Microstructure study of $Bi_4Ti_3O_{12}$ - $SrBi_4Ti_4O_{15}$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$- $SrBi_4Ti_4O_{15}$ ceramics

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TEM study is preformed on mixed-layer type Bismuth compounds: $Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$ (BT-SBTi) and $Bi_{3.25}La_{0.75}Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$ (BLT-SBTi) ceramics. Meeting the prediction of space group theory, APBs and 90° domain wall are observed by bright- and dark-field imaging in both materials. Besides, other planer defects are found and confirmed to be stacking faults.

INTRODUCTION

In recent years ferroelectric materials have generated wide interest for their applicabilities to nonvolatile ferroelectric random access memories (NvFeRAM)[1]. Many ferroelectric materials, such as $PbZr_xTi_{1-x}O_3$ (PZT), $SrBi_2Ta_2O_9$ (SBT) and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) have been studied as candidates for NvFeRAM [2, 3, 4].Among them PZT has the largest Pr, but poorest fatigue; BLT and SBT, on the other hand, significantly improve the fatigue, but their Prs are still insufficient for practical use. Hence, an alternative material is yet desired. Mixed-layer type bismuth layer-structured ferroelectrics (BLSFs) are studied for promising candidates to that aim. Bismuth-layered ferroelectrics are known to possess a structure expressed by general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A is mono-, di-, or trivalent ions, B is tetre-, penta-, or hexavalent ions with appropriate size and valence, and m is the number of BO_6 octahedra in the perovskite blocks (m=1, 2, 3, 4 and 5)[5]. These compounds are built up by regular intergrowth of $(Bi_2O_2)^{2+}$ layers and perovskite layers $(A_{m-1}B_mO_{3m+1})^{2-}$. Some mixed-layer type are composed of two BLSFs[6]. Most recently, $Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$ is studied by Y. Noguchi *et. al.*[7], which shows larger Pr than BTO and SBTi, and relative high Tc (610°C). However, it was found that BT-SBTi shows fatigue failure after 10^{10} switch circles. And it is reported the fatigue property is significantly improved when Bi ions are partially substituted by La^{3+} [8]

In this paper, microstructures of BT-SBTi and BLT-SBTi are studied by TEM. APBs and 90° domain walls of them are reported. Stacking faults are also observed in both of them.

EXPERIMENTS

Ceramic samples of BT-SBTi and BLT-SBTi were prepared by conventional solid-state reaction technique. The crystalline structures of the samples are determined by x-ray diffraction. TEM specimens were prepared by mechanical thinning, followed by Ar^+ ion milling at 4kV. A 120kV Philips CM12 transmission electron microscopy, equipped with a side-entry double-tilt specimen stage, as used in this study.

In general, the space group of the prototype structure of BLSFs is close to F4/mmm, and the ferroelectric phase structure of BT-SBTi is defined as $P2_1am$[7]. The exact structure of BLT-SBTi has not been reported yet. Taking into account the case of BTO ans BLT, the BLT-SBTi structure is expected to change less due to the less effective percentage of La doped-in[9]. According to a group theory anylesis[10], we could anticipate there exist APBs, 90° domain walls and 180° domain walls in both materials.

RESULTS AND DISCUSSION

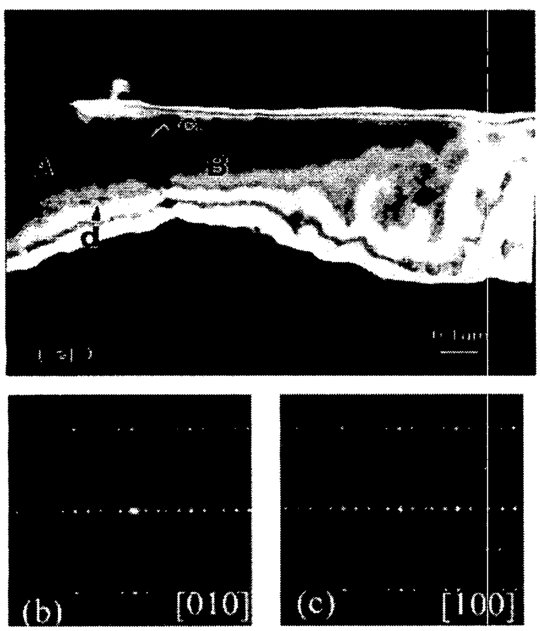

FIGURE 1 (a) bright-field image of BT-SBTi (b) [010] zone-axis SAED pattern of the single domain A. (c) [100] zone-axis SAED pattern of the single domain B.

Fig 1 (a) shows bright-field image of BT-SBTi, where symmetrical fringe is observed as indicated by marked as "c". Distinct diffraction patterns are detected on domains (A and B) separated by such fringe. Fig 1 (b) is the [0 1 0] zone-axis selected area electron diffraction (SAED) pattern from A domain whereas fig 1 (c) is the [1 0 0] zone-axis SAED pattern from B domain. This indicates the fringe represents a 90° domain wall. In this observation, the 90° domain wall has a flat figuration. Some planer defects marked "d" in fig 1 (a) are also noticed, which will be discussed at later.

