Chemical Bonding and Magnetic Properties of Gadolinium (Gd) Substituted Cobalt Ferrite

Venkata Sreenivas Puli^{1,*}, Shiva Adireddy², and C.V. Ramana¹

¹*Department of Mechanical Engineering, University of Texas, El Paso, Texas 79968, USA*

²*Department of Physics and Engineering Physics, Tulane University, New Orleans, Louisiana, 70118, USA*

* Author to whom correspondence should be addressed; Email: vspuli@utep.edu

Abstract

Polycrystalline gadolinium (Gd) substituted cobalt ferrites ($\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$; $x=0-0.3$, referred to CFGO) ceramics have been synthesized by solid state reaction method. Chemical bonding, crystal structure and magnetic properties of CFGO compounds have been evaluated as a function of Gd-content. X-ray diffraction and Raman spectroscopic analyses confirmed the formation of inverse spinel structure. However, a secondary ortho-ferrite phase (GdFeO_3) nucleates for higher values of Gd-content. A considerable increase in the saturation magnetization has been observed upon the initial substitution of Gd ($x=0.1$). The saturation magnetization drastically decreases at higher Gd content ($x \geq 0.3$). No contribution from ortho-ferrite GdFeO_3 phase is noted to the magnetic properties. **The increase in the magnetic saturation magnetization is attributed to the higher magnetic moment of Gd^{3+} ($4f^7$) residing in octahedral sites is higher when compared to that of Fe^{3+} ($3d^5$) and as well due to the migration of Co^{2+} ($3d^7$) ions from the octahedral to the tetrahedral sites with a magnetic moment aligned anti-parallel to those of rare earth (RE^{3+}) ions in the spinel lattice. Increase in coercivity with increase in Gd^{3+} is content is attributed to magnetic anisotropy in the ceramics.**

Keywords: Cobalt Ferrite; Gd-Substitution; Raman Spectroscopy; Magnetic properties; Neel temperature;

1. Introduction

Ferrimagnetic materials, are an important class of magnetic ceramics, have drawn much attention for the past few decades due to their remarkable properties like high saturation magnetization, large permeability at high frequency, low eddy current, and high electrical resistivity to be utilized in solid state electronics and magneto-electronics [1-15].

Particularly, rare earth (RE) ion substituted spinel ferrites are reported to be promising candidates for applications in high-density storage (magnetic cores of read write heads for high-speed digital tape or disk recording), magnetic sensors, magnetic fluids, telecommunication equipments, magnetically guided drug or radioactive nuclide delivery, and remote detoxification, radio frequency coils, transformer cores, rod antennas, and are also good candidates for microwave applications [2-3].

In AB_2O_4 type centrosymmetric spinel ferrites, the metal ions are situated in two different sub-lattices designated tetrahedral (A-site) and octahedral (B-site) in a unit cell. Magnetic and electrical properties of these ferrites depend on the nature and distribution of their cations in the two tetrahedral and octahedral sub-lattices of a cubic structure [4,5]. These high Curie temperature magnetic insulators can also be used in spintronics [6] and spin caloritronics (spin-transfer torque devices) [7] applications due to their natural non-zero magnetic moment along with spin dependent band gaps. Recently, AB_2O_4 spinel crystalline structured ceramics ($CoFe_2O_4$, $NiFe_2O_4$, $Ni_{0.65}Zn_{0.35}Fe_2O_4$, $Co_{0.65}Zn_{0.35}Fe_2O_4$) were also utilized in multiferroic composites [3,8-15].

