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CRYSTALLOGRAPHIC AND MAGNETIC IDENTIFICATION OF SECONDARY PHASE IN ORIENTATED $\text{Bi}_5\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_3\text{O}_{15}$ CERAMICS

Meghdad Palizdar¹, Tim P. Comyn¹, Mike B. Ward¹, Andrew P. Brown¹, John Harington¹, Santosh Kulkarni², Lynette Keeney², Saibal Roy², Martyn Pemble², Roger Whatmore², Christopher Quinne³, Susan H. Kilcoyne³, Andrew J. Bell¹

1- Institute for Materials Research, SPEME, University of Leeds LS2 9JT, Leeds, UK

2- Tyndall National Institute, University College Cork, Cork, Ireland

3- Institute for Materials Research, University of Salford, Salford, UK

Email: ml07m2p@leeds.ac.uk

Abstract— Oxide materials which exhibit both ferroelectricity and ferromagnetism are of great interest for sensors and memory applications. Layered bismuth titanates with an Aurivillius structure, $(\text{BiFeO}_3)_n\text{Bi}_4\text{Ti}_3\text{O}_{12}$, can possess ferroelectric and ferromagnetic order parameters simultaneously. It has recently been demonstrated that one such example, $\text{Bi}_5\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_3\text{O}_{15}$, where $n = 1$ with half the Fe^{3+} sites substituted by Co^{3+} ions, exhibits both ferroelectric and ferromagnetic properties at room temperature. Here we report the fabrication of highly-oriented polycrystalline ceramics of this material, prepared via molten salt synthesis and uniaxial pressing of high aspect ratio platelets. Electron backscatter images showed that there is a secondary phase within the ceramic matrix which is rich in cobalt and iron, hence this secondary phase could contribute in the main phase ferromagnetic property. The concentration of the secondary phase obtained from secondary electron microscopy is estimated at less than 2.5 %, below the detection limit of XRD. TEM was used to identify the crystallographic structure of the secondary phase, which was shown to be cobalt ferrite, CoFe_2O_4 . It is inferred from the data that the resultant ferromagnetic response identified using VSM measurements was due to the presence of the minor secondary phase. The Remanent magnetization at room temperature was $M_r \approx 76$ memu/g which dropped down to almost zero ($M_r \approx 0.8$ memu/g) at 460 °C, far lower than the anticipated for CoFe_2O_4 .

Keywords-component; multiferroic, texture, microstructure

I. INTRODUCTION

Aurivillius compounds, with the general formula $A_{m+1}\text{Bi}_2\text{B}_m\text{O}_{3m+3}$, have a layered perovskite-like structure where the 12-coordinated A site can be occupied by such cations such as Bi^{+3} , Ba^{+2} , Sr^{+2} etc. while Fe^{+3} , Ti^{+4} , Na^{+5} occupy the octahedral coordinated B site. Each perovskite layer

$([A_{m+1}\text{B}_m\text{O}_{3m+3}]^{2-})$ is sandwiched between two $(\text{Bi}_2\text{O}_2)^{2+}$ layers [1]. Ismailzade reported $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$, $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ and $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$ structures, prepared from 1 mole $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and n mole BiFeO_3 which resulted in $(\text{BiFeO}_3)_n\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [2]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has a crystal structure consisting of layered perovskite compounds which possess a high ferroelectric Curie temperature. It changes from a tetragonal structure at high temperatures to a ferroelectric phase on cooling through a temperature of $\sim 675^\circ\text{C}$ [3].

BiFeO_3 is a well known lead-free material possessing both ferroelectric and antiferromagnetic properties at room temperature. The electric ordering (spontaneous polarization) is due to bismuth on the A-site and the magnetic properties (antiferromagnetism) are due to the iron on the B-site [4].

Increasing the texture in materials could improve both the ferroelectric and the ferromagnetic properties. This improvement may be due to either increasing poling efficiency (due to easier alignment of electric dipoles with the applied electric field) [5] or by utilizing the inherent anisotropy [6] which is induced via texture methods such as die pressing, hot forging and templated grain growth. Rango et al reported an improvement of a factor of 2 of the remanent magnetization of $\text{YBa}_2\text{Cu}_3\text{O}_7$, using a magnetic field to induce texture during preparation, whilst the sample was in solution. [7]. Also Ma et al showed the positive effect of texture on Nd-Fe-B magnets [8].

