

Synthesis of BiFeO₃ by carbonate precipitation

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Abstract. Magnetolectric multiferroic BiFeO₃ (BFO) was synthesized by a simple carbonate precipitation technique of metal nitrate solutions. X-ray powder diffraction and thermo-gravimetric analysis (TGA) revealed that the precipitate consists of an intimate mixture of crystalline bismuth carbonate and an amorphous hydroxide of iron. The precipitate yielded BiFeO₃ at an optimal calcination temperature of ~560°C. Energy dispersive X-ray (EDX) analysis showed 1:1 ratio between Bi and Fe in the oxide. X-ray photoelectron spectroscopy (XPS) studies confirmed that Fe to be in +3 oxidation states both in the precipitated powder and BiFeO₃. The synthesized BFO exhibits a very weak ferromagnetic correlation at room temperature and the degree of which increases slightly on cooling down to 10 K suggesting alteration in the long range spatial modulation of the spins arrangement as compared to the bulk BiFeO₃.

Keywords. BiFeO₃; carbonate precipitation technique.

1. Introduction

Interest in magnetolectric multiferroic materials has increased significantly over the years in view of their projected potential applications in sensors and recording media. BiFeO₃ (BFO) is the most interesting magnetolectric multiferroic compound and has attracted considerable attention because of its magnetic and ferroelectric ordering temperatures which are well above the room temperature. It possesses a rhombohedrally distorted perovskite structure with lattice parameters $a_r = 5.56 \text{ \AA}$ and $\alpha = 59.35^\circ$ (hexagonal parameters $a_{\text{hex}} = 5.59 \text{ \AA}$ and $c_{\text{hex}} = 13.869 \text{ \AA}$) and belongs to the space group $R3c$ (Bucci *et al* 1972). Its ferroelectric Curie temperature is 810°C and acquires a long range spatially modulated canted G-type antiferromagnetic structure below 370°C (Michel *et al* 1969; Fischer *et al* 1980). As a result of the long range modulation, bulk BFO does not exhibit ferromagnetic correlation. Interest in this compound grew significantly after the discovery of very large value of spontaneous polarization in epitaxially strained thin films (Wang *et al* 2005).

Unlike for the majority of the oxide perovskites, conventional ceramic synthesis approach of mixing and heating the oxides of Bi and Fe in stoichiometric ratio does not yield a single phase BiFeO₃. This is because, under equilibrium sintering conditions, phases such as Bi₂Fe₄O₉, Bi₂₅FeO₃₉ and Bi₄₆Fe₂O₇₂ are prone to form in significantly large fraction as compared to the desired BFO phase (Speranskaya *et al* 1965). These phases have detrimental effect on the overall insulating property of the ceramic body, resulting in high leakage current and deterioration in the ferroelectric proper-

ties. Hence several special synthesis methods were developed over the years to get single phase BFO such as solid state method (Mahesh Kumar *et al* 2000; Valant *et al* 2007), rapid sintering method (Wang *et al* 2004), hydrothermal synthesis (Chen *et al* 2006; Wang *et al* 2007), solgel method (Wei and Xue 2008; Xu *et al* 2009), combustion (Fruth *et al* 2007; Paraschiv *et al* 2008), solution evaporation route (Ghosh *et al* 2005) and wet chemical method (Fruth *et al* 2007; Selbach *et al* 2007). In the present paper, we report the synthesis of bismuth ferrite by carbonate co-precipitation method of nitrate solution of stoichiometric Bi and Fe metal cations.

2. Experimental

Bismuth ferrite powder was synthesized by precipitation using metal nitrates as precursors. Equimolar Bi(NO₃)₃·5H₂O and Fe(NO₃)₃·9H₂O were dissolved in distilled water. Saturated solution of ammonium carbonate was separately prepared and added to the beaker containing the nitrate solution which was continuously stirred with a magnetic stirrer. The precipitate named as BFC was filtered, thoroughly washed with deionised water and dried. For the sake of comparison Bi(NO₃)₃·5H₂O and Fe(NO₃)₃·9H₂O were precipitated separately by ammonium carbonate. These precipitates were named as BC and FC, respectively. Thermogravimetric analysis (TGA) of the precipitates was performed in air at the rate of 5°C min⁻¹. Phase identification was carried out by X-ray powder diffraction using a PANalytic diffractometer with Cu-K α radiation. Rietveld analysis of the X-ray diffraction patterns was carried out using Fullprof Program (Rodrigues-Carvajal). Scanning electron microscopy (SEM) (Quanta) was used to characterize the phase composition and microstructure of the BFO.

