Imaging of domains in single crystals of BiFeO$_3$-PbTiO$_3$ using various microscopy techniques

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Abstract
Single crystals of BiFeO$_3$-PbTiO$_3$ have been grown from a PbO:Bi$_2$O$_3$ flux by cooling at a rate of 2°C/hour from the melt. Faceted crystals of various morphologies were produced and the size of the crystals ranged from less than 0.5mm to 5mm. Initial measurements were made using the scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) semi-quantifying the composition of the crystals as well as electron probe microanalysis (EPMA). Powder X-ray diffraction (XRD) of the crushed and sieved crystals established that the structure was rhombohedral perovskite for the (BiFeO$_3$)$_{0.75}$-(PbTiO$_3$)$_{0.25}$ composition and tetragonal perovskite for the (BiFeO$_3$)$_{0.50}$-(PbTiO$_3$)$_{0.50}$ composition and mixed phase for the (BiFeO$_3$)$_{0.65}$-(PbTiO$_3$)$_{0.35}$ and (BiFeO$_3$)$_{0.70}$-(PbTiO$_3$)$_{0.30}$ compositions. X-ray pole figures verified that the (BiFeO$_3$)$_{0.75}$-(PbTiO$_3$)$_{0.25}$ crystal had grown with a single orientation, the [100] direction. Structures that are believed to be domains have been observed through optical and electron microscopy in backscattered mode. This interim report of on going investigations seeks to eventually confirm the domain structure in the crystals with electron back-scattered diffraction (EBSD).

Introduction
Bismuth ferrite is a multi-ferroic [1] material which exhibits ferromagnetic and anti-ferroelectric properties. It is a perovskite with a rhombohedrally distorted lattice [2] and has a Curie point of 836°C [3]. Characterisation of the ferroelectric and piezoelectric properties of bismuth ferrite has been limited due to its semi-conducting nature at room temperature [4].

Lead titanate is a perovskite with a tetragonally distorted lattice and a Curie temperature of 490°C [5]. Most commonly utilised in the mainstay piezoelectric lead zirconate titanate (PZT) compositions close to the morphotropic phase boundary (MPB) between its tetragonal and rhombohedral forms, where the highest piezoelectric coefficients are exhibited due to phase equivalence.

The solid solution between bismuth ferrite and lead titanate was first reported in 1960 [6]. Later work revealed that bismuth ferrite-lead titanate (BFPT) exhibits a morphotrophic phase boundary (MPB) at around 70 wt% bismuth ferrite [7]. The potential for BFPT to deliver high performance as a piezoelectric is still yet to be confirmed, however it has been reported that a tetragonal spontaneous strain of 18% [8] exists at the MPB. It is suggested that this will translate to similarly exceptional piezoelectric performance. The Curie point at the MPB is also reported to be 632°C; this is in comparison to 386°C for PZT, hence BFPT is a potential high temperature piezoelectric material.

Single crystals of various complex perovskites, most notably Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_7$-PbTiO$_3$ and Pb(Zn$_{1/3}$,Nb$_{2/3}$)$_3$O$_7$-PbTiO$_3$, have previously demonstrated much higher performance than their ceramic analogues [9]. The outstanding properties of single crystals are attributed to a field-induced rhombohedral-tetragonal transformation coupled with the high electrical and mechanical strength of the materials, which allows them to experience very high fields without breaking down.

BFPT has already been shown to have a high Curie point and an exceptional spontaneous strain. Single crystals of this material may provide performance beyond that of any piezoelectric to date.
The work reported here investigates the imaging of domains in single crystals of BFPT grown using the flux growth method. This interim report of ongoing investigations seeks to eventually confirm the domain structure in the crystals with electron back-scattered diffraction (EBSD).

