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Size effect study in magnetoelectric $BiFeO_3$ system

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Abstract. In this paper, we report for the first time finite size effects on Néel temperature (T_N) of magnetoelectric $BiFeO_3$ system. Novel wet chemical route has been developed to produce fine particles of $BiFeO_3$ with controlled size and size distribution. Unlike other oxide systems, lattice volume contraction has been observed with decrease in particle size. The decrease in T_N is co-related to unit cell volume contraction occurring with reduction in particle size.

Keywords. Nanoparticles; size effects; magnetoelectric materials.

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1. Introduction

The discovery of compounds which exhibit simultaneously electric and magnetic dipole long-range order by Smolenskii *et al* [1] stimulated an intense search for new substances with similar properties. Such systems with coexistence of magnetic and ferroelectric ordering are also known as signetomagnets. Very few signetomagnets exist in nature or have been synthesized in the laboratory. Bismuth ferrite ($BiFeO_3$) is one of the few known signetomagnets. $BiFeO_3$ exhibits rhombohedrally distorted perovskite structure. The parameters of the hexagonal elementary cell are: $a = 5.5876$ Å and $c = 13.867$ Å at room temperature. It has antiferromagnetic ordering with $T_N \sim 370°C$ and ferroelectric properties with a high Curie temperature of about $\sim 830°C$. Conditions for synthesizing single phase $BiFeO_3$ are critical since the temperature stability range of the phase is very narrow. Moreover, it is also difficult to control oxygen stoichiometry in the sample. Hence, various aspects of $BiFeO_3$ are yet to be studied.

Finite size effect study has been carried out on various oxide systems. Earlier we have reported size induced structural changes in magnetic (Fe_2O_3), ferroelectric ($PbTiO_3$) and antiferroelectric ($PbZrO_3$) systems. In all the cases lattice acquired higher symmetry structure. Observed size induced structural changes were also associated with unit cell volume expansion with decrease in particle size. The suppression of the physical properties [2–4] suggest structure property co-relationship. It is, therefore, thought to be interesting to find out effects of size reduction in the system like $BiFeO_3$, which is characterized by co-existence of magnetic and ferroelectric ordering.

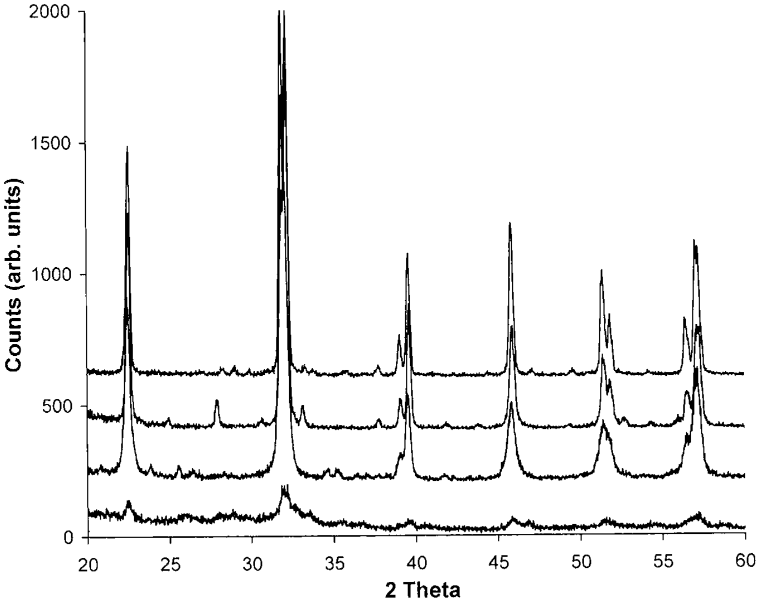

Figure 1. XRD patterns of $BiFeO_3$ fine particles calcined at different temperatures for 1 hour.

2. Experimental

A new wet chemical route has been developed in our laboratory to synthesize fine particles of $BiFeO_3$ with controlled size and size distribution. Bismuth trioxide (Bi_2O_3) and ferric oxide (Fe_2O_3) having 99.9% purity were weighed in stiochiometric proportion. The oxides were dissolved in concentrated nitric acid and then diluted with deionized water to bring the solution concentration to $\sim$ 10% (w/v). Both the cations (Bi and Fe) in the solution were co-precipitated as hydroxide using ammonia as the precipitating agent. The pH of the solution was adjusted to $\sim$ 9 to ensure complete precipitation of both the cations. The precipitate was filtered and washed with deionized water till pH of the filtrate reduced to 7. The precipitate was then dried under infrared lamp. The dried complex was subjected to thermo gravimetric analysis (TGA) to determine the calcination temperature. TGA curve indicated that the weight loss is complete by 500°C. Hence the complex was heated above 500°C to obtain the reacted material. The calcination temperature was varied between 550–750°C for 1 hour so as to obtain $BiFeO_3$ particles with different sizes. To obtain bulk material for comparison, $BiFeO_3$ sample was prepared by oxide mixing technique and calcined at 810°C for 1 hour. The unreacted impurity phase present in calcined $BeFeO_3$ samples was leached out with dilute nitric acid.

