Enhanced Room Temperature Multiferroicity in Gd Doped BFO

S. K. Pradhan[1], J. Das [1], S. Samantray[1] , D. R. Sahu[2], A. K. Pradhan[3], K. Zhang[3], R. B. Konda[3], R. Mundle[3], V. V. Srinivasu[4], B. K. Roul[1]

[1] Institute of Materials Science, Bhubaneswar, India
[2] National Cheng-Kung University, Taiwan
[3] Norfolk State University, Virginia, USA
[4] National Center for Nano Structured Materials & Microfluidics group Materials & Manufacturing division, CSIR, Pretoria, South Africa.
ims@iopb.res.in

ABSTRACT

A signature of enhanced multiferroic behavior at room temperature has been observed in Gd doped Bismuth Ferrite system. This paper reports the preliminary findings / observations of structural and magnetization measurement of bismuth rich iron deficient Gd doped multiferroic BFO system. At particular doping level of Gd, this bulk ceramics showed spectacular M~ H behavior at room temperature which is likely to be opened a new avenue for the potential applications in information storing technology as well as in the emerging field of spintronics and high sensitive magnetoelectronic sensor devices.

INTRODUCTION

Some specific materials that have the intrinsic ability to couple electric, magnetic and structural order parameters resulting the co-existance of ferroelectricity, Ferromagnetism & Ferroelesticity are defind as multiferroics. Coupling between electric and magnetic ordering leads to electromagnetic effect which provides an additional degree of freedom in designing & engineering of functional sensor, current devices , transducers and multistage memory devices. On the other hand there is a derth of materials to exhibit magnetoelectric behavior at room temperature which is probably due to the fact that the tansition metal *d* electron , essential in the presence of magnetic moment, also reduce lattice distortion. Lattice distortion is essential in the presence of the ferroelectric behavior. The Perovskite $BiFeO_3$ (BFO) is one of the few magnetoelectric multiferroics in which ferroelectric (Tc ~ 830 ^{0} C) and antiferromagnetic (AF) (T_N ~ 370 ^{0} C) order parameters coexist up to quite high temperature [. In BFO , Bi-O orbital hybridization due to Bi $6s^2$ lone pair is responsible for ferroelectric instability while Fe-O-Fe Dzyaloshinski Moriya antisymmetric interaction (DMI) gives rise to complicated magnetic structure [1]. The structural properties of bulk BFO single crystal have been extensively studied and have been shown to posses rhombohedral distorted perovskite structure and space group *R3C* at room temperature [2]. The spontaneous polarization of bulk BFO was expected to be 90-110 μC / cm^2 [3] because of large atomic displacement and a high Curie temperature . However, a small polarization has been observed in bulk BFO single crystal [4] and BFO bulk ceramics [5] , and their hysteresis loops were not saturated , which were attributed to the high leakage current density and is

related to the oxygen vacancies / charge defects , oxidation state of Fe and nonstoichiometry [6,7] .

APPROACH TO THE PROBLEM

To overcome above mentioned leakage problem , attempt has been made to tailor the said materials by ion substitution or solid solution with other perovskite materials or by introducing dopents and using different fabrication methods. Well saturated hysteresis loop with remanent polarization has also recently been reported in single phase $BiFeO_3$ ceramics. In order to address above issue , we have prepared a series of Gd doped BFO bulk ceramics system and studied their basic properties using XRD , SEM and SQUID Magnetization measurement technique.