Sabolsky et al showed how texture could affect the piezoelectric properties of $0.675\text{PbMgO}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – 0.325PbTiO_3 ceramics. With an increase in texture, the d_{33} piezoelectric coefficient increased to 1.2-1.5 times greater than that of randomly oriented samples [9].

$(\text{BiFeO}_3)_n\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compounds have been reported to show ferroelectricity and simultaneous weak magnetic ordering [10]. Mao et al recently reported $\text{Bi}_5\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_3\text{O}_{15}$ (BFCT), in which half the Fe^{3+} sites have been replaced by Co^{3+} ions, shows simultaneous ferroelectric and ferromagnetic ordering at room temperature [11]. In our previous work, we identified existence of a magnetic secondary [12]. In this present work, X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM) have been employed to identify and investigate the type of secondary phase formed in BFCT prepared by a molten salt method.

II. EXPERIMENTAL

The molten salt method was employed to synthesize platelets of $\text{Bi}_5\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_3\text{O}_{15}$ (BFCT). Comparing the molten salt method with a solid state reaction reveals that the sintering time and temperature is lower in the molten salt method, due to the much higher rate of diffusion [13]. The constituent oxide powders, Bi_2O_3 , TiO_2 , Fe_2O_3 and Co_2O_3 (purity, 99.9%, Aldrich, Germany) were mixed (in the stoichiometric quantities required to produce $\text{Bi}_5\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_3\text{O}_{15}$) by ball milling with zirconia balls in iso-propanol for 24 hours. After drying, the powders were sieved and mixed with an equal weight of 1:1 mole ratio $\text{NaCl}:\text{KCl}$ with an agate pestle and mortar and then placed into an alumina crucible. The crucible and charge were then heated to 1000°C , soaked for 1 h, then cooled to room temperature. The products were crushed and washed with hot deionized water to remove the salts from the mixture. Also pellets were made from the powders using die and iso-pressing. The pellets were sintered at 1000°C for 1 hour. [12] Note that die pressing alone was used to impart crystallographic texture.

X-ray diffraction (XRD) and VSM measurements were used to investigate the crystallographic and magnetic properties of BFCT. The VSM used allowed measurements in the temperature range of -223°C up to 727°C , generating an applied magnetic field of $-30,000$ up to $30,000$ Oersteds using a helium compressed cryogenic magnet system. In addition, for crystallographic identification of the secondary phase present, TEM selected area electron diffraction patterns were obtained on a FEI Tecnai TF20 field emission gun-TEM operated at 200 keV, fitted with a Gatan SC600 digital camera and an Oxford Instruments 80mm^2 X-Max SDD EDX detector.

Thin sections were prepared for TEM using a Focused Ion Beam (FIB) microscope (FEI Nova 200 NanoLab, high resolution FEGSEM with Ga Ion Beam).

III. RESULTS

a) Powders

Fig.1 shows the morphology of BFCT crystallites prepared in molten salt at 1000°C for 1h, and subsequently drop cast onto an aluminium substrate for imaging. The powder has a platelet form with a large aspect ratio and range of platelet sizes, with average thickness $\sim 0.2\ \mu\text{m}$, and lateral width $5\text{-}20\ \mu\text{m}$.

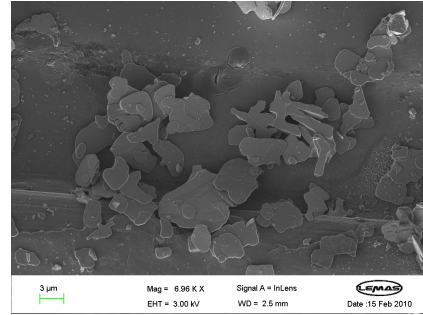


Fig.1. Scanning electron microscope (SEM) image of $\text{Bi}_5\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_3\text{O}_{15}$ powders, prepared at 1000°C for 1h., via the molten salt method.

Figures 2(a) and (b) show X-ray diffraction (XRD) patterns of BFCT powders, produced using the two preparation methods; molten salt and solid state reaction (conventional method), respectively. Samples were prepared for XRD by top loading a conventional aluminium sample holder. Note that no attempt was made to orient the materials. Clearly, using the molten salt method, BFCT is highly oriented along the (002) direction (Fig.2 (a)). Using conventional mixed oxide synthesis, where the stoichiometric powder mixture was sintered at 640°C for 8 h, results in a randomly oriented BFCT, which compared well with patterns in the literature [11],(Fig. 2(b)). The product obtained from the molten salt method differs significantly from BFCT prepared using conventional mixed oxide synthesis [11].