The fine particles of $BiFeO_3$ are then characterized by using various techniques. X-ray diffraction (XRD) study is carried out for phase determination and lattice parameter calculations (figure 1). The coherently diffracting domain size d_{XRD} is calculated from X-ray line broadening using Scherrer's formula. Scanning electron microscopy (SEM) is used to find out grain size and morphology (figure 2). Differential scanning calorimeter (DSC)

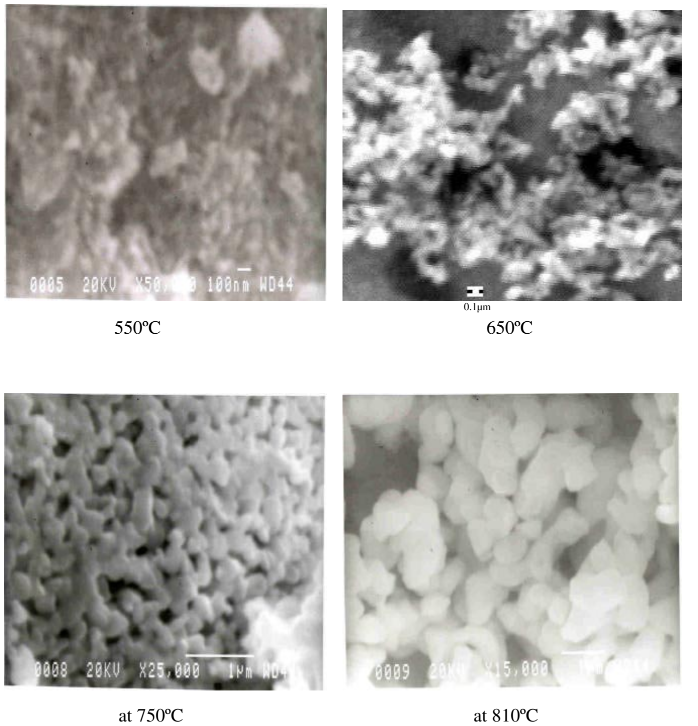

Figure 2. Scanning electron micrographs of $BiFeO_3$ fine paraticles calcined at different temperatures for 1 hour.

is used to determine Néel temperature (T_N) of the sample. DSC experiments were carried out in nitrogen ambient with the heating rate of 10°/min.

3. Results and discussion

XRD patterns shown in figure 1 reveal that as the calcination temperature progresses, peaks become sharper. It is an indication of the development of crystalline nature and grain growth in the sample. Grain growth with temperature is also clear from SEM pictures shown in figure 2. The observed difference in particle size for each sample, obtained from XRD and SEM confirms that particles are multi-domain.

It is clear from table 1 that particle size decreases with the reduction in calcination temperature. It also shows that with reduction in particle size, there is a decrease in lattice parameter a, while the c parameter increases. However, overall there seems to be contraction in unit cell volume with the reduction in particle size. Antiferromagnetic to paramagnetic transition gets diffused with reduction in particle size and reduction in Néel temperature (T_N) is also observed. These results could be explained on the basis of theoretical model suggested by Wang *et al* [5] for magnetic nano-structured materials. Accordingly, the surface atoms have fewer neighbors than interior atoms and the proportion of surface atoms

Table 1. Effects of particle size reduction on lattice parameters, cell volume and Néel temperature in $BiFeO_3$ system.

Heating schedule	Av. grain size (Å)	d_{XRD} (Å)	Lattice parameters a (Å)	c (Å)	Cell volume (Å^3)	T_N (°C)
550°C/1	615.5	233	5.574	6.927	186.36	339
650°C/1	1250	477	5.581	6.915	186.50	354
700°C/1	2417	541	5.584	6.912	186.66	378
810°C/1*	7240	738	5.591	6.918	187.28	400

*Sample prepared by oxide mixing technique.

in the entire particle increases as the particle size decreases. Due to increased surface to volume ratio there is bond-length contraction. Hence, there is decrease in Néel temperature with reduction in particle size. However, in the reported model, this kind of behavior is expected for the particles below 5 nm, while we have observed the effect at much higher range of particle size (23–54 nm). The behavior could be perhaps attributed to cell volume contraction observed in $BiFeO_3$ particles even in the size range much above 5 nm.

4. Conclusion

In $BiFeO_3$, reduction in particle size leads to decrease in a but increase in c parameter of the lattice. However, overall system experiences unit cell volume contraction with decrease in particle size. The observed decrease in Néel temperature with decrease in size is correlated to lattice volume contraction. Such a behavior could be explained on the basis of theoretical model suggested by Wang *et al* [5] for magnetic materials.

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