Among the spinel ferrites, large magnetostrictive cobalt ferrite $CoFe_2O_4$ (CFO) is widely studied due to its high Curie temperature ($T_C \sim 793$ K), large magneto-crystalline anisotropy, high

coercivity, moderate saturation magnetization, chemical stability and mechanical hardness [1]. Rare-earth ions substitution into Fe^{3+} -site in AB_2O_4 type spinel ferrites has been reported to induce structural distortion and strain and thus significantly modifies the electrical and magnetic properties [16-21]. Rare-earth (Ho, Er, Tm, Yb, Lu) ion doping/substitution into cobalt ferrite tend to decrease the room-temperature magnetization as well as the Curie point [22]. Magnetic properties of nanocrystalline Sm-substituted CFO synthesized by citrate precursor method was reported by Rashad et al. [5]. However addition of Sm^{3+} ions resulted in decreased saturation magnetization and coercivity. Decreased saturation magnetization with an increase in samarium content was also observed for samarium substituted CFO nanopowder synthesized by sol-gel method and this decrease is attributed to the decrease in the net magnetic moment due to the substitution of nonmagnetic ion in the octahedral site [19]. The temperature dependence of magnetization studies of gallium (Ga)-substituted cobalt ferrite ($\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$) revealed the magnetization increase for lower Ga^{3+} content ($x=0.2$ and 0.4) when compared to pure CFO at low temperature and as the temperature increased from 10 K to 400 K magnetization decreased ($x=0.4$) [23]. Negligible room temperature magnetization with more than two-fold increase in coercivity [~ 29 kA/m for $x=0$ to ~ 66 kA/m for $x=0.02$] was reported for Er-doped cobalt-ferrite nanocrystals by a sol-gel assisted auto combustion method because of their low magnetic-ordering temperature ($<90\text{K}$) [24]. Substitution of Gd^{3+} and Nd^{3+} for Fe^{3+} induces a decrease in the saturation magnetization and Curie temperature of the nickel ferrite [20]. Similarly, substitution of Dy^{3+} for Fe^{3+} causes a decrease in the saturation magnetization and Curie temperature of the nickel ferrite [25]. Recent results by our group proved that the larger ionic size Gd^{3+} ($0.938 \text{ \AA}$) ion substitution at Fe^{3+} ($0.645 \text{ \AA}$) in spinel cobalt ferrites will have a profound influence on the structural, electrical conduction and dielectric properties [1,26,27].

The obvious aim and relevance of the present work is to understand the Gd-induced chemical changes in cobalt ferrite and magnetic properties of cobalt ferrite. To examine the effect of gadolinium (Gd^{3+}) incorporation into CFO and understand the Gd-induced chemical bonding changes, Raman spectroscopy coupled with X-ray diffraction has been employed. Understanding the chemical structure changes and correlating with magnetic properties of these CFGO materials is expected to further enhance our current understanding of the RE-ion substitution in ferrites. The effect of Gd substitution on the chemical structure magnetic properties is reported in this paper.

2. Experimental section

The CFGO polycrystalline compounds were prepared from 99.99% pure CoO , Fe_2O_3 , and Gd_2O_3 by the solid state reaction method. Powders of the starting materials were ground in an agate mortar and pestle for 2 h in an ethanol medium and the mixtures were heat treated in air at $1200\text{ }^\circ\text{C}$ for 12 h employing controllable furnace with a ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ for both heating and cooling. Calcined powders were mixed with PVA binder and pressed in a Carver press at 4.5 tons, sintered at $1300\text{ }^\circ\text{C}$ for 12 hours. The pellet diameter and thickness were $\sim 7.9\text{ mm}$ and 1.5 mm , respectively. Phase identification and crystal structure of the materials synthesized were investigated using X-ray diffraction (XRD) measurements employing a Bruker D8 Discover X-ray diffractometer. Measurements were made at room temperature using $\text{CuK}\alpha$ radiation ($\lambda=1.5406\text{ \AA}$). The Raman spectral analysis (Lasos 77, argon laser source: $\lambda=488\text{ nm}$ and 10 mW power, and range: $200\text{--}900\text{ cm}^{-1}$) was performed on the sintered samples. The magnetic characterization was performed using Quantum-Design MPMS-3 superconducting quantum interference device magnetometer.

