

# Induced Magnetization in Antiferromagnetic GdFeO<sub>3</sub> by Nonmagnetic Titanium Substitution for Magnetic Switching and Storage Application

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**Abstract:** Room temperature ferromagnetism has been induced in antiferromagnetic GdFeO<sub>3</sub> by substituting titanium at Gd site Gd<sub>1-x</sub>Ti<sub>x</sub>FeO<sub>3</sub> (x=0.00 - 0.25). Perovskite GdFeO<sub>3</sub> has been synthesized at lower temperature by chemical co-precipitation. Titanium substitution in gadolinium orthoferrite has transformed the perovskite phase to garnet phase confirmed by X-ray diffraction analysis. Tolerance factor of perovskite structure has been reduced from 0.81 to 0.78 for x=0.25 Ti substitution. Antiparallel G-type electron spins of GdFeO<sub>3</sub> has been distorted by structural change induced due to titanium substitution. Ferromagnetism has been increased to 0.74 emu/g from 0.5 emu/g by titanium substitution. Retentivity and coercivity has been also increased from 0.005 emu/g to 0.28 emu/g and 27 Oe to 218 Oe respectively. The increase in magnitude of ferromagnetic transition with respect of temperature has been significantly observed by high temperature magnetization measurement. Present process is easy to induce room temperature ferromagnetism in antiferromagnetic GdFeO<sub>3</sub> by distorting the structure at lower temperature by titanium substitution. The retentivity and coercivity produced at x=0.25 titanium substitution is useful for magnetic memory and switching application.

**Keywords:** Multiferroics, Antiferromagnetic, GdFeO<sub>3</sub>, Magnetic Memory

**1. Introduction:** Rare earth orthoferrites exhibits distorted perovskite structure crystallize in *Pbnm* space group and exhibit weak ferromagnetic properties [1]. However, recently it is reported that some RFeO<sub>3</sub> systems such as EuFeO<sub>3</sub> and GdFeO<sub>3</sub> prepared by a low temperature chemical route exhibit better ferromagnetic properties [2]. The magnetic properties of rare earth orthoferrites are interesting because of the magnetic interactions of the two different types of magnetic ions: Fe<sup>3+</sup> and R<sup>3+</sup>. The spin-exchange interaction mechanism among Fe–Fe, R–Fe and R–R ions leads to a few interesting phenomena in rare earth ortho-ferrite materials [3,4]. The magnetic properties of RFeO<sub>3</sub> systems at high temperature depend majorly on the Fe–Fe interactions that

lead to an antiferromagnetic type spin ordering with Neel temperatures ranging from 620 to 740 K [5,6]. With decrease in temperature about 100–200 K, the competition of the Fe–Fe and R–Fe interactions leads to a so-called spin-reorientation transition of the ordered Fe<sup>3+</sup> magnetic moments [7]. Spin reorientation is a more general phenomenon observed in many compounds containing rare earth and iron ions. The crystal structure examined by X-ray photography reported to be twinned on a (110) plane. The displacements of the Gd<sup>3+</sup> ions from the ideal positions were not very large, but the displacement was considerably larger in the *b* direction than in the *a* direction [8]. Gadolinium compounds are used as contrasting agents for magnetic resonance imaging due to its florescent

properties [9]. Antiferromagnetic gadolinium ortho ferrite has been studied for multiferroic properties by disturbing G-type antiferromagnetic spins by generating strain in the distorted perovskite structure [10-12].