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Magnetization measurement was carried out using SQUID (MPMS XL-5 Quantum Design).

3. Results and discussion

Figure 1 shows the X-ray powder diffraction patterns of BFC, BC and FC precipitates. It is evident from this figure that the patterns of BFC and BC are identical. This pattern was found to match with the standard X-ray powder diffraction pattern of orthorhombic Bi_2CO_5 (Greaves and Blower 1988). The orthorhombic lattice parameters of BC and BFC were obtained by least squares refinement of the prominent Bragg peak positions. The lattice parameters and unit cell volume of BC were obtained as $a = 5.4516(2) \text{ \AA}$, $b = 27.254(1) \text{ \AA}$, $c = 5.4680(3) \text{ \AA}$ and $v = 815.60(9) \text{ \AA}^3$; for BFC the corresponding values were obtained as $5.4621(7) \text{ \AA}$, $27.352(2) \text{ \AA}$, $5.4591(4) \text{ \AA}$ and $v = 812.42(5) \text{ \AA}^3$, respectively. The slightly smaller cell volume of BFC can be attributed to partial replacement of bigger-sized Bi^{+3} (Shannon radius = 1.17 \AA) ions by smaller-sized Fe^{+3} ions (Shannon radius 0.78 \AA) in the structure. The shrinkage in cell volume is, however, only 0.4%, which is very insignificant because of the radius of Fe^{+3} is $\sim 22\%$ smaller than that of Bi^{+3} . Even if it is assumed that a significant fraction of Fe to be in a +2 state, ($r(\text{Fe}^{2+}) = 0.92 \text{ \AA}$), the ionic size difference between Fe^{+2} and Bi^{+3} is still considerably large and hence Fe occupying Bi sites in the Bi_2CO_5 structure should have led to considerable large reduction in the cell volume. From the above,

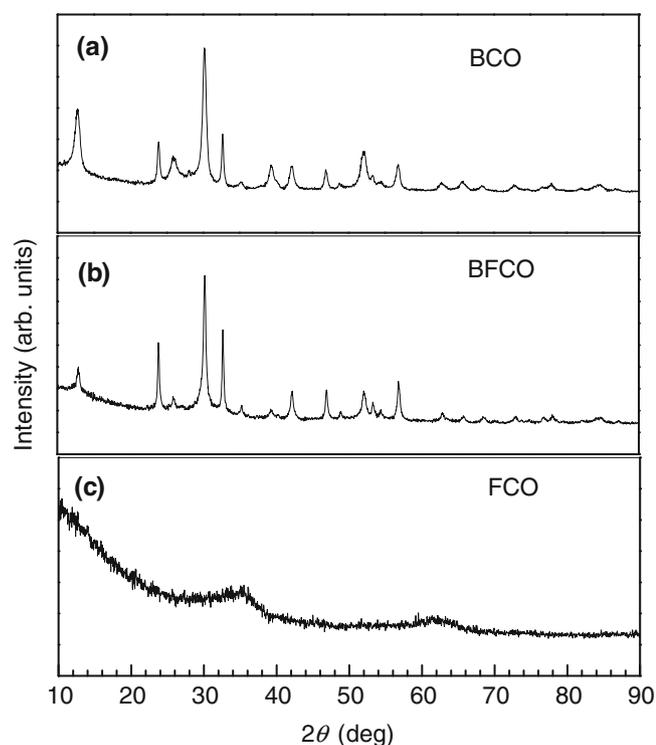


Figure 1. X-ray powder diffraction patterns of precipitated powders of (a) BC, (b) BFC and (c) FC.

