Equilibrium phases in the multiferroic BiFeO$_3$-PbTiO$_3$ system – a revisit

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Abstract. The (1-x) BiFeO$_3$-(x) PbTiO$_3$ solid solution exhibiting a Morphotropic Phase Boundary (MPB) has attracted considerable attention recently because of its unique features such as multiferroic, high Curie point (T$_C$ ~ 700°C) and giant tetragonality (c/a -1 ~ 0.19). Different research groups have reported different composition range of MPB for this system. In this work we have conclusively proved that the wide composition range of MPB reported in the literature is due to kinetic arrest of the metastable rhombohedral phase and that if sufficient temperature and time is allowed the metastable phase disappears. The genuine MPB was found to be x=0.27 for which the tetragonal and the rhombohedral phases are in thermodynamic equilibrium. In-situ high temperature structural study of x=0.27 revealed the sluggish kinetics associated with the temperature induced structural transformation. Neutron powder diffraction study revealed that the magnetic ordering at room temperature occurs in the rhombohedral phase. The magnetic structure was found to be commensurate G-type antiferromagnetic with magnetic moments parallel to the c-direction (of the hexagonal cell). The present study suggests that the equilibrium properties in this solid solution series should be sought for x=0.27.

1 Introduction

Interest in multiferroic materials has increased significantly over the years in view of their potential applications in sensors and recording media. BiFeO$_3$ is the only multiferroic compound that exhibits both magnetic and ferroelectric ordering well above the room temperature. The displacement of Bi^{3+} along the pseudocubic [111] direction from the centro-symmetric position permits high spontaneous polarisation and the magnetism is due to Fe^{3+}. Conventional ceramic synthesis of this compound invariably leads to the formation of several other thermodynamically stable non-perovskite phases near the sintering temperature [1]. Suitable chemical modifications can stabilize pure perovskite phase in BiFeO$_3$. Among them PbTiO$_3$ substitution imparts unique features: (i) inducing Morphotropic phase boundary (MPB) consisting of tetragonal and rhombohedral ferroelectric phase, (ii) high Curie point, and (iii) extremely large tetragonality [2-5]. However, so far there is no unanimity among the various research groups about the compositional range for the MPB state [2-9]. In this work we have resolved this issue by undertaking a systematic sintering temperature-time study on the reported MPB compositions of (1-x) BiFeO$_3$-(x) PbTiO$_3$. We found that for most of the

reported MPB compositions the rhombohedral phase is metastable in nature. The rhombohedral nuclei have finite life time which is very sensitive to slight changes in sintering temperature[10]. If the system is cooled before these nuclei vanish it would result in a MPB like state. Otherwise the equilibrium situation corresponds to the tetragonal state. A strong correlation between the structural integrity of the solid specimen and the phase formation behaviour was also found; formation of pure tetragonal phase invariably led to disintegration of the dense pellet. Our results show that the equilibrium MPB state corresponds to x=0.27. The structural and magnetic phase transition behaviour of this composition is reported in this paper.

2 Experimental

The solid solutions of (1-x) BiFeO$_3$-(x) PbTiO$_3$ were prepared by conventional solid state route. The powder X Ray Diffraction (XRD) at room temperature and high temperature were carried out in the PAN Anlaytic X Ray diffractometer using CuKα radiation with the wavelength of 1.5406Å. The neutron powder diffraction experiment was done in SPODI diffractometer at FRM II Germany [11]. The measurement was done with the neutron

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wavelength of 1.548Å in the niobium container from room temperature, 24°C to the high temperature 890°C. Rietveld refinement was carried out using FULLPROF program [12]. The Neel temperature of the sample was measured by Differential Scanning Calorimeter (METTLER-TOLEDO-DSC 822 e) with the heating rate of 5°C/min. The dielectric constant was measured using Novocontrol impedance analyzer (Alpha AN) in the temperature range 30-700°C during heating and cooling.

3 Results and Discussion

3.1 Identification of the equilibrium MPB composition

Fig. 1 shows the room temperature XRD patterns for x=0.35 and x=0.28. Both the compositions yielded pure tetragonal (P4mm) and also tetragonal + rhombohedral (R3c) phase mixture even when prepared under nearly similar conditions. The sample exhibiting pure P4mm was found to have disintegrated into powder whereas those exhibiting phase coexistence remained as pellets after sintering. For x=0.35 the volume fraction of rhombohedral phase was found to be ~5% (figure1b).
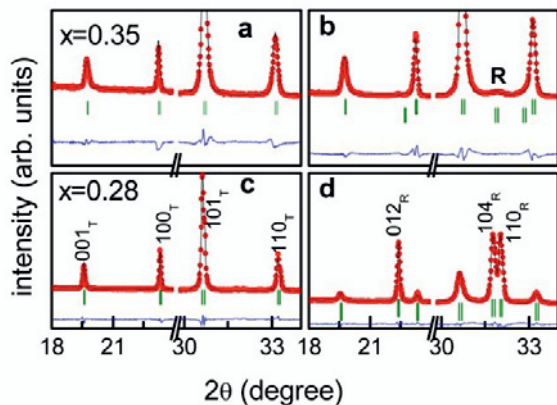