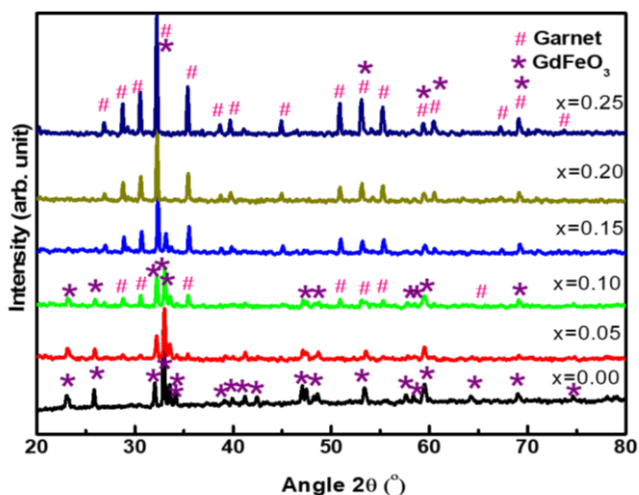
In present work G-type antiferromagnetic ordering of  $\text{GdFeO}_3$  has been disturbed by substituting titanium at Gd site synthesis by co-precipitation method. Characterization of pure and substituted nanocrystalline  $\text{GdFeO}_3$  powder for the purpose of multiferroic effect has been analyzed. Room temperature magnetism has been obtained in  $\text{GdFeO}_3$  perovskite system by titanium substitution. Phase analysis of the composition is done by taking X-ray diffraction pattern. A study of magnetic property of the composition is carried out using Vibrating Sample Magnetometer. Dielectric constant measurement of the compositions at room temperature is done by Impedance analyzer.

**2. Experimental:** Gadolinium ferrate  $\text{Gd}_{1-x}\text{Ti}_x\text{FeO}_3$  ( $x=0.0, 0.05, 0.10, 0.15, 0.20, 0.25$ ) was prepared by chemical co-precipitation method. Analytical grade precursors  $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  has been taken in stoichiometric ratio in DI water. Precursor's solution kept at  $80^\circ\text{C}$  on magnetic stirring for homogeneous mixing. After one hour stirring solution was precipitated by ammonia solution. The precipitate was washed with DI water until neutral pH is reached. Filtrates were kept in oven for overnight drying at  $100^\circ\text{C}$ . The dried samples were presintered at  $750^\circ\text{C}$  for 24 h followed by pelletization and sintered at  $1000^\circ\text{C}$  for 8 h. Structural, electrical and magnetic measurements were done on sintered pellets.

### 3. Results and discussion

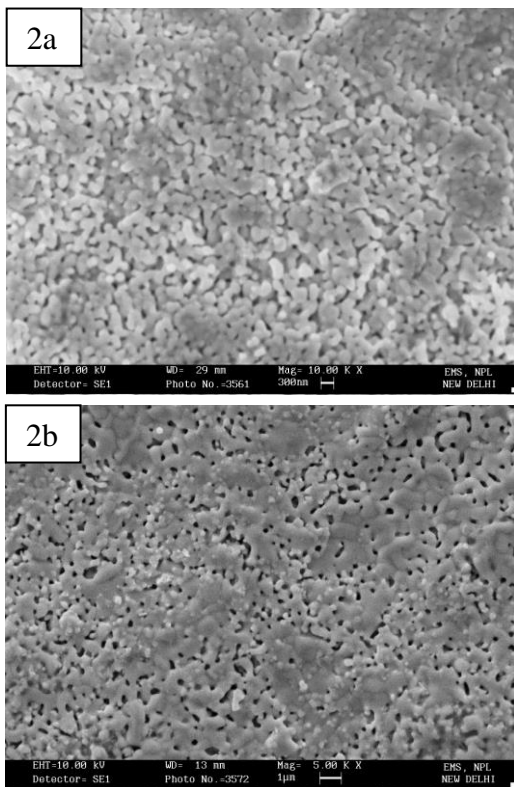
**3.1. X-Ray Diffraction:** X-ray diffraction pattern was carried out by Philips X-ray diffractometer (X-pert Pro). X-ray pattern was taken from angle  $2\theta = 20$  to  $80$  with a step  $0.02^\circ$  with Cu  $K\alpha$  source. The operating condition of