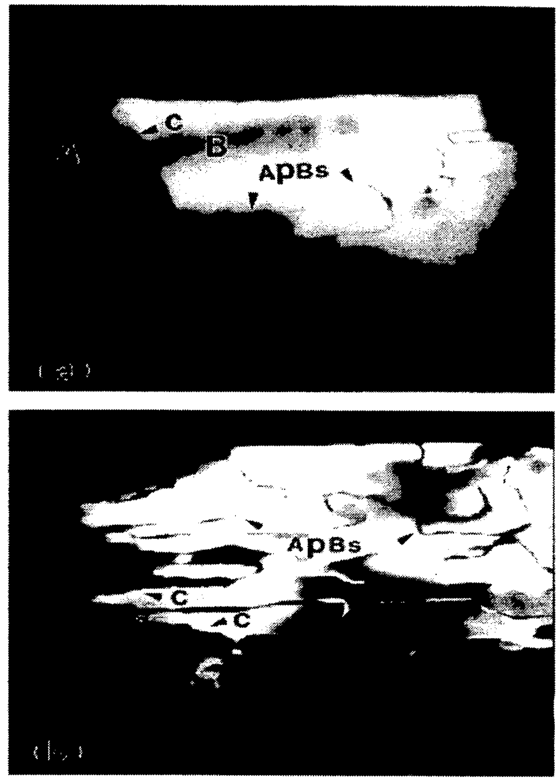

FIGURE 2 showing (0 3 1) superlattice dark-field images of BT-SBTi (a) and BLT-SBTi (b). 90° domain walls marked as "c"

Fig 2 (a) is (0 3 1) superlattice dark-field image taken at the same area as fig 1 (a). "A" domain is dark because the domain does not give such reflection. According to electron diffraction theory, the images of the APB can only be observed when $2\pi g \cdot R=(2n+1)\pi$ (n is integer), where **R** is one lattice translation vector of the prototype unit cell, but half of that in the low symmetry phase. APBs are observed in bright B domain. Fig 2 (b) is (0 3 1) superlattice dark-field image of a grain of BLT-SBTi. Similarly, the APBs and irregular 90° domain walls are observed. It is note-worthy that the figuration of 90° domain walls, which is irregular, is different from that observed in BT-SBTi.

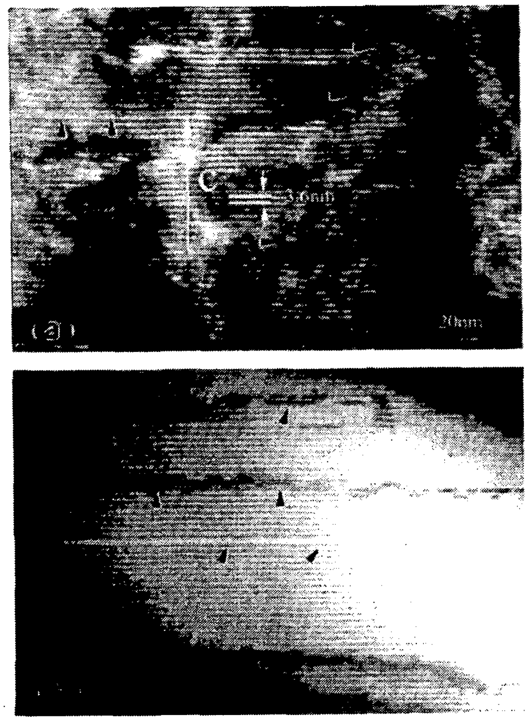

FIGURE 3 showing dark-field images of BT-SBTi (a) and BLT-SBTi (b).

Fig 3 (a) and (b) are dark-field images of BT-SBTi and BLT-SBTi under two-beam conditions with higher magnification. One can see some dark lines, which are separated by a distance about 3.6 nm, close to c-lattice constant. As c-axis is normal to these lines and c is much larger than a and b, we identify these lines with lattice stripes. Stacking faults is a simple type of planer defect. Structurally, a displacement relates the parts on the two sides of the fault[11]. The stacking faults are observed and marked in fig 3 (a) and (b). The planer defects in fig 1 (a) is stacking faults too.

APBs and 90° domain walls exist in both materials. Densities of APBs and 90° domain walls seem different in BT-SBTi and BLT-SBTi. But a rational analysis should be based on the statics, which is difficult to preform in TEM experiment. Furthermore, 180° domain wall is not confirmed in this paper.

CONCLUSION

The microstructures of BT-SBTi and BLT-SBTi are studied by TEM. APBs and 90° domain walls are identified in both of them. The domain density in BLT-SBTi is higher than that in BT-SBTi. The figuration of 90° domain walls in BT-SBTi becomes irregular after La doping, which may be caused by released strain in BLT-SBTi. The stacking faults are also observed in both materials.

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