3. Results and Discussion

3.1 X-ray diffraction

XRD patterns of pristine CFO and Gd-substituted CFO (CFG0) are shown in Fig. 1(a). XRD patterns revealed that the pristine CFO and CFG0 ceramics were in the inverse spinel phase, along with the peaks corresponding to minor amount of ortho-ferrites (GdFeO_3) is also observed for $x \geq 0.2$ in CFO. As shown in the Fig.1, all the diffraction peaks were indexed to a simple cubic structure with **$\text{Fd}\bar{3}\text{m}$** space symmetric group, according to the standard CFO powder diffraction data (JCPDS 22-1086). Formation of these Ortho-ferrites (REFeO_3) is common for rare-earth ion doped ferrites [1,26-34]. Lattice parameters for the CFO and CFG0 ceramics were in the range of 8.373-8.394 Å. As the Gd content increases, there is an increase in both lattice parameter and volume of the unit cell, this volume expansion is due to complete incorporation of the rare-earth Gd ions into the unit cell leading to expansion. Complete incorporation of large ionic radius Gd^{3+} (0.938 Å) into smaller Fe^{3+} (0.645 Å) in CFO lattice leads to increase in lattice parameter. When compared to lattice parameters of Dy substituted NiFe_2O_4 [31], Hf substituted CFO powders, Gd substituted CFO powders have shown higher magnitude of lattice expansion [32]. Similar behavior was also observed in Sm and Ho substituted NiFe_2O_4 [33].

3.2 . Raman spectroscopy

Raman spectroscopy measurements in the wave number region $150\text{--}900\text{cm}^{-1}$ at room temperature are carried out to further reveal to structural characteristics of the cobalt ferrite with the doping of the Gd^{3+} ions. Inverse spinel structured cobalt ferrite with cubic O_h^7 (**$\text{Fd}\bar{3}\text{m}$**) symmetry space group has 39 normal vibrational modes, out of which the five active Raman

modes are $3T_{2g}+E_g+A_{1g}$ [35, 36]. However there are additional 12 Raman modes which are inactive include: T_{1g} , $2A_{2u}$, $2E_u$, $4T_{1u}$ (IR), T_{1g} (acoustic), and $2T_{2u}$ are largely inactive in spinel structure. These additional Raman modes may be expected in inverse spinel structured ferrites due to random distribution of cations among A and B sites, defects induced lattice distortions, and short range ordering of cations on B sites [37, 38]. In spinel structure the metallic cations occupy either surrounded by six oxygen ions to form an octahedron, or by four oxygen ions to form a tetrahedron.

Fig.2 shows the room temperature Raman spectra for pristine and Gd substituted CFO ($x=0.0-0.3$). Furthermore, the spectra in Fig. 2, did not exhibit any other Raman modes that corresponds to impurity phases confirming the chemical quality of CFGO compounds. As shown in the Fig.2, all the Raman modes are consistent with those reported for other cubic inverse spinel ferrite structures, which belong to the O_h^7 ($Fd\bar{3}m$) space group. The vibrational modes observed were in close agreement with those reported for polycrystalline $CoFe_2O_4$ [36,39]. CFO and CFGO ceramics have shown six peaks. Table 1 presents the wavenumber corresponding to Raman active peaks, most of which are the typical modes of the cubic inverse-spinel ferrite structure. The two Raman modes at around $T_{1g}(2) \sim 468-471 \text{ cm}^{-1}$ and $A_{1g}(1) \sim 687-693 \text{ cm}^{-1}$ are the characteristic modes of spinel ferrite: the low-frequency mode at $T_{1g}(2)$ is assigned as the vibrations of the octahedral sublattice, whereas the high energy phonon mode at $A_{1g}(1)$ originates from vibrations of the tetrahedral sublattice.