X-ray instrument was 40kV, 30mA. Figure 1 shows the diffraction pattern of  $\text{Gd}_{1-x}\text{Ti}_x\text{FeO}_3$  ( $x=0-0.25$ ). For  $x=0.00$  and  $x=0.05$  Ti substitution  $\text{GdFeO}_3$  crystallized in perovskite phase [13]. Lattice constants for pure  $\text{GdFeO}_3$  were calculated  $a=5.30 \text{ \AA}$ ,  $b=5.54 \text{ \AA}$ , and  $c=7.59 \text{ \AA}$  (orthorhombic) by hkl and d values obtained by X-ray diffraction pattern. For  $x=0.10$  some garnet phase  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$  peaks start to appear with perovskite phase [14]. Perovskite structure tolerance factor  $t = (r_A + r_X) / \sqrt{2}(r_B + r_X)$  has been calculated for Ti substitution at Gd site in table 1. Where A is Gd & Ti, B is Fe and X is Oxygen. According to Goldschmidt rule the tolerance factor  $t$  for a perovskite structure is below 0.7 and above 1 beyond which non-perovskite structure is formed. Structure of the minerals is dependent on the chemical composition. The compositions have been synthesized by chemical process so the diffusion of Ti and Fe ions is fast in sintering process. The valency of the Ti ions can be changed by sintering the material and may occupy tetrahedral and octahedral Fe sites. The ionic radii of  $\text{Ti}^{4+}$  ( $0.605 \text{ \AA}$ )/ $\text{Ti}^{3+}$  ( $0.67 \text{ \AA}$ ) is comparable to  $\text{Fe}^{3+}$  ( $0.645 \text{ \AA}$ )/ $\text{Fe}^{2+}$  ( $0.78 \text{ \AA}$ ) thus have a possibility to replace octahedral/tetrahedral site of Fe. Titanium substitution somehow relaxed the distorted perovskite into symmetric cubic garnet structure. Gadolinium is located in the center of eight coordinated dodecahedral distorted site.



**Figure 1. X-ray diffraction pattern of  $Gd_{1-x}Ti_xFeO_3$  ( $x=0-0.25$ ).**

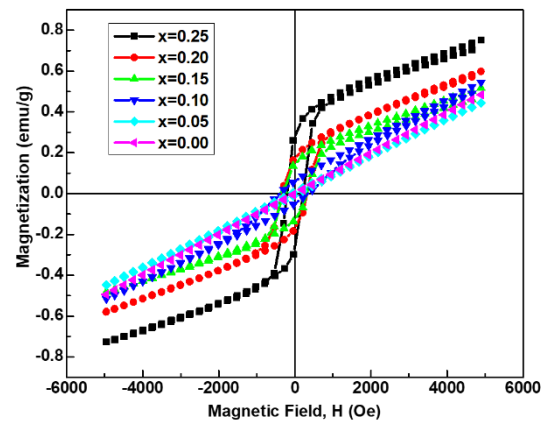
**3.2. Scanning Electron Microscope:** Surface microstructure of sintered  $GdFeO_3$  and  $x=0.25$  Ti substituted  $GdFeO_3$  has been shown by SEM image in Figure 2 (a, b). SEM image shows small grains distribution and open pores present throughout the sample. The smaller grains are obtained due to chemical co-precipitation synthesis method. Grains seem to be fused by titanium substitution and collapse of pores visible in Fig 2b.



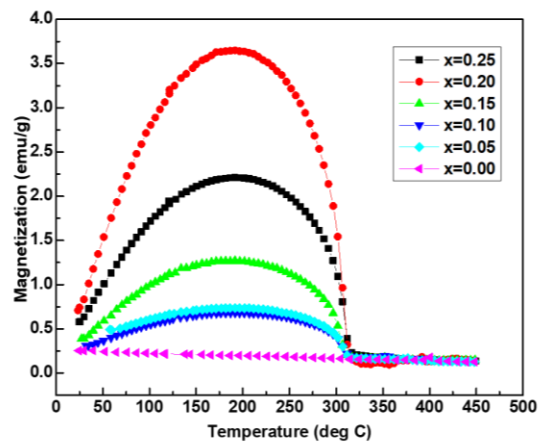
**Figure 2. SEM image of  $GdFeO_3$  (2a), and  $Gd_{0.75}Ti_{0.25}FeO_3$  (2b).**