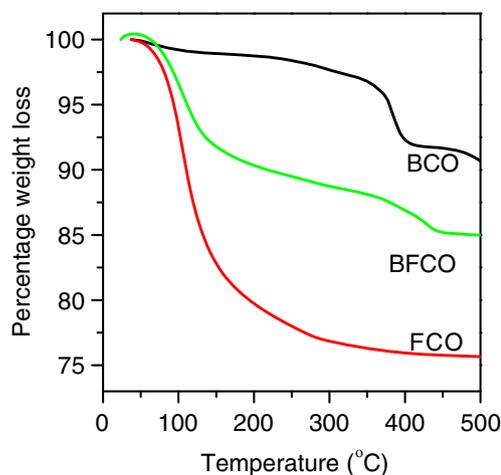


Figure 2. Thermogravimetric graph of decomposition of the precipitated powders of BC, BFC, and FC.

it is obvious that only a very insignificant fraction, if any, of the total Fe ions in the starting solution have entered the Bi_2CO_5 matrix. Therefore, a question arises regarding the fate of the remaining Fe-ions of the nitrate solution during precipitation by ammonium carbonate. To resolve this issue, a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was precipitated separately (FC) and X-ray powder diffraction pattern recorded (figure 1c). It is obvious from the pattern that the precipitate FC is amorphous in nature. The BFC precipitate is therefore a mixture of crystalline Bi_2CO_5 and an amorphous matrix containing Fe^{3+} ions. As shown latter X-ray photoelectron spectroscopy study revealed that Fe exists in +3 oxidation state in the BFC precipitate. This implies that the amorphous phase is formed by a complex of Fe^{3+} network. A perusal of literature suggests that in strong alkaline medium, Fe in +3 oxidation state can form amorphous ferric oxyhydroxide $\text{FeO}_x(\text{OH})_{3-2x}$ (Misawa *et al* 1974). It was also reported that, left to itself, this compound gradually age at room temperature to yield a crystalline FeOOH . We also found that the weight of FC precipitate continuously decreased when the powder was dried under a table lamp (temperature $\sim 60\text{--}80^\circ\text{C}$). This similarity with the reported result (Misawa *et al* 1974) suggests that Fe-ions present in the nitrate solution are precipitated as ferric oxyhydroxide and not as carbonate.

Figure 2 shows the TGA curves of the precipitated powders BC, BFC and FC. On heating FC shows a continuous increase in the weight loss from the room temperature onwards. This is consistent with the reported aging behaviour of amorphous ferric oxyhydroxide (Misawa *et al* 1974). However, since the temperature is continuously increased in the TGA experiment, the decomposition product is not expected to be FeOOH , but an oxide of iron. The TGA of FC suggests that the decomposition of FC is complete at $\sim 300^\circ\text{C}$. X-ray powder diffraction of the decomposed FC precipitate revealed that the oxide formed after decomposition to be Fe_2O_3 (figure 3). It may be remarked that the weight loss measured until decomposition of FC in TGA

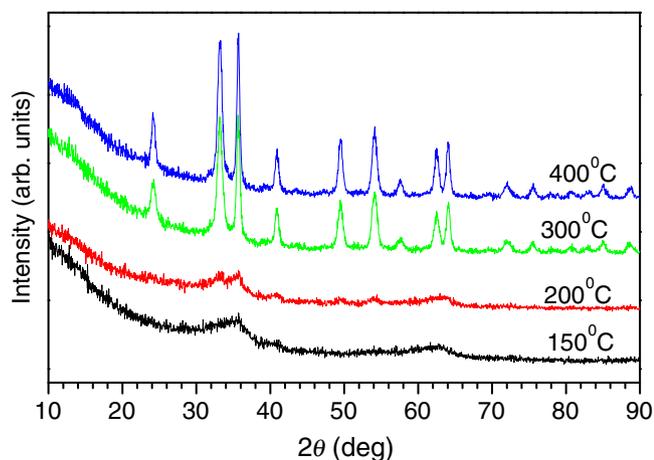


Figure 3. X-ray powder diffraction patterns of FC calcined at different temperatures for 1 h.