EXPERIMENTAL

High pure (99.999 %) oxides of Bismuth (Bi), Iron (Fe) and Gadolinium (Gd) were taken as starting materials for preparation of Gd doped Bismuth Ferrite (BFO) ceramics. Appropriate proportion of required metal oxides were mixed and ground in a agate mortar and placed in alumina tube furnace at 500 ^{0} C for five hours . In order to reduce particle size of the mixed powder, intermediate quenching (from 500 ^{0} C to room temperature) and grinding were repeatedly carried out . Mixed powders were palletized using a hydraulic press of 30 ton base capacity with a applied pressure of 8 tonn / cm^2 . Circular pellets with approximately 2mm thickness and 10 mm diameter were prepared out of the above mentioned processed powder which were subjected to sintering at 800 ^{0}C for achieving high density product. Sintering temperature was controlled by using a programmable temperature controller (Eurotherm make). Surface morphology of the sintered specimen and powder were studied by SEM (Philips FEG XI'30). Phase identification was performed by the X-ray powder diffraction (XRD) method on a Rigaku X-ray diffractometer using Cu Kα radiation. The magnetization was measured using Quantum Design superconducting quantum interference device (SQUID) magnetic property measurement system (MPMS)]

RESULT DISCUSSION

A typical XRD pattern of the sintered sample (Bi_1 $Gd_{0.1}$ $Fe_{0.9}$ O) is shown in figure-1a where in it is noted that sharp crystalline peaks are appeared at lower 2θ angle where as broad peaks are appeared at higher 2θ angle of the XRD pattern . As per Gd was substituted at the Fe site, some unreacted species (not indexed) along with a few small shoulder peaks are appeared which posed the problem of indexing the XRD lines. However, Gd substituted at Fe site with Bismuth rich sample showed perfect crystalline XRD peaks which are indexed and shown in figure -1b . It is evident from the figure-1b that the Bi rich Gd substituted BFO is highly in crystalline character.

