

Effect of Gd substitution on structure and magnetic properties of BiFeO₃

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Abstract. Multiferroic ceramic samples of Gd_xBi_{1-x}FeO₃ ($x = 0 - 0.35$) have been prepared by solid state reaction method. The results of XRD show a transition from rhombohedral to orthorhombic structure with increase in composition. Ferromagnetic order is observed with an enhanced magnetization (M) and coercivity (H_C) for all the doped samples. Maximum magnetization is observed at the field of 5T for $x = 0.3$. The temperature dependant magnetization shows the anomalous magnetic behaviour in this system. A minimum in the M-T curve and double hysteresis loop behaviour were observed for the samples with $x=0.1$ and 0.2

1. Introduction

Multiferroic materials have attracted the focus of many researchers recently because of the co-existence of the spin order as well as the charge order. The coupling between charge and spin ordering drives these materials for device application such as multiple state memory elements. Bismuth ferrite (BFO) is one of the most widely studied multiferroic material with $T_N = 370^\circ\text{C}$ and $T_C = 810^\circ\text{C}$. The magnetic order of BFO is G-type ordering with a cycloidal spiral with a period of 620\AA [1]. Unfortunately, the aforementioned magneto electric coupling is very small in BFO and its spin cycloid structure constraints the magnetic properties. To enhance the magnetic properties different strategies are adopted in terms of partial chemical substitution, reducing the particle size etc. Partial substitution of rare earth element at Bi site, Bi_{1-x}R_xFeO₃ (R= La, Gd, Ho, Sm etc.), is one such ways to improve the magnetic properties as it is expected to modify the spin structure due to the difference in ionic radius. Also, it has an additional advantage that it stabilizes pure phase and reduces the leakage current. Moreover, the introduction of rare earth element suppresses the spin cycloid and improves the magnetic properties [2]. To this end, as Gd³⁺ has a magnetic moment of $7.9 \mu_B$, effect of doping on the magnetic properties of BFO has been investigated.

2. Experimental details

Bi_{1-x}Gd_xFeO₃ (BGFO) ($x = 0 - 0.3$) powders were prepared using solid state reaction method. Stoichiometric amounts of Bi₂O₃, Fe₂O₃ and Gd₂O₃ oxides were milled for 5 hours in ball mill and pre-calcinated at 600°C . These powders are further milled and calcinated at 820°C for 30 minutes. The powders were then pressed into pellets and finally sintered at 820°C for 2 h. Phase analysis was carried out by X-ray diffraction (XRD) using Cu K α radiation. Field and temperature dependent magnetic properties were measured using Quantum design Physical Property Measurement System (PPMS).



3. Results and discussion

3.1. X-ray Analysis:

The X-ray diffraction spectra for BGFO samples are shown in Figure.1. For $x = 0$ the structure is rhombohedral with R3c space group and a shift in the peak positions is observed with increase in x . The doublets seen in pure BFO disappear with doping, signifying the change in the structure from Rhombohedral R3c to Orthorhombic Pnma due to the difference in the ionic radii of Gd^{3+} and Bi^{3+} as reported in literature [3, 4].

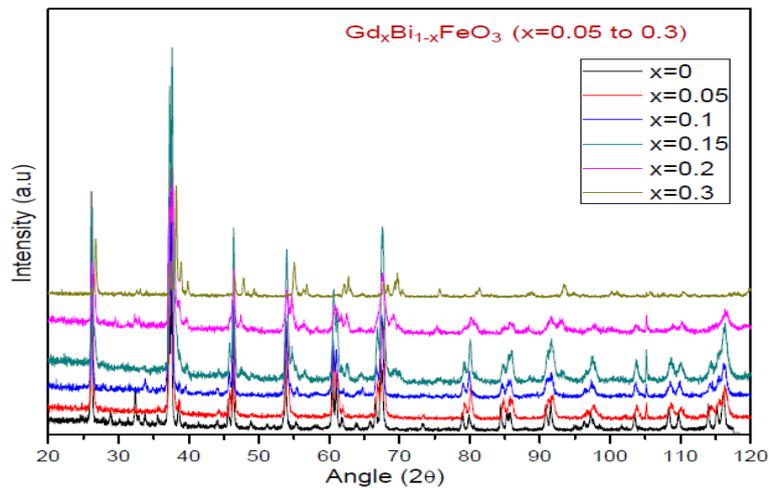


Figure.1. XRD pattern of Gd doped BFO.