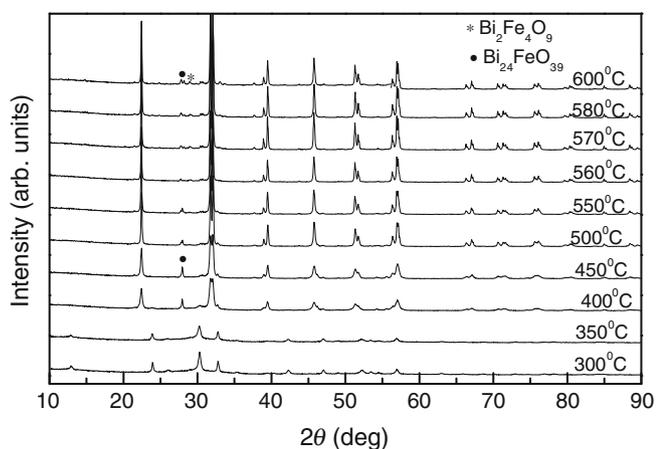


Figure 4. X-ray powder diffraction patterns of BFC calcined at different temperatures for 1 h.

experiments would vary from sample to sample because of the continuous loss (aging) taking place even at the room temperature. It is therefore not possible to correlate the weight loss observed in the TGA experiment with any specific decomposition reaction. The same argument holds true for the BFC precipitate since it contains FC as a separate phase. In contrast to FC and BFC, the TGA of the BC precipitate suggests that it is stable until $\sim 350^\circ\text{C}$. Complete decomposition occurs in the temperature range $350\text{--}400^\circ\text{C}$, and the weight loss after decomposition is $\sim 9\%$ which is in good agreement with the decomposition reaction: $\text{Bi}_2\text{CO}_3 \rightarrow \text{Bi}_2\text{O}_3 + \text{CO}_2$. As expected, the TGA plot of BFC shows features of both BC and FC. This analysis suggests that nascent oxides of bismuth and iron are available for reaction to form bismuth ferrite at temperature as low as $350\text{--}400^\circ\text{C}$.

The phase formation behaviour on heating the BFC precipitate in air was investigated by calcining the precipitate powders at different temperatures for 1 h at close temperature intervals. Figure 4 shows the X-ray powder diffraction

patterns of the calcined powders in the temperature interval of $300\text{--}620^\circ\text{C}$. As per the TGA results discussed above, at 350°C the powder should consist Bi_2CO_3 and Fe_2O_3 . The diffraction pattern of the BFC powder calcined at 350°C , however, shows predominantly Bragg peaks corresponding to the Bi_2CO_3 phase though both are present in equimolar ratio in the powder. This can be attributed to the large difference in the magnitude of the structure factors of Bi_2CO_3 and Fe_2O_3 phases. Since Bi_2CO_3 decomposes in the temperature range $350\text{--}400^\circ\text{C}$, the nascent Bi_2O_3 formed soon after decomposition would be highly reactive and would react with the readily available Fe_2O_3 in its surrounding to form BiFeO_3 . The diffraction pattern of the powder calcined at 400°C shows the formation of BiFeO_3 phase. However, a weak reflection at $2\theta = 27.9^\circ$ corresponding to an undesired phase of $\text{Bi}_{24}\text{FeO}_{39}$ was also noticed in the pattern of the powder calcined at 400°C . The formation of this phase could be attributed to local kinetic constraints associated with the low temperature reaction. The intensity of this impurity peak was found to decrease as the calcination temperature was gradually raised above 400°C . For the powder calcined at 560°C , the diffraction pattern is nearly free from $\text{Bi}_{24}\text{FeO}_{39}$ phase. Interestingly, however, the intensity of this impurity peak starts increasing when the calcination temperature is raised above 570°C . For the pattern corresponding to 620°C , other impurity peaks corresponding to another phase $\text{Bi}_2\text{Fe}_4\text{O}_9$ become visible. The intensity of these peaks increase significantly on further increase of the calcination temperature. This reveals that the optimum calcination temperature for obtaining nearly impurity free BiFeO_3 powder lies in the narrow temperature range of $550\text{--}570^\circ\text{C}$. As mentioned in § 1, it is a well known fact that these impurity peaks dominate the diffraction pattern when attempt is made to synthesise BiFeO_3 by conventional ceramic synthesis route of oxides of bismuth and iron at $\sim 800^\circ\text{C}$. Since in the conventional ceramic synthesis method, there is a necessity to keep the reaction temperature reasonably high so as to allow the reacting species to diffuse over a relatively large distance, one cannot avoid the impurity phases such as $\text{Bi}_{24}\text{FeO}_{39}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$ as they are thermodynamically stable phases at such high temperatures. In the present study, since the reaction leading to the formation of BiFeO_3 was made possible at 400°C , the formation of stable impurity phases was avoided to a significantly large extent. Rietveld analysis was carried out for the diffraction pattern corresponding to the powder calcined at 560°C . The refined lattice parameter was obtained as $a = 5.580 \text{ \AA}$ and $c = 13.8723 \text{ \AA}$, which matches very well with the values reported in the literature ($a = 5.59 \text{ \AA}$ and $c = 13.869 \text{ \AA}$) (Bucci *et al* 1972). The corresponding Rietveld plot is shown in figure 5.