To get more detail and accurate information from Raman spectra, both low and high frequency Raman spectra were fitted by superposition of Lorentz peaks expressed by **using equation number (1):**

$$I(\omega) = I_0 + \frac{2A}{\pi} \frac{W}{W^2 + 4(\omega - \omega_0)^2} \quad (1)$$

where ω_0 is phonon frequency of the peak, W is its FWHM, A is a constant, and I_0 is intensity of the background. From fitting as shown in Fig.3, the Raman peak positions of the three modes are listed in Table 2 with a very little shift to higher wavenumber region to that of unfitted data (Table1). The deconvoluted Raman spectra for all the major peaks at for pristine CFO and Gd substituted CFO ($x=0.0-0.3$) are shown in the Fig. 3.

In general, CFO Raman vibrational modes below 600 cm^{-1} and above 600 cm^{-1} were attributed to vibrations of oxygen within the octahedral site, while vibrations within tetrahedral sites respectively [40]. The Raman spectra for the CFO and CFGO ceramics exhibit an intense and major peaks near $689-694 \text{ cm}^{-1}$ associated with CFO (A_{1g} mode) is due to symmetric stretching of Fe (Co)-O bonds, $T_{1g}(2)$ around $470-472 \text{ cm}^{-1}$, E_g at about $300-307 \text{ cm}^{-1}$ is due to symmetric bending of Fe (Co)-O bonds and a relatively weak shoulder peak together with most intense near $205-210 \text{ cm}^{-1}$ which is attributed to the T_{1g} mode, which is due to translational motion of the whole tetrahedron. Most intense $T_{1g}(2)$ Raman mode at around 470 cm^{-1} is due to asymmetric stretching of Fe(Co)-O bonds. $T_{1g}(2)$ is related to the octahedral site mode that reflects the local lattice effect in the octahedral sub-lattice and the other intense A_{1g} mode at about 700 cm^{-1} and a small peak at 620 cm^{-1} are the symmetry vibrations of the metal in the tetrahedral site of CoFe_2O_4 [36]. As the Gd content increases in CFO, weakening of $T_{1g}(1)$ Raman mode is noted which indicates dilution of the long range order of cations in B sites [37]. **Raman mode shift towards lower wavenumber region may be attributed to complete incorporation of Gd into the lattice and as well due to the largest atomic mass of Gd when compared to the Fe. As**

state in case of X-ray diffraction patterns, the increase in lattice parameters with volume expansion might be due to complete incorporation of larger ionic radii Gd^{3+} (0.938 Å) into smaller Fe^{3+} (0.645 Å) in CFO lattice. And the Raman mode shift towards lower wave number region is in complete agreement with increase in lattice parameter and volume expansion of unit cell in case of XRD measurements.

3.3 Magnetization measurements (*M-H*)

Magnetic field dependence of magnetization measurements were carried out on a vibrating sample magnetometer at room temperature with a maximum applied field of 8 kOe. Fig.4 (a-d) shows the magnetization (*M-H*) curves for Gd substituted cobalt-ferrites. Clearly, the *M-H* hysteresis loops vary with Gd content in CFO. The saturation magnetization (*M_s*), remnant magnetization (*M_r*), the coercivity (*H_c*), and remnant squareness ratio *R* and the magnetic moment (*μ*) values are listed in Table 3. The saturation magnetization (*M_s*) for CoFe_2O_4 is ~ 39 emu/gm. With increasing Gd^{3+} substitution, *M_s* increases from 39 emu/gm (*x*=0) to 132 emu/gm (*x*=0.1) followed by a drastic decrease to 47 emu/gm (*x*=0.3). The Gd^{3+} substituted cobalt-ferrites (*x*≤0.2) have shown an anomalous improvement in *M* values compared to CoFe_2O_4 . **This enhancement in the magnetic properties is attributed to the higher magnetic moment of Gd^{3+} ($4f^7$ orbital) which is residing in octahedral sites is higher when compared to that of Fe^{3+} ($3d^5$) [36,44]. This can also be ascribed due to the migration of Co^{2+} ($3d^7$) ions from the octahedral to the tetrahedral sites with a magnetic moment aligned anti-parallel to those of rare earth (RE^{3+}) ions in the spinel lattice and this increase magnetic properties is also theoretically expected [36,44]. Decrease in magnetization once Gd^{3+} content is beyond *x*=0.1 in CFGO might be attributed to compositional saturation in the CFO lattice. Substitution**

