010) 3986-3990
[18] Pawan Kumar, NishaShankhwar, A. Srinivasan, ManoranjanKar,Oxygen octahedra distortion induced structural and magnetic phase transitions in $Bi_{1-x}Ca_xFe_{1-x}Mn_xO_3$ ceramics**,** J. Appl. Phys. 117 (2015), 194103.
[19] N. L. A. Ross, J. Zhao, and R. J. Angel,General Rules for Predicting Phase Transitions in Perovskites due to Octahedral Tilting,Phys. Rev. Lett. (2005) 95, 025503.
[20] Whitfield PS, Herron N, Guise WE, Page K, Cheng YQ, Milas I, Crawford MK,Structures, Phase Transitions and Tricritical Behavior of the Hybrid Perovskite Methyl Ammonium Lead Iodide,Sci Rep. (2016) 6, 35685.
[21] M. Kuceraa, V. Kolinsky, S. Visnovsky, D. Chvostova, N. Venkataramani, S. Prasad, P.D. Kulkarni, R. Krishna,Faraday effect in cubic and tetragonal copper ferrite $CuFe_2O_4$ films Comparative studies, J. Magn. Magn. Mater. 316 (2007) e688-e691
[22] S.S. Ata-Allah, A. Hashhash, Jahn – Teller effect and superparamagnetism in zn substituted copper-gallate ferrite, J. Magn. Magn. Mater. 307 (2006) 191-197
[23] T. Caronna, F. Fontana, I.NataliSora, R. Pelosato,Chemical synthesis and structural characterization of the substitution compound $LaFe_{1-x}Cu_xO_3$ (x=0-0.4), Mater. Chem. Phys. 116 (2009) 645–648
[24] Carlos Moure, Octavio Pena, Magnetic features in $REMeO_3$ perovskites and their solid solutions (RE = rare-earth, Me = Mn, Cr), J. Magn. Magn. Mater. 337-338 (2013) 1-22
[25] R. Gimenes, M. R. Baldissera, M. R. a Da Silva, C. a. Da Silveira, D. a W. Soares, L. a. Perazolli, M. R. Da Silva, and M. a. Zaghete, Structural and magnetic characterization of $Mn_xZn_{1-x}Fe_2O_4$ (x = 0.2, 0.35, 0.65, 0.8, 1.0) ferrites obtained by the citrate precursor method, Ceram. Int. 38 (2012) 741-746.



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