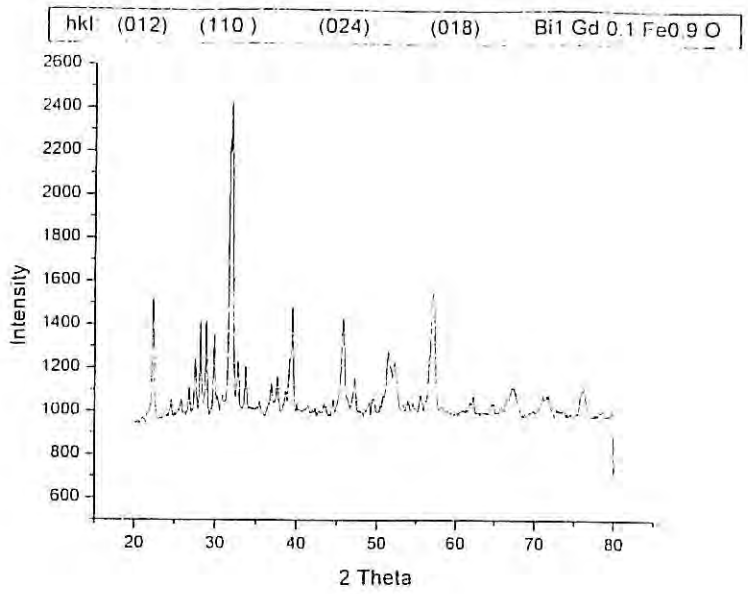

Figure-1a

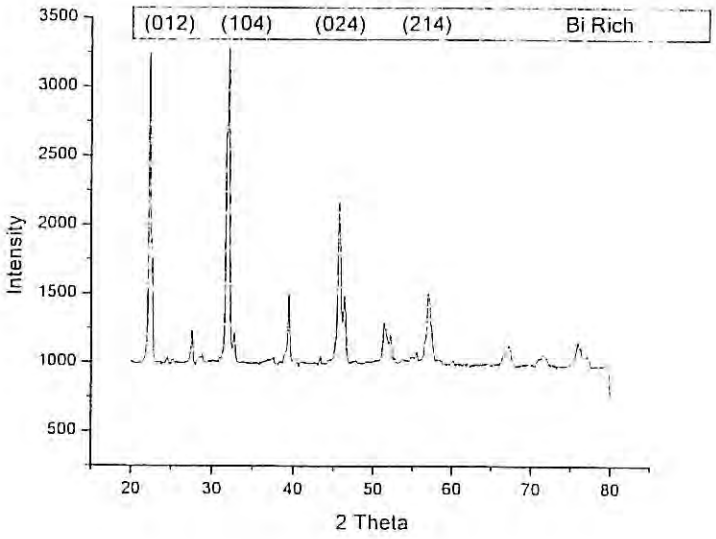

Figure-1b

This result has also been observed in our SEM analysis as shown in figure-2 . It is evident from the scanning electron micrograph (Fig-2) that highly regular & cubic crystallites with sharp boundary/edges of micron size semi oriented grains were grown, which is the primary cause for exhibiting highly crystalline character in our XRD pattern as shown in figure-1b. It is expected that the substitution of Gd in Fe site for bismuth rich BFO promotes the physical densification of the sintered product which in turns also act like a nucleation center for rapid grain growth of cubical crystallite. Further details on experimental findings in connection with cubic size crystallites grain growth habits are required to understand the above mentioned grain growth kinetics.

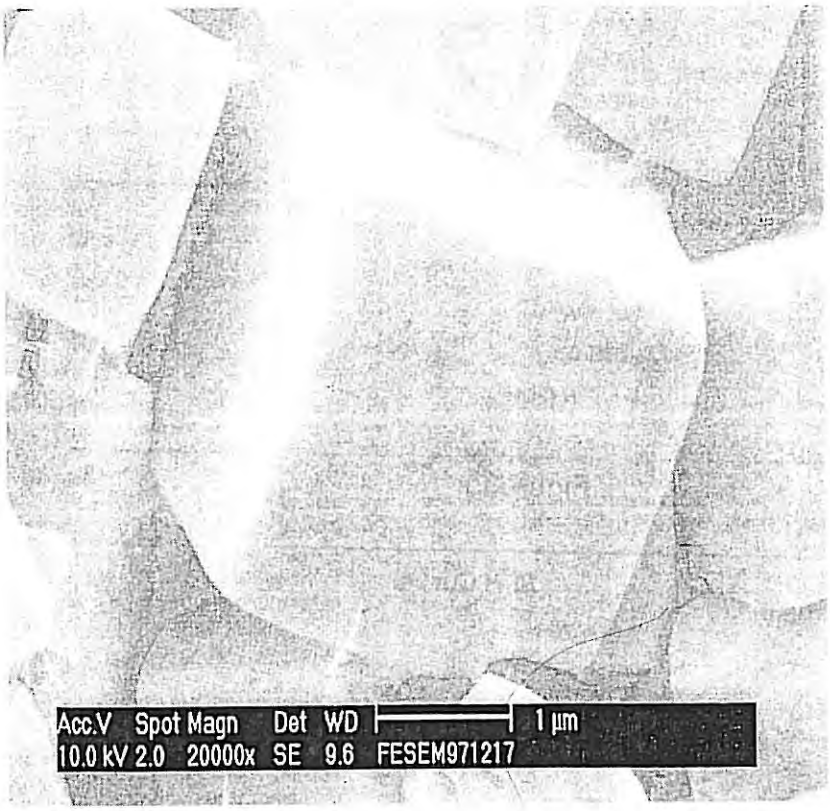

Figure-2

Magnetization behavior of Gd-doped sintered BFO specimens are shown in figure 3a & 3b. Figure –3a presents the M~H characteristic of Gd-doped BFO at room temperature . It is noted that a linear field dependent magnetization line exists and the materials show antiferromagnetic behavior at room temperature . However, for Gd doped bismuth rich BFO , the M~H behavior is totally different and exhibit a clear M~H hysteresis loop at room temperature . This observation clearly suggest the room temperature application of Gd doped BFO multiferroics system.