of larger ionic radii ($0.938 \text{ \AA}$) Gd^{3+} into smaller Fe^{3+} ($0.645 \text{ \AA}$) in CFO lattice leads to increase in lattice parameter, the contribution of the larger ionic radius in the enhancement of these values is very significant. The M-H loops although non-saturating with increasing content of Gd, indicating weak ferromagnetism in the system. The non-saturation of hysteresis loops might be due to magnetic disorder i.e. spins are canted instead of parallel and anti-parallel.

The GdFeO_3 phase is a canted antiferromagnetic with a Néel temperature of 674 K with feeble magnetization. Therefore, there is no considerable contribution from the GdFeO_3 phase to the magnetic properties [41]. The magnetic properties of doped/ substituted ferrites mainly arise due to strong superexchange interactions between A- and B-sites cations in the inverse spinel ferrites [42]. However, at higher Gd content ($x=0.3$) formation of antiferromagnetic GdFeO_3 phase leads to decrease in M. **Zoomed portion of M-H loops with coercivity (H_c) for CFO and CFGO ceramics is shown in Fig. 4(e & f). It is clearly seen from the M-H loops that these materials are ferromagnetic in nature with some remnant magnetization and coercivity values as listed in Table.3. H_c increases with increase of Gd content, the greater the magnetic anisotropy in the material, the greater coercive field. Hence enhancement in H_c is attributed to magnetic anisotropy [45].** Formation of Ortho-ferrite (REFeO_3) phase is a common feature for rare-earth doped/substituted ferrites, which in turn decreases the magnetization [1,26,27]. Fig.4 gives the dependence of the coercive force on the substitution content for Co–Gd ferrites. It was observed that the coercivity of $\text{CoFe}_{1.9}\text{Gd}_{0.1}\text{O}_4$ was larger than that of a pure CFO ceramics. Calculated squareness ratio ($R=M_r/M_s$) for all measured compositions is also followed the magnetization trend and these values were $\sim 0.106, 0.314, 0.175$ for x values of 0.0, 0.1 and 0.3, respectively. **According to the Stoner–Wohlfarth model, in the case of an ensemble of uniformly magnetized and isotropically distributed particles**

without intergrain interactions the squareness ratio ($R = M_r/M_s$) should be 0.5 and if the exchange coupling between adjacent grains take place, then the R value will exceed 0.5, however it is not in the present CFO and CFGO ceramics [45].

The saturation magnetization M_s value (132 emu/gm) of the Gd substituted CFO sample at room temperature is greater than that of Dy-doped Ni ferrite ~47 emu/g [25]. From the hysteresis loops, the coercive force (H_c), saturation magnetization (σ_s) and magnetic moments (μ) were obtained (Table 3). The magnetic-moment values were calculated from the σ_s values at room temperature using the relation (equation number 2) [43]:

$$\frac{\mu}{\mu_B} = \frac{\sigma_s \times \text{Molecular Weight}}{5585} \quad (2)$$

Magnetic moment followed similar trend to that of magnetization, with increasing Gd substitution, μ/μ_B increases from 0.806 ($x=0$) to 3.086 emu/gm ($x=0.1$) followed by a marginal decrease 1.386 ($x=0.3$). Similar results were observed for Ga substituted CFO with spin glass behavior [42].

4. Conclusions

Chemical bonding, crystal structure and magnetic properties of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ polycrystalline ceramics were investigated. The CFGO ceramics exhibit the inverse spinel structure with slightly enlarged cell lattice constants at the substitution content $x \leq 0.2$. The Gd

substituted ions studied in the present work are considered to be ferromagnetic at room temperature, an initial increase in magnetization was observed for $x \leq 0.2$ and then monotonous decrease in magnetization for $0.3 \geq x \geq 0.4$ of CFGO was therefore observed for Gd content in CFO.