**Experimental**

Compositions of \((\text{BiFeO}_3)_{0.75-}(\text{PbTiO}_3)_{0.25}\) (75:25), \((\text{BiFeO}_3)_{0.70-}(\text{PbTiO}_3)_{0.30}\) (70:30), \((\text{BiFeO}_3)_{0.65-}(\text{PbTiO}_3)_{0.35}\) (65:35) and \((\text{BiFeO}_3)_{0.50-}(\text{PbTiO}_3)_{0.50}\) (50:50) were produced by ball milling the precursor metal oxides of \(\text{Bi}_2\text{O}_3\), \(\text{Fe}_2\text{O}_3\), \(\text{PbO}\) and \(\text{TiO}_2\) (Aldrich, purity \(>99.9\%\)) in acetone for two hours. Excess additions of \(\text{PbO}\) and \(\text{Bi}_2\text{O}_3\) were added to produce a flux : BFPT ratio of 40:60 by weight. The composition of the flux was 70:30 \(\text{PbO}:\text{Bi}_2\text{O}_3\) by weight which was chosen to coincide with the \(\text{PbO}:\text{Bi}_2\text{O}_3\) eutectic (635°C) [10] and due to its chemical compatibility with BFPT. The mixed powders were dried before being packed into a 100ml platinum crucible. For each crucible a total charge of 50g of powder was used.

The platinum crucibles were fitted with a lid and then placed within an alumina crucible which was subsequently sealed using alumina cement in order to suppress \(\text{PbO}\) and \(\text{Bi}_2\text{O}_3\) loss. Alumina fibre (Saffil) was packed between the platinum crucible and alumina crucible to absorb any potential leakage that may damage the furnace.

Melting was carried out in a box furnace with a dwell of two hours at 1200°C before cooling at a rate of 2°C per hour to 800°C. Cooling continued at the slightly accelerated rate of 5°C per hour down to 600°C. This was employed in an effort to reduce the stresses that are thought to occur as the charge descends through the paraelectric/ferroelectric phase transition and the flux solidification temperature. Below 600°C the samples were cooled at a rate of 50°C per hour. Once cooled, the platinum crucibles were removed from the furnace and immersed in glacial acetic acid to dissolve the flux which surrounds the crystals. Over a period two days the crystals were loosened from the flux and were removed with a minimum of force.

The samples for electron microscopy and composition analysis were Syton polished. This process was preceded by the polishing of the samples down to 1µm with diamond and consists of a combined chemical and mechanical polish using colloidal silica and a highly alkaline solution which gently attacks the surface to leave a virtually damage free surface, which would be the result of normal polishing techniques. The samples for powder x-ray diffraction consisted of a selection of crystals which had been crushed with a pestle and mortar and sieved to ensure a maximum particle size of 100µm.

Backscattered electron imaging and EDX was carried out on a CamScan 4 scanning electron microscope with an accelerating voltage of 20KV. EPMA was carried out on a Cameca SX50 EPMA microprobe with wavelength dispersive spectrometer (WDS) and XRD measurements on a Philips APD 1700.

**Results and discussion**

For each of the compositions it can be seen from the Table 1 that the intended composition was not achieved even taking into account the errors in the techniques the composition is quite far from what was desired, the remaining components must have remained in the flux as the charge cooled. The errors usually associated with EDX are up to 10% relative and around 1% for the EPMA but each system uses standards for each element which are often very different than the material being analysed. This introduces a further degree of as yet un-quantified error which will need to be addressed with the production of suitable standards.

| Intended composition (BF:PT) | EPMA composition (BF:PT) | EDX composition (BF:PT) | Powder XRD phase |
|-----------------------------|--------------------------|-------------------------|------------------|
| 50:50                       | 37:63                    | 40:60                   | Tetragonal (T)   |
| 65:35                       | 42:58                    | 49:51                   | Mixed R & T      |
| 70:30                       | 45:55                    | 51:49                   | Mixed R & T      |
| 75:35                       | 50:50                    | 53:47                   | Rhombohedral (R) |

Figures 1 to 4 are back-scattered electron micrographs which are typical for each of the samples of the different compositions. It should be emphasised at this point that these samples are completely flat and this
has been confirmed with secondary electron imaging, where the only visible features are the cracks (i.e. no topographical contrast) and also that there is no variation in composition between the areas of differing tone. This has been confirmed with EPMA.