Figure 6 shows the X-ray photoelectron spectroscopy (XPS) of the core level of Fe-2p orbitals for the BFC precipitate and also for BiFeO_3 obtained after calcination at 560°C . The Fe- $2p_{3/2}$ and Fe- $2p_{1/2}$ peaks are seen at ~ 711 and 725 eV , respectively. It is known that the satellite peak of the Fe- $2p_{3/2}$ appears at $\sim 8 \text{ eV}$ and $\sim 6 \text{ eV}$ higher in binding energy for +3 and +2 oxidation states of Fe, respectively

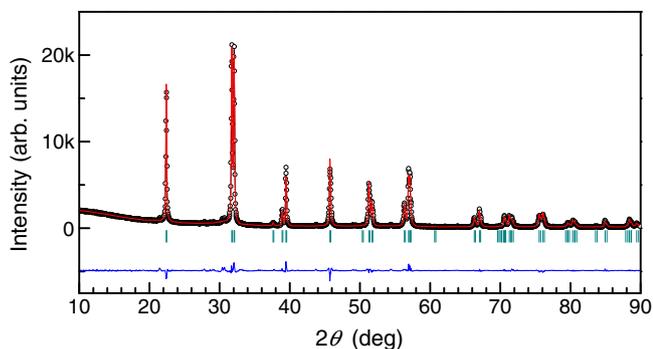


Figure 5. Rietveld plot of X-ray powder diffraction pattern of BiFeO_3 obtained after calcination at 560°C . Refinement was carried out using rhombohedral ($R3c$) structure.

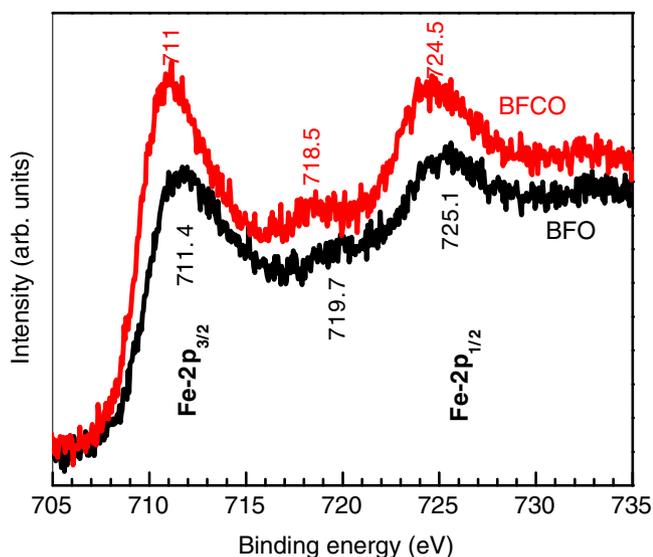


Figure 6. X-ray photoelectron spectra of core level Fe-2p in the BFC precipitate and BiFeO_3 .

