Hydrothermal synthesis is an attractive method for the deposition of ferroelectric thin films because it can realize a low processing temperature of 200 °C or less. In this study, micron-sized PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals and thin films were fabricated on a Ti substrate at 160 °C by hydrothermal synthesis. The ferroelectricity of the crystals was investigated using local piezoresponse hysteresis, while their domain structure was investigated using high-resolution transmission electron microscopy (HRTEM) measurement. The isolated PZT single crystal exhibited hysteresis behavior of the piezoresponse, which represents ferroelectricity. From the HRTEM observations of a crystallite in polycrystalline PZT thin film, we found a twinned domain structure in the form of a $c/a$ polydomain pattern. On the basis of the HRTEM observations, we proposed a three-dimensional domain structure for the isolated PZT single crystal; the $c/a$ domain walls form along coherent {101} planes in the tetragonal cell. This structure was experimentally verified by scanning nonlinear dielectric microscopy. © 2004 American Institute of Physics. [DOI: 10.1063/1.1702129]
(SEM) image of a typical PZT crystal and the surface image of PZT thin film (inset) on Ti substrate. The PZT crystal takes a micron-sized hexahedron shape with well-developed facets. Noticeably, a crystallite in the PZT thin film takes the same shape as the PZT crystal. Figure 1(b) shows the piezoresponse ($A \cdot \cos \varphi$) of the PZT crystal, where $A$ is the tip vibration amplitude, which is a parameter proportional to the piezoelectric coefficient, and $\varphi$ is the phase difference between the applied ac signal and the tip vibration due to the state of polarization direction. It reveals a hysteresis curve; the curve represents the polarized domain switching. As expected from the piezoresponse of the PZT crystal, the XRD pattern in the inset of Fig. 1(b) shows that the crystal had a perovskite structure with a tetragonal ratio ($c/a$) of 1.036. By WDS analysis, the composition of PZT thin film was determined to be Zr/Ti = 40/60. The chemical formula of the PZT crystal shown in Fig. 1(a) is therefore expected to be PbZr$_{0.4}$Ti$_{0.6}$O$_3$.

Figure 2(a) shows the plane-view TEM image of a crystallite in PZT thin film and Fig. 2(b) shows a corresponding HRTEM image with a selected area diffraction (SAD) pattern. The periodic arrays of dark streaks are oriented in two directions. As shown in Fig. 2(a), one direction is perpendicular to the other. These streaks can also be seen in the HRTEM image in Fig. 2(b). They form a broad region about 2 nm wide and each side contrasts with the other. Our PZT crystal has a tetragonal ratio of 1.036; this makes it difficult to determine exactly whether the zone axis is the [100] or [001] direction from the SAD pattern. Therefore, it is not clear whether the streak direction is the [100]/[010] or the [110] direction of the tetragonal cell as shown in Fig. 2(b).

In Fig. 3(a), the cross-sectional TEM image of a crystal-

![FIG. 1. (a) SEM photograph of a typical micron-sized PbZr$_{1-x}$Ti$_x$O$_3$ crystall. The inset shows the surface SEM image of polycrystalline PbZr$_{1-x}$Ti$_x$O$_3$ thin film. (b) Piezoresponse hysteresis obtained on an isolated PbZr$_{1-x}$Ti$_x$O$_3$ single crystal using a contact mode of AFM. The inset shows an XRD pattern obtained from polycrystalline PbZr$_{1-x}$Ti$_x$O$_3$ thin film. The single crystal and the thin film are fabricated using hydrothermal synthesis at 160 °C.](image1)

![FIG. 2. (a) Plane-view TEM image of a crystallite within polycrystalline PbZr$_{1-x}$Ti$_x$O$_3$ thin film. (b) HRTEM image focused on the dark streaks where the SAD with the [100] or [001] is inserted.](image2)

![FIG. 3. (a) Cross-sectional TEM image of a crystallite within PbZr$_{1-x}$Ti$_x$O$_3$ thin film. (b) HRTEM image focused on a wedge-shaped band where the SAD with the [100] is inserted.](image3)

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the formation of the crossed a-domain on the (001) plane with a plane-view TEM in 450-nm-thick epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ film on a (001) SrTiO$_3$ substrate.

SNDM observations easily confirmed the proposed polydomain structure of the PZT crystal; one example of the results is shown in Fig. 4(b). To be equivalent to Fig. 4(a), the corresponding crystallographic plane indices are indicated on the figure. The inset is a three-dimensional topography image of the observed PZT crystal. The lines on the SNDM image show the crystal edges and another PZT crystal stands close to the observed crystal. Our PZT crystal clearly shows the c/a/c/a domain walls on both the (001) and (010) planes as depicted in Fig. 4(b). The [001] axis of the observed crystal tilts away from the normal to the crystal-substrate interface. Therefore, the probe scans not only the (001) plane, but also the (010) plane. This makes it possible to obtain the same SNDM signal from both the (001) and (010) planes simultaneously. The crystal uses only one twin variant; that is, the (011) twinned a-domain in Fig. 4(a). However, the crystal tilt that revealed the plane-view TEM of Fig. 2(a) uses at least two [101] twin variants because the c/a domain walls in the A and B region are at right angles to each other.

From the PbTiO$_3$–PbZrO$_3$ subsolidus phase diagram, we know that PZT ceramics have a Curie temperature of about 425 °C. At this temperature, the phase transition from the cubic paraelectric phase to the tetragonal ferroelectric phase occurs. Our PZT crystal was grown in a hydrothermal solution at 160 °C under hydrostatic pressure. Even with the effect of hydrostatic pressure, our PZT crystals experienced no phase transition; they were grown in a temperature range where the tetragonal phase is stable. Nevertheless, contrary to expectations, they exhibited the twinned domain structure observed in epitaxial ferroelectric thin films such BaTiO$_3$, PbTiO$_3$, and PbZr$_{1-x}$Ti$_x$O$_3$, which were grown on a cubic substrate with a high processing temperature. Furthermore, the thermal expansion mismatch of the PZT crystal and Ti substrate is unlikely to be responsible for the observed domain structure because the crystal growth temperature was 160 °C. Therefore, our experimental results clearly suggest that another mechanism forms the twinned domain structure of the PZT crystal fabricated by hydrothermal synthesis. A study of this phenomenon is in progress.

In summary, submicron and micron-sized isolated PZT crystals and thin films on a Ti substrate were hydrothermally synthesized at 160 °C. The results confirm that isolated PZT crystal has an hysteresis behavior of piezoresponse, which represents ferroelectricity. From HRTEM observations on a crystallite in polycrystalline PZT thin film, we found a twinned domain structure of the ... c/a/c/a ... polydomain pattern. On the basis of the HRTEM observations, we proposed a three-dimensional domain structure of the isolated PZT crystal, in which the c/a walls form along coherent {101} planes in the tetragonal cell. This structure was experimentally verified by SNDM.

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![Diagram](https://example.com/diagram.png)