The similarities between all samples can be seen in the cracking and the alternative light/dark patterning. There are also other dimensions of tone which are not constricted by the most predominant bands.

Fig. 1 Backscattered electron micrograph of a polished (BiFeO$_3$)$_{0.50}$-(PbTiO$_3$)$_{0.50}$ crystal prepared from a charge with 40% PbO:Bi$_2$O$_3$ as a flux.

Fig. 2 Backscattered electron micrograph of a polished (BiFeO$_3$)$_{0.65}$-(PbTiO$_3$)$_{0.35}$ crystal prepared from a charge with 40% PbO:Bi$_2$O$_3$ as a flux.

Fig. 3 Backscattered electron micrograph of a polished (BiFeO$_3$)$_{0.70}$-(PbTiO$_3$)$_{0.30}$ crystal prepared from a charge with 40% PbO:Bi$_2$O$_3$ as a flux.

Fig. 4 Backscattered electron micrograph of a polished (BiFeO$_3$)$_{0.75}$-(PbTiO$_3$)$_{0.25}$ crystal prepared from a charge with 40% PbO:Bi$_2$O$_3$ as a flux.

This allows for the assertion that the contrast in the images is a result of the crystallographic structure, either due to a difference in phase or direction, more commonly referred to as ferroelastic domains. The relationship between the domains and the cracks is quite striking. This is well demonstrated in Fig 1 which shows the presence of cracks at the junction of two different domain groups. An enlargement of Fig. 3 can be seen in Fig. 5 and it can be seen in several instances, cracks which run across one domain and are constrained by the domain and do not propagate into the adjacent domains.

Figures 5 and 6 show a further refinement of the domain structure which can be seen within the larger domains. Again a light/dark alternation is present and in Fig. 5 these exists at an angle not 90° to the large domain. In Fig. 6 the fine domains are as far as can be seen at approximately 90° or parallel to the larger domains, these domains are interesting in that they translate across the light coloured dividing domain into the next adjacent darker domain. It is possible that these domains could be ferroelectric.

The cracking which appears in all samples in especially the larger cracks could be affected by domains but equally may come about either through macroscopic stress such as that which may be produced by
differential cooling. However the cracks shown in Fig. 5 are an effect related purely to differences in adjacent domains.

![Fig. 5 Backscattered electron micrograph of a polished (BiFeO$_3$)$_{0.70}$-(PbTiO$_3$)$_{0.30}$ crystal prepared from a charge with 40% PbO:Bi$_2$O$_3$ as a flux.](image1)

One possible explanation for the presence of the cracks is that they are formed by the movement of the domains and indeed it is possible that all the cracks in the sample are initiated by such movement. One possible cause for this internal stress could be a result of the very high spontaneous strain of the tetragonal phase the lattice parameters for the 70:30 as found with powder XRD are $a = 3.874$ Å and $c = 4.317$ Å and for the rhombohedral phase $a = 3.975$ Å. A study into the PZT system [11] has highlighted domains as giving rise to stresses which could analogous to this system. It is argued that two adjacent domains which see a tetragonal phase domain alongside a rhombohedral phase domain would result in a huge lattice mismatch of the order of 10% and the effect of this would give rise to large stresses being developed.

**Conclusions**

Single crystals of BiFeO$_3$-PbTiO$_3$ have successfully been synthesised although the actual composition differs quite significantly from the intended composition and this was confirmed with both EDX and EPMA and taking into account the potential errors. Powder XRD confirmed the phase of the four compositions and the lattice parameters. Domains have been successfully imaged using back-scattered electrons in a scanning electron microscope. A relationship between the cracks and the domains is obvious and it is suggested that this may initiate at domain boundaries where there is a mismatch between the lattice parameters. Analysis with electron back-scattered diffraction (EBSD) is needed as the next step in order to characterise the orientation of the domains.

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