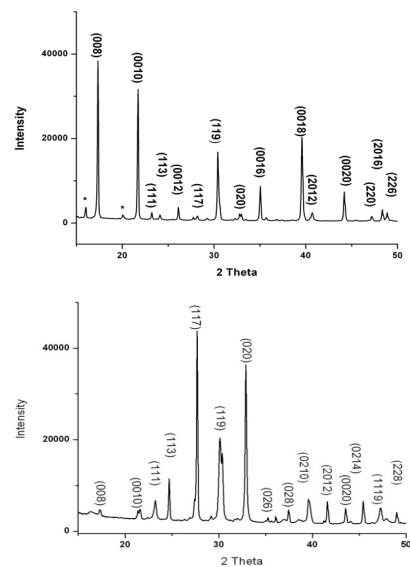


Fig.2. X-ray diffraction patterns for BFCT (a) prepared from the molten salt method at 1000°C for 1h and (b) made from conventional sintering at 640°C for 8 h.

In the XRD pattern obtained from the conventional sintering method, the intensity of the [00l] peaks, with $l = 8, 10, 12, \dots$, is lower than powders prepared via molten salt synthesis, and (117) is the most intense (Figure 2). This

decrease shows that the molten salt method produces a material highly textured along the c axis.

b) Pellets

Fig. 3 shows XRD pole figures for the BFCT pellet ceramic which is made from the molten salt method, for (008) and (117) reflections. The source and detector were positioned at a fixed 2θ Bragg angle to reflect from the BFCT (008) and (117) planes, and the samples rotated about 360° , and tilted from 0 to 85° . Figure 3-a shows the (008) peak which is clearly orientated normal to the sample surface; conversely (Fig. 3-b) the (117) reflection, which is the most intense in a conventional polycrystal, has low intensity normal to the surface, and reaches a maximum at ca. 30° to the surface normal.

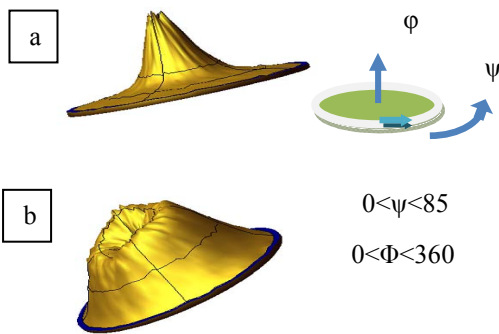


Fig. 3. XRD pole figures for BFCT pellets made from powders produced by the molten salt method at 1000°C for 1h; a) (008) peak and b) (117) peak

c) Identification of the secondary phase

In previous work it was shown from SEM electron backscatter (EBS) imaging of a BFCT pellet, that an unidentified secondary phase was present in BFCT, which accounted for approximately 2.5% by area [13]. To clarify exactly what the secondary phase was, TEM in conjunction with electron diffraction was used.

Fig. 4 shows the different stages required for preparing the TEM sample. FIB systems use a finely focused ion beam, (in this case a 30 keV Ga ion source), for site specific sputtering or milling [14]. The target area was chosen in a way to section both the main phase and the secondary phase. The darker area in the SEM image identifies the secondary phase.

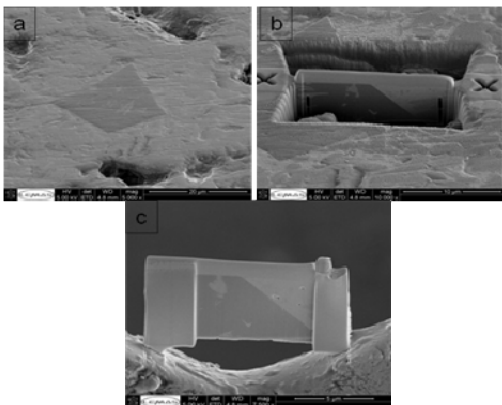


Fig. 4-a, b. FIB sectioning of the BFCT around the secondary (dark) phase, a) before and b) after FIB milling. Fig.4-c, FIB milled thin section of BFCT after lift out and mounting on TEM grid

Fig. 5 shows the TEM electron diffraction pattern of the secondary phase. The pattern matches with ICSD file 00-022-1086, for cobalt ferrite, which is cubic with $a = 8.3919 \text{ \AA}$. XRD was unable to identify the secondary phase, presumably due to (a) the low concentration and (b) the interaction of the x-rays with the light CoFe_2O_4 phase in a heavy Bi-based matrix was relatively weak. The electron diffraction pattern clearly demonstrates that cobalt ferrite has been generated during the molten salt method for the production of BFCT. EDX results were in agreement with TEM diffraction data. CoFe_2O_4 , in the form of a bulk powder, is a ferromagnetic material with a ferromagnetic Curie temperature around 520°C [15].