**3.3. Magnetization:** Room temperature M-H loops were taken by vibrating sample magnetometer as shown in Figure 3. M-H loop shows a typical antiferromagnetic nature of  $GdFeO_3$ . At 5KOe the magnetic moment was quite low 0.5 emu/g as characteristic of antiparallel arranged spin moments. By increasing Ti substitution, low magnetic field magnetization starts to appear as well as

magnetic moment also increased. For the  $x=0.25$  Ti substitution the retentivity of the composition increased to 0.28 emu/g signifies the spin are aligned at low applied magnetic field. This shows the switching behavior of the magnetic moment with reversible applied magnetic field. From XRD pattern it is observed that with Ti substitution perovskite phase converting towards garnet phase. The magnetic moment in garnet appears due to the antiparallel alignment as a result of exchange interaction between  $Fe^{3+}$  ions at tetra and octahedral sites with magnetic moment of Gd ions in c site give the net magnetic moment [15]. Thus, replacement of Gd ions by Ti ion is resulted into net magnetic moment observed by M-H loop. It has been clearly observed by X-ray diffraction that the perovskite structure is transforming to cubic garnet structure by titanium substitution in  $GdFeO_3$ .



**Figure 3. Room temperature magnetization vs. field of  $Gd_{1-x}Ti_xFeO_3$  ( $x=0.00-0.25$ ).**



**Figure 4. Magnetization vs. temperature plot for  $Gd_{1-x}Ti_xFeO_3$  ( $x=0.00-0.25$ ) series.**

$Gd_{1-x}Ti_xFeO_3$	Tolerance Factor	Magnetic Moment (emu/g)	Retentivity (emu/g)	Coercivity (Oe)
X=0	0.810	0.50	0.005	27
X=0.05	0.806	0.45	0.01	86
X=0.1	0.801	0.54	0.06	367
X=0.15	0.796	0.52	0.14	313
X=0.2	0.792	0.61	0.17	321
X=0.25	0.787	0.74	0.28	218

**Table 1. Tolerance factor calculated for perovskite structure.**

Figure 4 shows the plot between magnetization vs temperature graph of  $Gd_{1-x}Ti_xFeO_3$  ( $x=0.0-0.25$ ) series. Magnetization vs temperature plot shows typical ferrimagnetic sublattice Curie temperature curve. It is known that  $Fe^{3+}$  spins form an antiferromagnetic order along the **a** axis below  $T_{FeN} = 661$  K with a weak ferromagnetic (WFM) component along the **c** axis due to the spin canting in the **ac** plane, which results from the Dzyaloshinskii-Moriya interaction. On the other hand,  $Gd^{3+}$  moments order antiferromagnetically along **a** axis below  $T_{GdN} = 2.5$  K. Magnitude of ferrimagnetic spins increased upto  $x = 0.20$ , Ti substitution then with further substitution it decreased. This type of Curie temperature  $T_c$  (comp) often observed in sublattice-structured compounds. This  $T_c$  (comp) at which the net magnetisation is zero because the individual magnetisation of the sublattices have equal magnitudes but opposite signs. It is evident even from this short discussion that the magnetism of garnets, and especially the compensation temperature, is strongly dependent on crystallographic parameters.

**4. Conclusions:** Antiferromagnetic  $GdFeO_3$  has been transformed to low field ferromagnetic garnet has been obtained by titanium substitution using chemical synthesis process. Perovskite phase has been formed at low temperature  $750^\circ C$  while by solid state reaction it requires prolong

heating above  $1300^\circ C$  for phase formation. By replacing Gd ions with Ti ions shows

ferrimagnetism at room temperature has been observed by inducing structural change. Magnetization vs. temperature plot confirms the

sublattice magnetization of the compound with transformation of phase. Highest retentivity of 0.28 emu/g at low applied magnetic field approximately 150 Oe at  $x=0.25$ , titanium substitution is applicable in magnetic switching and storage of magnetic moment at room temperature.