Acknowledgements: Authors at the University of Texas at El Paso acknowledge, with pleasure, the support from the National Science Foundation (NSF) for the grant # DMR-1205302.

References

- [1] Md. T. Rahman, M. Vargas, and C. V. Ramana, *J. Alloys Compd.* 617 (2014) 547.
- [2] A. Paul Blessington Selvadurai , V. Pazhanivelu , R. Murugaraj, *Appl. Phys. A* 119 (2015) 229.
- [3] Dhiren K. Pradhan, Pankaj Misra, Venkata S. Puli, Satyaprakash Sahoo, Dillip K. Pradhan, and Ram S. Katiyar, *J. Appl. Phys.* 115 (2014) 243904.
- [4] L. Ben Tahar , M. Artus , S. Ammar, L.S. Smiri , F. Herbst, M.-J. Vaulay , V. Richard ,J.M. Grene`che, F. Villain , F. Fie´vet, *J. Magn. Magn. Mater.* 320 (2008) 3242.
- [5] M. M. Rashad, R. M. Mohamed, and H. El-Shall, *J. Mat. Proc. Tech.* 198 (1–3) (2008) 139.
- [6] J. C. Slonczewski, *Phys. Rev. B* 82 (2010) 054403.
- [7] G. E. W. Bauer, E. Saitoh, and B. J. van Wees, *Nature Mater.* 11 (2012) 391.
- [8] Babusona Sarkar, Biswajit Dalal, Vishal Dev Ashok, Kaushik Chakrabarti, Amitava Mitra and S.K.De, *J. Appl. Phys.* 115 (2014) 123908 .
- [9] A.Srinivas, R.V.Krishnaiah, T.Karthik,P.Suresh, Saket Asthana and S.V.Kamat, *Appl. Phys. Lett.* 101 (2012) 082902.
- [10] R. Muralidharan, N. Dix,V. Skumryev, M. Varela, F. Sánchez, and J. Fontcuberta, *J. Appl. Phys.* 103 (2008) 07E301.
- [11] S.Narendra Babu and Leszek Malkinski, *J. Appl. Phys.* 111 (2012) 07D919.
- [12] Dhiren K.Pradhan,Venkata.S.Puli,Satya N.Tripathy, Dillip K.Pradhan,J.F.Scott and Ram S.Katiyar, *J. Appl. Phys.* 114 (2013) 234106 .

- [13] Dhiren K.Pradhan, Satyaprakash Sahoo, Sujit K.Barik, Venkata S.Puli, Pankaj Misra and Ram S.Katiyar, J. Appl. Phys. 115 194105 (2014).
- [14] J.L. Gunjekar, A.M. More, V.R. Shinde and C.D. Lokhandea, J. Alloys Compd. 465 (2008) 468.
- [15] S. H. Song, C. C. H. Lo, S. J. Lee, S. T. Aldini, J. E. Snyder and D. C. Jiles, J. Appl. Phys. 101 (2007) 09C517.
- [16] Zhijun Gu, Xu Xiang, Guoli Fan, and Feng Li, J. Phys. Chem. C 112 (2008) 18459.
- [17] Fuxiang Cheng, Chunsheng Liao, Junfeng Kuang, Zhigang Xu, Chunhua Yan, Liangyao Chen, Haibin Zhao and Zhu Liu, J. Appl. Phys. 85 (1999) 2782.
- [18] S. J. Lee, C. C. H. Lo, P. N. Matlage, S. H. Song, Y. Melikhov, J. E. Snyder and D. C.Jiles,J. Appl. Phys. 102 (2007) 073910.
- [19] Sheena Xavier, Smitha Thankachan, Binu P. Jacob, and E.M.Mohammed, J. Nanosci. 2013 (2013) 1 (Article ID 524380).
- [20] K. K. Bharathi, J. A. Chelvane, and G. Markandeyulu, J.Magn. Magn. Mater. 321(22) (2009) 3677.
- [21] E. E. Sileo and S. E. Jacobo, *Physica B*. 354(1–4) (2004) 241.
- [22] Fu-Xiang Cheng, Jiang-Tao Jia, Zhi-Gang Xu, Biao Zhou, Chun-Sheng Liao, and Chun-Hua Yan, J.Appl.Phys. 86(5) (1999) 2727 .
- [23] N. Ranvah, Y. Melikhov, D. C. Jiles, J. E. Snyder, A. J. Moses, P. I. Williams,¹ and S. H. Song, J. Appl.Phys. 103 (2008) 07E506.
- [24] Sateesh Prathapani,M. Vinitha, T. V. Jayaraman, and D. Das, J.Appl.Phys. 115 (2014) 17A502.