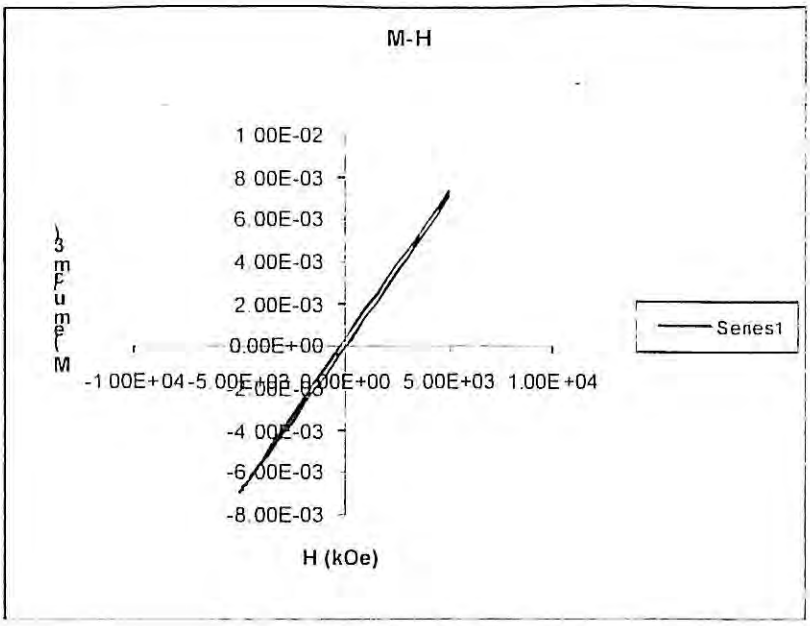

Figure3a

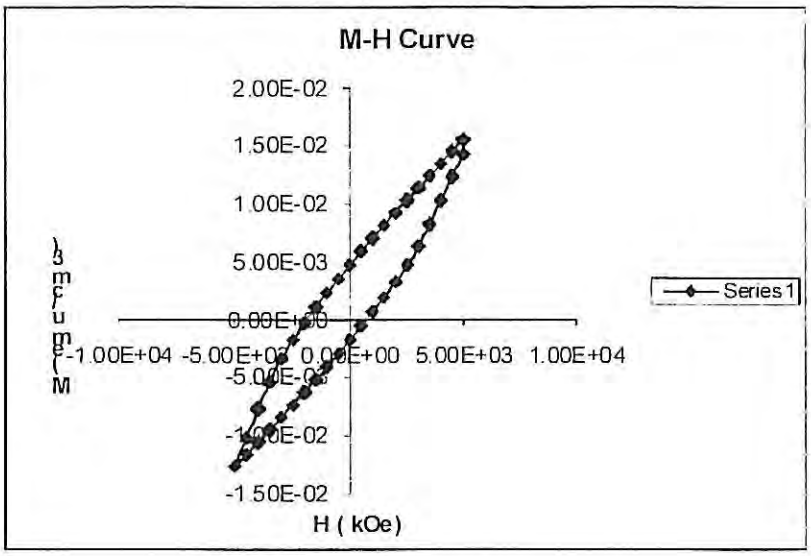

Figure-3b

CONCLUSION

It is possible to tailor the multiferroics BFO system for room temperature application by suitably engineering the chemical and magnetic unit cell by doping appropriate rare earth ions.

ACKNOWLEDGEMENT

Authors are thankful to the Director, IMS (Prof. S. N. Behera) for his constant encouragement and academic support to carry out this research programmee in the institute.

REFERENCES

1. H. Schmid , Ferroelectrics **162**, 317 (1994)
2. F. Kubel and H. Schmid, Acta Crystallography, Sect. B: Structure Sci. **46**, 698
   (1990)
3. J. B. Neaton, C. Ederer, U. V. Waghmare, N. A,. Spaldin, and K. M. Rabe, Phys. Rev. B **71**, 014113 (2005)
4. J. R. Teague , R. Gerson, and W. J. James, Solid state commu. 8, 1073 (1970)
5. Y. P Wang , L. Zhou , M. F. Zhang, X. Y. Chen, J. M. Liu, and Z. G. Liu, Appl. Phys. Lett. 84 , 1731 (2004)
6. V. R. Palkar et el, Appl. Phys. Lett. 80 , 1628 (2002)
7. K. Singh et el, J. Appl. Phys. 93, 142904 (2008)