#### References:

1. S. Geller, Crystal structure of gadolinium orthoferrite  $GdFeO_3$ . J. Chem. Phys. 24, 1956, 1236–39.
2. Room temperature magnetoelectric coupling enhancement in Mg-substituted polycrystalline  $GdFeO_3$ , Scripta Materialia 67, 2012, 316–19.
3. S. Sahoo, P.K. Mahapatra, R.N.P. Choudhary, M.L. Nandagoswami, A. Kumar, Structural, electrical and magnetic characteristics of improper multiferroic:  $GdFeO_3$ . Mat. Res. Express 3, 2016, 065017.
4. C.S. Vandana, B.H. Rudramadevi, Effect of  $Cu^{2+}$  substitution on the structural, magnetic and electrical properties of gadolinium orthoferrite. Mat. Res. Express 5, 2018, 046101.
5. Landolt-Börnstein; Numerical Data and Functional Relationships in Science and Technology Group III, Vol 27f3, ed H P J Wijn; 1994
6. R.L. White, Review of Recent Work on the Magnetic and Spectroscopic Properties of the

- Rare Earth Orthoferrites, *Journal of Applied Physics* 40, 1969, 1061.
7. T. Yamaguchi, Theory of spin reorientation in rare-earth orthochromites and orthoferrites, *Journal of Physics and Chemistry of Solids*, 35(4) 1974, 479-500.
  8. J. D. Cashion, A.H. Cooke, D.M. Martin, M.R. Wells, Magnetic interactions in gadolinium orthoferrite. *J. Phys. C* 3, 1970, 1612–20.
  9. D. V. Korolev, G. A. Shulmeyster, M. S. Istomina, N. V. Evreinova, I. V. Aleksandrov, A. S. Krasichkov, V. N. Postnov, M. M. Galagudza, Fluorescently Labeled Gadolinium Ferrate/Trigadolinium Pentairon (III) Oxide Nanoparticles: Synthesis, Characterization, In Vivo Biodistribution, and Application for Visualization of Myocardial Ischemia–Reperfusion Injury, *Materials*, 15 (11), 2022, 3832.
  10. J. Shah, P. Bhatt, D. K. Dayas and R K Kotnala, Significant role of antiferromagnetic GdFeO<sub>3</sub> on multiferroism of bilayer thin films, *Materials Research Express*, 5 (2), 2018.
  11. E E. Ateia, B. Hussein, C. Singh and M. M. Arman, Multiferroic properties of GdFe<sub>0.9</sub>M<sub>0.1</sub>O<sub>3</sub> (M = Ag<sup>1+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup>) nanoparticles and evaluation of their antibacterial activity, *The European Physical Journal Plus*, 137(443) 2022.
  12. F. Bzour, A. Gismelseed, I. Z. Al-Yahmadi, et al. Structural, magnetic and mössbauer studies of GdFe<sub>x</sub>Mn<sub>1-x</sub>O<sub>3</sub> multiferroic materials. *Hyperfine Interact*, 242(54), 2021.
  13. A. Ruffo, M. C. Mozzati, B. Albini, P. Galinetto and M. Bini, Role of non-magnetic dopants (Ca, Mg) in GdFeO<sub>3</sub> perovskite nanoparticles obtained by different synthetic methods: structural, morphological and magnetic properties, *Journal of Materials Science: Materials in Electronics*, 31, 2020, 18263–77.
  14. Y. Takumi, A. Junji, K. Yusuke, E Shuji, C Susumu, N Shoichi, Ferrimagnetic order in the mixed garnet (Y<sub>1-x</sub>Gd<sub>x</sub>)<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, *Philosophical magazine*, 85(17), 2005, 1819-33.
  15. M-lan Li, L. Zhang, N. Jiang, S-juan Zhong and L. Zhang, Influences of silicon carbide nanowires' addition on IMC growth behavior of pure Sn solder during solid–liquid diffusion, *Journal of Materials Science: Materials in Electronics*, 32, 2021, 18067–75.