- [25] K. Kamala Bharathi, K. Balamurugan, P. N. Santhosh, M. Pattabiraman, and G. Markandeyulu, Phys. Rev. B 77 (2008) 172401(1-4).
- [26] Md. T. Rahman and C. V. Ramana, J.Appl..Phys.116 (2014) 164108.
- [27] Md.T. Rahman, C.V. Ramana, Ceramics International 40 (2014) 14533.
- [28] K. Kamala Bharathi, G. Markandeyulu, and C. V. Ramana, J. Phys. Chem.C 115 (2010) 554.
- [29] K. Kamala Bharathi and C. V. Ramana, J. Mater. Res. 26 (2011) 584.
- [30] K. Kamala Bharathi, G. Markandeyulu, and C. V. Ramana,J. Electrochem. Soc. 158 (2011) 71.
- [31] K. Kamala Bharathi,a M. Noor-A-Alam,a R.S. Vemuriab and C. V. Ramana, RSC Advances 2 (2012) 941.
- [32] S. Wells, C.V. Ramana, Ceramics International 39 (2013) 9549.
- [33] K. Kamala Bharathi, G. Markandeyulu and C. V. Ramana, Electrochem. Solid-State Lett. 13 (2010) G98.
- [34] Jianhong Peng , Mirabbos Hojamberdiev, Yunhua Xu, Baowei Cao, Juan Wang and Hongn Wu, J. Magn. Magn. Mater. 323 (2011) 133.
- [35] M.A.G. Solera, T.F.O. Melo, S.W. da Silva, E.C.D. Lima, A.C.M. Pimenta, V.K. Garg, A.C. Oliveira, P.C. Morais, J. Magn. Magn. Mater. 272–276 (2004) 2357.
- [36] S.R. Naik , A.V. Salker , S.M. Yusuf, S.S. Meena, Journal of Alloys and Compounds 566 (2013) 54.

- [37] K.S. Aneesh Kumar, R.N. Bhowmik, *Mater. Chem. Phys.* 146 (2014) 159.
- [38] V. G. Ivanov, M. V. Abrashev, M. N. Iliev, M. M. Gospodinov, J. Meen, and M. I. Aroyo, *Phys. Rev. B* 82, (2010) 024104.
- [39] M.A.G. Solera, T.F.O. Melo, S.W. da Silva, E.C.D. Lima, A.C.M. Pimenta, V.K. Garg, A.C. Oliveira, P.C. Morais, *J. Magn. Magn. Mater.* 272–276 (2004) 2357.
- [40] S. Urcia-Romero, O. Perales-Pérez, and G. Gutiérrez, *J. Appl. Phys.* 107 (2010) 09A508.
- [41] Jyoti Shah and Ravinder Kumar Kotnala, *Scripta Materialia* 67 (2012) 316.
- [42] Mohamed Bakr Mohamed , M. Yehia, *J. Alloys Comp.* 615 (2014) 181.
- [43] Utpal Bhattacharya and Vishu S. Darshane, *J. Mater. Chem.* 3(3) (1993) 299.
- [44] S. R. Naik and A. V. Salker *J. Mater. Chem.* 22 (2012) 2740.
- [45] Fenlian Zan, Yongqing Ma, Qian Ma, Yuanfeng Xu, Zhenxiang Dai, Ganhong Zheng, Mingzai Wu and Guang Li, *J. Am. Ceram. Soc.*, 96 [10] (2013) 3100.