There are small traces of non-magnetic $Bi_{25}FeO_{40}$ [5] and $Bi_2Fe_4O_9$, antiferromagnetic (AFM) below 264 K, secondary phases were observed. However, the influence of $Bi_2Fe_4O_9$ phase is not significant in the magnetic properties of these samples.

3.2. Magnetic properties:

The temperature variation of zero-field-cooled (ZFC) and field-cooled (FC) magnetization at a field of 500 Oe is depicted in Figure 2. Both ZFC and FC magnetization (for $x = 0, 0.1, 0.2, 0.3$) increase gradually with decrease in temperature from 300 K. For $T \leq 25$ K there is a sudden increase in magnetization which is due to the ordering of Gd^{3+} magnetic moments [4]. A bifurcation in the ZFC and FC magnetization below 200K indicates the presence of magnetic frustration. There is a linear increase in the moments with x at low temperatures.

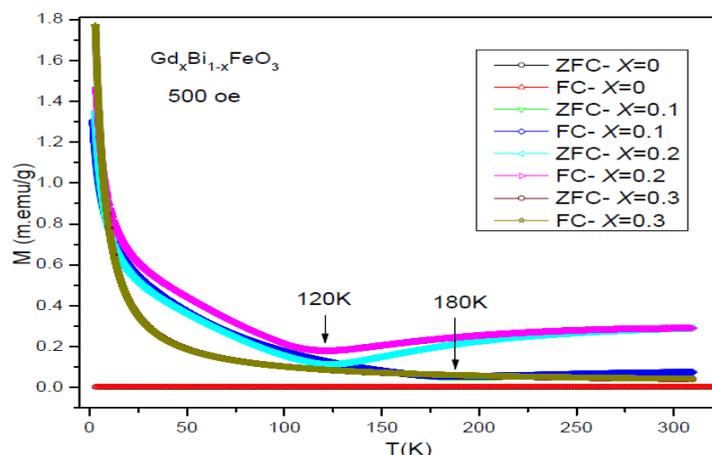


Figure.2. Zero Field cooled M-T curve of $Gd_xBi_{1-x}FeO_3$ at 500 Oe

Only for samples $x = 0.1$ and $x = 0.2$, the magnetization shows a minimum in both FC and ZFC at 180 K and 120 K respectively [Figure.2]. A similar kind of result was observed in single crystal BFO with a minimum at 100K, which indicates a change in spin ordering [6]. The minimum observed in $x=0.1$ and $x=0.2$ samples may be due to spin re-orientation, typically seen in orthoferrites [7]. This behavior is more prominent in the M-H loops at 300K.

Figure 3 presents the magnetic hysteresis loops recorded at 300 K for BGFO. In pure BFO ($x = 0$), almost no net magnetization is observed due to the spiral spin structure but has a small residual magnetic moment results due to a canted spin arrangement. Gd doping at Bi site in BFO results in the appearance of ferromagnetism at room temperature. Pure BFO shows a weak magnetism with $M_r = 0.0005$ emu/g and $H_c = 8.3$ Oe. The values of magnetization and coercivity get enhanced remarkably with the doping. This magnetization increase is due to the breaking of spin cycloid structure of BFO with the introduction of Gd.

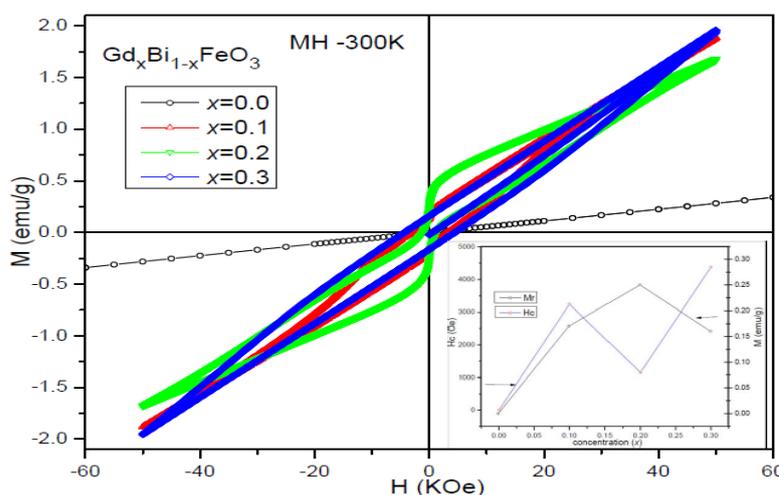


Figure.3. M-H loops for Gd doped BFO at RT. Inset shows H_c and M_r Values with x .