Fig . 1 Rietveld plot of X-ray powder diffraction pattern of (a) x=0.35 (T), (b) x=0.35 (R+T), (c) x=0.28 (T), (d) x=0.28 (R+T), where R- Rhombohedral and T- Tetragonal

This indicates that the R3c phase absorbs the stress induced in the system due to formation of tetragonal phases with very large tetragonality (c/a = 1.19) and prevents disintegration of the solid while cooling below the Curie point. To understand this seemingly unpredictable phase formation behaviour of the reported MPB compositions, phase formation behaviour was examined as a function of sintering temperature and time. Figure 2 shows the XRD pattern of x=0.27 sintered at 990°C for 2hr and 16hr. Both exhibit phase coexistence. Beyond 990°C the sample melted and stuck to the alumina plate and hence maximum temperature was limited to 990°C. For x=0.28, sample sintered at 980°C for two hour exhibits pure tetragonal phase. When the
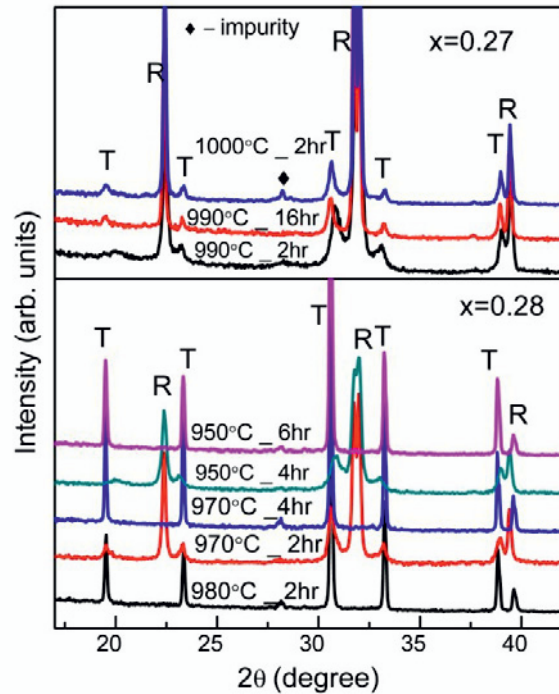

Fig. 2 X- ray powder diffraction of x=0.27 and x=0.28 sintered at different temperature – time combinations.R and T indicate Rhombohedral and Tetragonal peaks, respectively.

sintering temperature was decreased to 970°C and 950°C, it took 4 hr and 6 hr, respectively to form the pure tetragonal phase. For lesser sintering time at these temperatures both the phases coexist. In view of this, the stability of the two-phase nature (P4mm + R3c) even after 16 hours of sintering at 990°C suggests that for this composition both the phases are in equilibrium. x = 0.27 can therefore be considered as the genuine MPB state of this solid solution series.

3.2 Temperature induced structural and magnetic transformations in the MPB composition

The equilibrium MPB composition x=0.27 was chosen for detailed structural and magnetic phase transition study. In-situ high temperature XRD was performed in two rounds of heating-cooling cycles (figure 3). Before
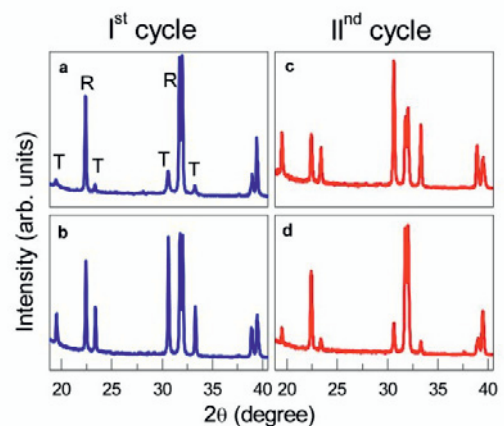

Fig.3 Room temperature XRD pattern of x=0.27 of the same sample at two heating cycles. 1st cycle (a) before heating (b) after heating, 2nd cycle (c) after 48hr ,of the first cycle (d) after heating upto 700°C and cooling to room temperature.