(Wandelt 1982). The occurrence of the Fe-2p_{3/2} satellite peak at ~ 719 eV for both the specimens suggests that Fe exists in +3 oxidation state in BFC and BiFeO_3 precipitates. As discussed above, the precipitate consists of crystalline Bi_2CO_5 and iron ions in a separate amorphous matrix; the contribution to the XPS signal in figure 6 comes from the amorphous phase of the precipitate. The +3 oxidation state of Fe in the amorphous matrix is consistent with the proposition of ferric-oxyhydroxide $\text{FeO}_x(\text{OH})_{3-2x}$ for the amorphous phase discussed above.

Figure 7 shows the SEM image of the BFO powder calcined at 560°C . It is evident from this figure that the grains are uniform in shape and size. The average grain size is ~ 300 nm. EDX analysis was also carried out on this specimen and the Bi : Fe ratio was found to be close to 1:1 confirming the powder to be chemically homogeneous.

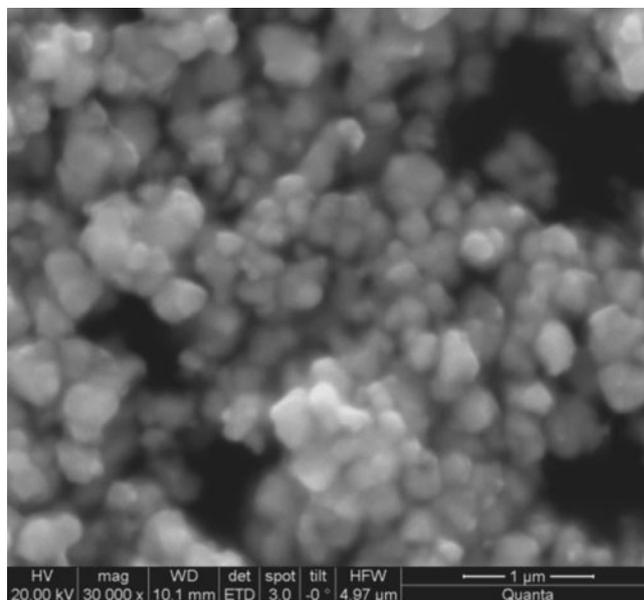


Figure 7. SEM micrograph of the BiFeO_3 powder calcined at 560°C .

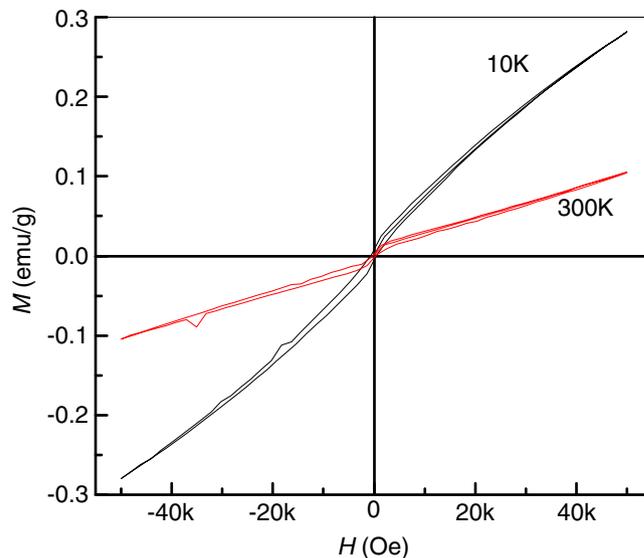


Figure 8. Magnetization vs magnetic field of BiFeO_3 at 300 and 10 K.