Figure Captions

- Figure 1** XRD patterns of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFGO) compounds as a function of x . The data indicate that pure and Gd-substituted CFO compounds crystallize in inverse spinel structure. As indicated, secondary phase GdFeO_3 peaks appear with increasing Gd content.
- Figure 2** Room temperature Raman spectra of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFGO, $x=0.0-0.3$) compounds as a function of wave number (cm^{-1})
- Figure 2** Experimental and fitted Raman spectra of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFGO, $x=0.0-0.3$) compounds as a function of wave number (cm^{-1}), (Solid lines are experimental data, blue line are individual peaks and red lines are whole spectrum peaks after fitting).
- Figure 4** Room temperature magnetization-field (M-H) hysteresis loops of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFGO, $x=0.0-0.3$) (inset show the zoomed portions of coercivity for different samples)

Table Captions

Table 1. Room temperature Raman peaks of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFGO, $x=0.0-0.3$) compounds.

Table 2. Room temperature Raman fitting peak position of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFGO, $x=0.0-0.3$) compounds.

Table 3. Effect of Gd substitution on magnetic parameters [Saturation Magnetization- M_s , Remanent Magnetization- M_r , Coercive field, Squareness ratio - $R = M_r / M_s$, Magnetic moment (μ/μ_B)] of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ compounds.

Fig.1

Fig.2

Fig.3

Fig.4

Graphical Abstract

Room temperature Raman spectra of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFGO, $x=0.0-0.3$) compounds as a function of wave number (cm^{-1})

Table 1. Room temperature Raman peaks of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFG0, $x=0,0.1,0.3$) compounds.

$\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$	$T_{1g}(3)$ Translational motion	E_g Symmetric bending	$T_{1g}(2)$ Asymmetric stretching	$T_{1g}(1)$ Asymmetric bending	$A_{1g}(1)$ Symmetric stretching	$A_{1g}(2)$ Symmetric stretching
$x=0$	210	307	471	575	615	694
$x=0.1$	210	306	472	573	611	693
$x=0.3$	205	300	470	572	603	689

Table 2. Deconvoluted room temperature Raman peaks of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFG0, $x=0,0.1,0.3$) compounds.

$\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$	$T_{1g}(3)$ Translational motion	E_g Symmetric bending	$T_{1g}(2)$ Asymmetric stretching	$T_{1g}(1)$ Asymmetric bending	$A_{1g}(1)$ Symmetric stretching	$A_{1g}(2)$ Symmetric stretching
$x=0$	210.984	307.575	471.212	572.222	618.181	695.454
$x=0.1$	210.985	307.333	472.933	572.819	625.821	693.601
$x=0.3$	204.869	304.716	469.875	565.684	613.080	689.524

Table 3. Effect of Gd substitution on magnetic parameters [Saturation Magnetization- M_s , Remnant Magnetization- M_r , Cercieve field, Squareness ratio - $R = M_r / M_s$, Magnetic moment (μ/μ_B) of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$.

$\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (Gd content)	M_s (emu/g)	M_r (emu/g)	H_c (kOe)	$R = M_r / M_s$ (squareness ratio)	Magnetic moment (μ/μ_B)
$x=0$	39.25	4.17	0.122	0.106	0.806
$x=0.1$	132.5	41.7	0.510	0.314	3.086
$x=0.2$	130.36	17.29	0.655	0.132	3.551
$x=0.3$	48.15	8.43	0.418	0.175	1.386