the first heating cycle the specimen shows 18% tetragonal phase and 82% rhombohedral phase (figure-3a) at room temperature. In the first heating cycle the sample was heated till 700°C and diffraction data was recorded at 10°C intervals. At each temperature it took about 50 minutes to collect the diffraction pattern. After reaching 700°C, the specimen was cooled at the rate of 20°C/min. The room temperature pattern after this first heating-cooling cycle appears different (figure3b) - the tetragonal fraction increased from 18% to 39%. When the diffraction pattern was recorded again at room temperature after a gap of 48 hours of the first heating-cooling cycle (figure-3c), the fraction of the tetragonal phase was found to be altered again - it increased from 39% to 57%. At this stage, the specimen was heated again up to 700°C (which is above the cubic transition temperature) and cooled. After this second cycle, the tetragonal phase fraction reverted back to 20%, close to its initial value (figure-3d). This experiment suggests that though the kinetics associated with the temperature induced transformation in x=0.27 is very sluggish, the system is able to recover its initial state.
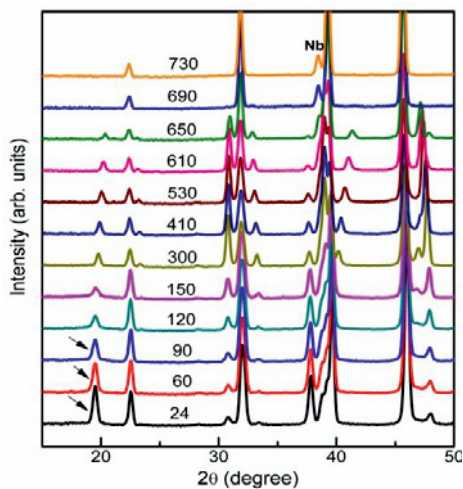

Fig.4 Temperature evolution of the neutron powder diffraction of x=0.27 in the range 24°C to 730°C. The arrows indicate the magnetic peak. Nb-container

Magnetic phase transition study of the equilibrium MPB composition x=0.27 was carried out using in-situ high temperature neutron powder diffraction (NPD) in the temperature range 24°C - 890°C. The NPD patterns in the two-theta range 15 -50 degree are shown in figure 4 for selected temperatures. Rietveld refinement was carried out by considering the rhombohedral and tetragonal phases. The sharp peak at 19.5 (shown by arrow in figure 4) could not be accounted by the nuclear Bragg reflections of rhombohedral and tetragonal phases. The magnetic peak merged with the nuclear peak of the tetragonal (001) reflection at this angle. As considered earlier for the pure rhombohedral composition, x=0.20 [8], the magnetic structural refinement of x=0.27 wascarried out using the collinear G-type antiferromagneticordering with the magnetic moments parallel to the c
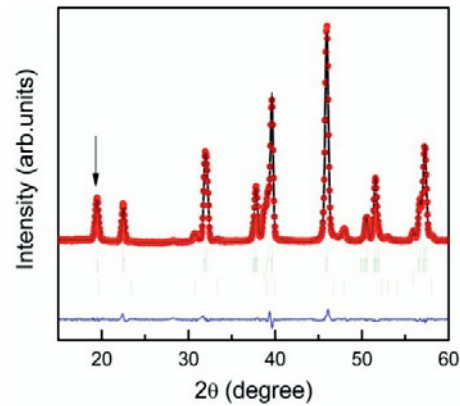

Fig. 5 Rietveld fitted neutron powder diffraction pattern of the x=0.27 at room temperature, arrow indicates the magnetic peak.
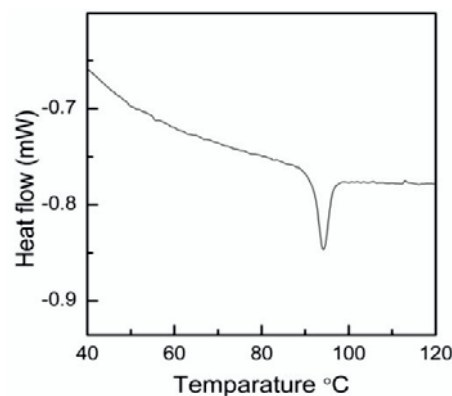