Figure 8 shows the magnetic hysteresis curve of 560°C calcined powder at 300 and 10 K. The hysteresis curve shows a very weak ferromagnetic correlation at room temperature with a coercive field of ~ 390 Oe and remanent magnetization of 0.003 emu/gm. On cooling down to 10 K, the coercive field and the remanent magnetization increase to 780 Oe and 0.008 emu/g, respectively. Since it is known that bulk BFO does not exhibit ferromagnetic correlation because of the long range modulation of the canted spin structure, the onset of a weak ferromagnetic correlation in our specimen suggests that the spatial modulation of the spin structure is altered with respect to its bulk counterpart.

4. Conclusions

In this paper, it is shown that using a simple and convenient precipitation of stoichiometric nitrate solution of bismuth and iron by ammonium carbonate, is possible to obtain a single phase BiFeO₃ at ~560°C, which is well below the temperature of ~800°C and used to synthesize this material by conventional ceramic synthesis method. Detailed examination of the precipitate revealed that it consists of bismuth crystalline carbonate and amorphous ferric oxyhydroxide. Though the Fe and Bi did not precipitate in one single matrix phase, the reaction temperature leading to the formation of BiFeO₃ could be lowered, and the formation of the thermodynamically stable impurity phases thereby controlled, due to the availability of highly reactive nascent Bi₂O₃ and Fe₂O₃ during the decomposition of the precipitate at such low temperatures. The BiFeO₃ thus formed exhibits a weak ferromagnetic correlation suggesting that the long range spatial modulation of the canted spin structure is altered, presumably due to reduced particle size.

References

- Bucci J D, Robertson B K and James W J 1972 *J. Appl. Cryst.* **5** 187
Chen C, Cheng J, Yu S, Che L and Meng Z 2006 *J. Cryst. Growth* **291** 135
Fischer P, Połomska M, Sosnowska I and Szymański M 1980 *J. Phys. C: Solid. State Phys.* **13** 1931
Fruth V, Mitoseriu L, Berger D, Ianculescu A, Matei C, Preda S and Zaharescu M 2007 *Prog. Solid State Chem.* **35** 193
Fruth V, Tenea E, Gartner M, Anastasescu M, Berger D, Ramer R and Zaharescu M 2007 *J. Eur. Ceram. Soc.* **27** 937
Ghosh S, Dasgupta S, Sen A and Maiti H S 2005 *Mater. Res. Bull.* **40** 2073
Greaves C and Blower S K 1988 *Mater. Res. Bull.* **23** 1001
Mahesh Kumar M, Palkar V R, Srinivas K and Suryanarayana S V 2000 *Appl. Phys. Lett.* **76** 2764
Michel C, Moreau J M, Achenbechi G D, Gerson R and James W J 1969 *Solid State Commun.* **7** 701
Misawa T, Hashimoto K and Shimodaira S 1974 *Corros. Sci.* **14** 131
Paraschiv C, Jurca B, Ianculescu A and Carp O 2008 *J. Therm. Anal. Cal.* **94** 411
Rodrigues-Carvajal J *FULLPROF. A Rietveld refinement and pattern matching analysis program*. Laboratoire Leon Brillouin (CEA-CNRS), France
Selbach S M, Einarsrud M A, Tybell T and Grande T 2007 *J. Am. Ceram. Soc.* **90** 3430
Speranskaya E I, Skorikov V M, Rode E Y and Terekhova V A 1965 *Bull. Acad. Sci. USSR Div. Chem. Sci.* **5** 873 (English Translation)
Valant M, Axelsson A K and Alford N 2007 *Chem. Mater.* **19** 5431
Wandelt K 1982 *Surf. Sci. Rep.* **2** 1
Wang J *et al* 2005 *Science* **307** 1
Wang Y, Xu G, Ren Z, Wei X, Weng W, Du P, Ge Shen and Han G 2007 *J. Am. Ceram. Soc.* **90** 2615
Wang Y P, Zhou L, Zhang M F, Chen X Y, Liu J M and Liu Z G 2004 *Appl. Phys. Lett.* **84** 1731
Wei J and Xue D 2008 *Mater. Res. Bull.* **43** 3368
Xu J-H, Ke H, Jia D C, Wang W and Zhou Y 2009 *J. Alloy Compd.* **472** 473