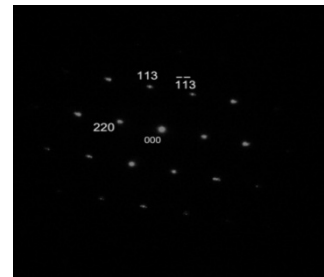


Fig. 5. TEM electron diffraction pattern from the secondary phase, which is formed during the preparation of BFCT from the molten salt method. The pattern can be indexed to CoFe_2O_4 viewed down the $[1\ -1\ 0]$ zone axis.

The magnetic properties of cobalt ferrite strongly depend on the cobalt content, particle size and particle shape [16-18]. CoFe_2O_4 can have remanent magnetization values between 25 and 60 emu/g (depending on crystallite size and calcination temperature) [19] and can reach up to 120 emu/cm^3 for CoFe_2O_4 thin films. [20] Hence, this secondary phase could be the dominant magnetic phase with limited contribution from main BFCT phase. Therefore it is important to differentiate the magnetic contributions of the main and secondary phase. Depending on the grain size, a Curie temperature range of between 520°C and 557°C has been identified for CoFe_2O_4 . [15, 20-22]. Mao et al [11] reported a ferromagnetic Curie temperature of 345°C for BFCT, far lower than that of CoFe_2O_4 . Consequently, by investigating the Curie temperature of BFCT prepared in this study, it may be possible to identify the influence of the CoFe_2O_4 secondary phase on the magnetic properties. Fig 6 shows the magnetic hysteresis loops for BFCT at a range of temperatures.

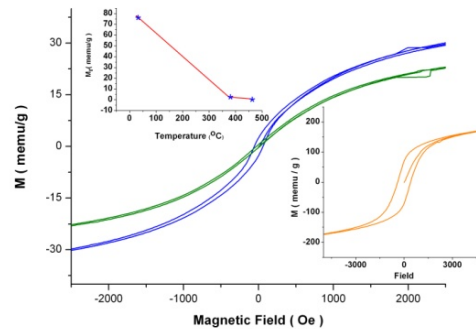


Fig. 6 .VSM hysteresis loops over a range of temperatures for BFCT, made from the molten salt method at 1000 °C for 1 h, The ceramic has magnetization above the 345 °C Curie temperature of BFCT

The magnetisation measurements show a remanent magnetization of 75 memu/g at room temperature, which drops to 0.8 memu/g at 460 °C. Clearly, this is not in keeping with the reported magnetic Curie temperature for CoFe_2O_4 of between 520 °C and 557 °C. We anticipate, however, that the CoFe_2O_4 phase does contribute to the bulk of the magnetic response at room temperature from a simple product of the concentration (2.5%) and the reported magnetisation (25 emu/g for CoFe_2O_4 at room temperature) for the secondary phase; clearly, then, the T_c has shifted significantly.

Having demonstrated the strong influence on the ferromagnetic properties of the current BFCT, different sintering temperatures were employed during the preparation to minimise or eliminate the formation of this phase (for more information see [12]). However, further investigation by electron backscattered diffraction or electron backscattered imaging reveals that the cobalt and iron rich secondary phase still exists at all sintering temperatures, showing that the conjunction of sintering temperature modification, and using additions of excess Bi_2O_3 is an insufficient solution.

IV. CONCLUSION

BFCT which is strongly textured along the (002) direction has been produced. However ca. 2.5% by area of a CoFe_2O_4 secondary phase was identified using electron backscattered imaging in the SEM. TEM electron diffraction and VSM measurement suggest that the secondary phase is CoFe_2O_4 . This ferromagnetic phase most likely dominates the magnetic properties of the prepared material, i.e. single phase of BFCT probably is not ferromagnetic.

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