

Induced Magnetization in Antiferromagnetic GdFeO₃ by Nonmagnetic Titanium Substitution for Magnetic Switching and Storage Application

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Abstract: Room temperature ferromagnetism has been induced in antiferromagnetic GdFeO₃ by substituting titanium at Gd site Gd_{1-x}Ti_xFeO₃ (x=0.00 - 0.25). Perovskite GdFeO₃ 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 GdFeO₃ 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 GdFeO₃ 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, GdFeO₃, 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 RFeO₃ systems such as EuFeO₃ and GdFeO₃ 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: Fe³⁺ and R³⁺. 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 RFeO₃ 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 Fe³⁺ 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 Gd³⁺ 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 GdFeO_3 has been disturbed by substituting titanium at Gd site synthesis by co-precipitation method. Characterization of pure and substituted nanocrystalline GdFeO_3 powder for the purpose of multiferroic effect has been analyzed. Room temperature magnetism has been obtained in 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°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°C . The dried samples were presintered at 750°C for 24 h followed by pelletization and sintered at 1000°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° 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 GdFeO_3 crystallized in perovskite phase [13]. Lattice constants for pure 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 Ti^{4+} (0.605 \AA) / Ti^{3+} (0.67 \AA) is comparable to Fe^{3+} (0.645 \AA) / Fe^{2+} (0.78 \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.

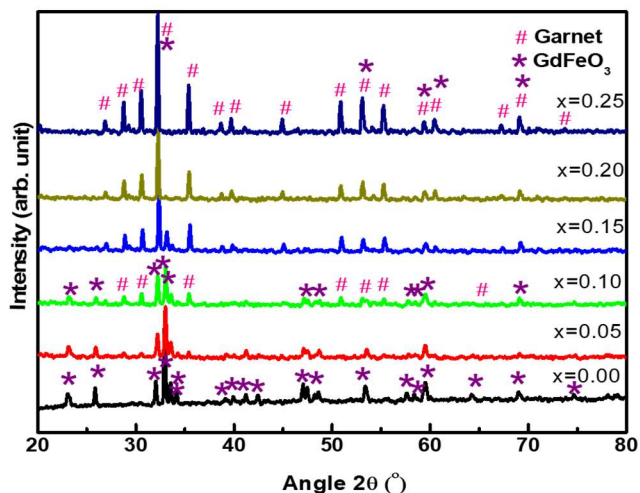


Figure 1. X-ray diffraction pattern of $Gd_{1-x}Ti_xFeO_3$ ($x=0-0.25$).

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.

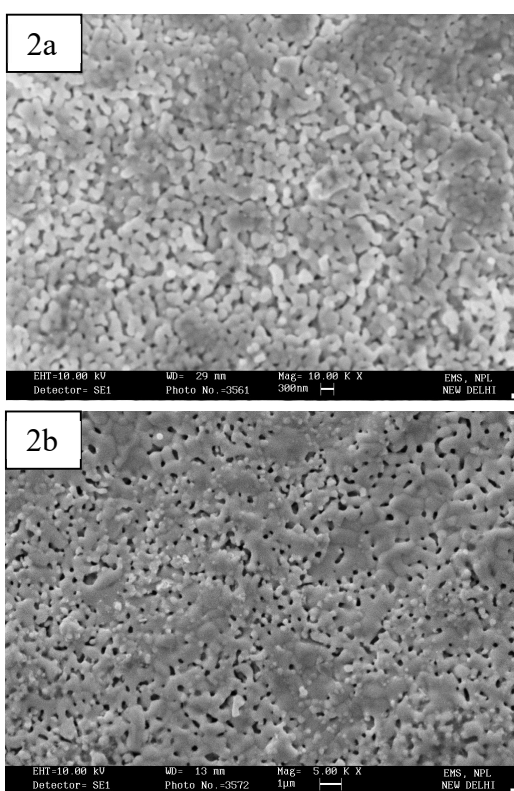


Figure 2. SEM image of $GdFeO_3$ (2a), and $Gd_{0.75}Ti_{0.25}FeO_3$ (2b).

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 $GdFeO_3$.

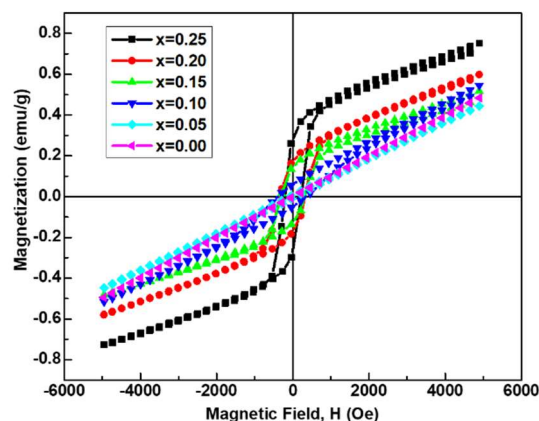


Figure 3. Room temperature magnetization vs. field of $Gd_{1-x}Ti_xFeO_3$ ($x=0.00-0.25$).

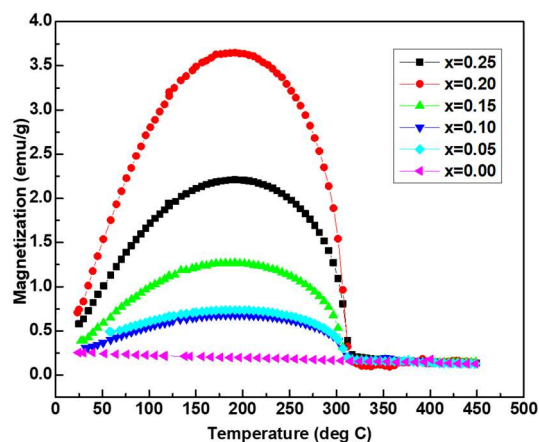


Figure 4. Magnetization vs. temperature plot for $Gd_{1-x}Ti_xFeO_3$ ($x=0.00-0.25$) series.

heating above 1300°C for phase formation. By replacing Gd ions with Ti ions shows

$Gd_{1-x}Ti_xFeO_3$	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°C while by solid state reaction it requires prolong

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.

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