Fig. 6 Differential Scanning Calorimeter (DSC) profile of x=0.27

direction of the hexagonal unit cell. The Rietveld fitted room temperature NPD pattern with combined magnetic and nuclear phase model is shown in the figure 5. The magnetic peak disappears at 120°C showing the magnetic transition to lie somewhere between 90°C and 120°C.The exact magnetic transition temperature was determined by differential scanning calorimetric (DSC) measurement which shows a sharp exothermic peak at $T_N \sim 95°C$ (figure 6). The singlet of all the Bragg peaks above 650°C (figure 4) suggests the system has become cubic. Rietveld refinement was carried out for all the temperatures. The spontaneous tetragonal strain and the weight fraction are plotted in the figure 7. Interestingly, though the tetragonal phase does not exhibit magnetic ordering, a slight non-monotonic tetragonal strain variation can be noted near the T_N suggesting that the magneto-elastic strain associated with the R3c lattice couples to the lattice of the tetragonal phase. The spin-lattice coupling also manifested in terms of weak dielectric anomaly (figure 8a) near 100°C. It is interestingto note that the T_N value observed by us is significantly less as compared to those reported earlier (200°C) for the same composition [7].
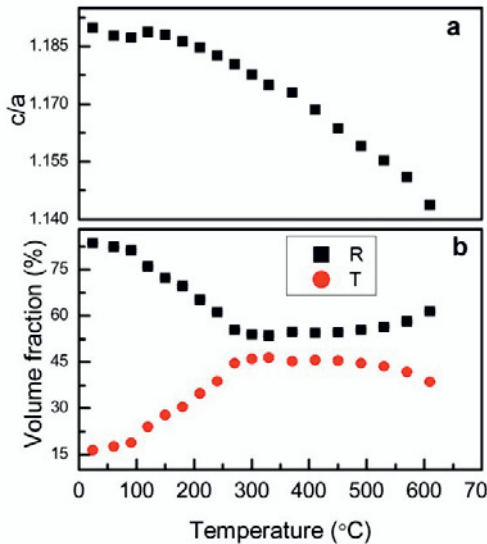
Fig. 7 Temperature variation of the (a) tetragonal strain, (b) volume fraction of R (rhombohedral) and T (tetragonal) phases, obtained from Rietveld refinement

This difference can be attributed to the difference in the synthesis conditions. Other groups have synthesized this composition at relatively lower temperatures (sintering temperature =900°C) than ours and have reported nearly pure rhombohedral phase. We feel that the presence of tetragonal phase in the lattice has effectively reduced the T_N, of the R3c phase.
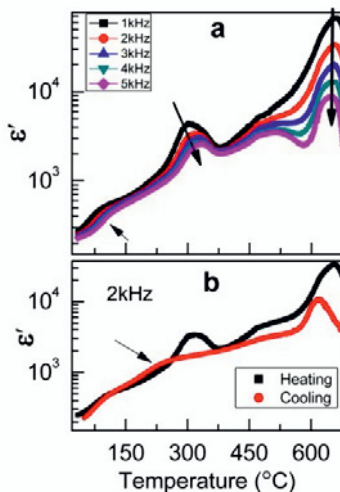

Fig.8 Temperature dependence of dielectric constant at (a) different frequencies (b) 2 kHz at heating and cooling

The volume fraction of the rhombohedral and tetragonal phases varies slightly till T_N. After 120°C the tetragonal fraction increases and the rhombohedral fraction decreases with both approaching ~50 % above 250°C. This state persists till 450°C. After 450°C the tetragonal fraction decreases and the rhombohedral fraction increases. Interestingly the relative permittivity exhibits weak relaxation peak around the same two temperatures in the heating cycle (figure 8a). In the cooling cycle these anomalies are not as pronounced (figure 8b). The

dielectric anomaly at 655°C (figure 8a) is due to the ferroelectric - paraelectric transitionand is in correspondence with the high temperature neutron powder diffractiondata.

4 Conclusion

A careful sintering time-temperature study of the reported MPB compositions of $BiFeO_3$-$PbTiO_3$ resolved the issue with regard to its erratic phase formation behaviour. For most of the reported MPB compositions, it was found that the R3c phase is of metastable nature. The life time of the R3c nuclei is highly sensitive to the chosen sintering temperature. If the specimen is cooled from its sintering temperature before the R3c nuclei have vanished, it would result in a MPB like state. The equilibrium MPB state was found for x=0.27. Structural and magnetic phase transition studies above room temperature carried out on this equilibrium MPB composition revealed that magnetic ordering occurs only in the R3c phase. The Neel temperature of the system was found to be ~95°C. The magnetic structure is commensurate G-type antiferromagnetic with magnetic moments parallel to the c-direction (of the hexagonal cell). The magneto-elastic coupling in the magnetically ordered R3c phase was also found to affect the lattice of the paramagnetic tetragonal phase.

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