The antiferromagnetic structure of pure BFO thus changes to ferromagnetic state at room temperature with doping. Gadolinium doping not only results in structural modification, affecting the Fe-O-Fe antiferromagnetic (AFM) exchange interaction and therefore modifying the magnetic structure but also brings in additional magnetic interaction involving Gd. The samples with $x=0.1$ and 0.2 have a magnetization (at $H=5$ T) of 1.85 and 1.69 emu/g and H_c is 3.2 KOe and 1.1 KOe at 300 K respectively. H_c and magnetization is maximum for $x = 0.3$ with a value of ~ 4.2 KOe and 1.95 emu/g respectively at 300 K. M-H loops for $x=0.1$ and 0.2 show an interesting double hysteresis kind of loop. This effect is more pronounced for $x=0.2$ thereby decreasing the H_c to 1.1 KOe. This may be attributed to the interactions between Fe^{3+} and Gd^{3+} . A similar kind of result was observed in previous studies, which is typical to orthoferrite structure [8] and also in Ho doped BFO [9].

M-H loops measured at 5 K are shown in figure 4. Although they are still unsaturated at 5T, exhibit a huge increase in magnetization reaching a value of 19.8 emu/g and 36.9 emu/g for $x = 0.1$ and $x = 0.3$ respectively compared to the pure BFO of 0.22 emu/g at 5T. The coercivity is maximum for $x = 0.2$ which has a value of ~ 0.95 KOe with the magnetization of 21.76 emu/g. The value of M_r increases linearly with x and reaches a maximum value of 0.25 emu/g and 0.97 emu/g for $x=0.2$ both at RT and 5K respectively and then starts decreasing for further doping of $x=0.3$.

The contribution to the magnetism occurred in this system is basically due to the Fe-O-Fe AFM interaction, contribution from Gd^{3+} ions and canted Fe sub lattice [4] As the doping level changes, the contributions from Gd and Fe sub lattice vary and hence results in the nonlinear variation in the M_r with x both at RT and 5K . However, a detailed magnetic structure analysis is required to understand this phenomenon more clearly.

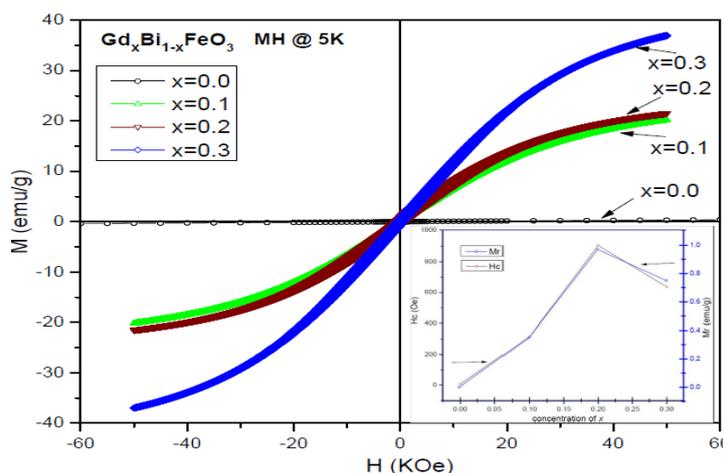


Figure.4. M-H loops for Gd doped BFO at 5K. Inset shows H_c and M_r values with x

4. Conclusions

In summary, we have prepared Gd doped BFO samples using solid state reaction method. Gd doping causes a structural change and accordingly enhance the magnetic properties. The magnetization reaches a maximum values for $x = 0.3$. High coercivity observed for $x=0.15$. The M-T curves for $x = 0.1$ and $x = 0.2$ have a minimum in the magnetic moment and a double hysteresis like M-H curve with a low coercive field was observed for the same samples, which is a characteristic of orthoferrites.

5. Acknowledgments

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6. References

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