INCOMMENSURATION IN ANTIFERROELECTRIC PZST

Incommensuration in Antiferroelectric Tin-modified Lead Zirconate Titanate

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ABSTRACT

The temperature dependence of the crystal structures of tin-modified lead zirconate titanate ceramics Pb_{0.98}Nb_{0.02}(Zr_{1-x}Sn_x)_{1-y}Ti_{1-y}O_3 was investigated by hot-stage transmission electron microscopy. The composition chosen for study, x=0.42 and y=0.04 (i.e., PZST 42/4/2), had a sequence of phase transformations on heating of antiferroelectric - multicell cubic - simple cubic. The presence of the multicell cubic phase was characterized by the existence of weak \( \frac{1}{2}[110] \) superlattice spots in the temperature range between the antiferroelectric and simple cubic phases. The antiferroelectric phase in both compositions was characterized by the presence of one-dimensional regular arrays of antiphase domain boundaries and \( \frac{1}{2}[110] \) superlattice spots. The modulation wavelength for the superlattice spot was found to be a strong function of temperature and was incommensurate with the lattice.

INTRODUCTION

Tin modified lead zirconate titanate (PZST) ceramics are amongst the best candidates for antiferroelectric to ferroelectric phase switching materials. The transformation from the antiferroelectric to the ferroelectric state can be driven by an electric field. Large changes in the physical properties accompany this induced-transformation, including large nonlinearities in the polarization and dielectric responses, and strong nonlinear electromechanical couplings. The PZST system was first investigated by Jaffe et al.\(^{1}\) for piezoelectric applications. A comprehensive study\(^{2}\) of the effects of chemical modifications on the relative phase stability was subsequently investigated. More recently a systematic study of the effects of temperature, pressure, and grain size was determined by Yang and Payne\(^{3,4}\). They found that PZST 42/4/2 was antiferroelectric at room temperature, transforming first to a multicell cubic state, and finally to the simple cubic phase. Strong dielectric anomalies were not observed at the antiferroelectric - multicell cubic phase transformation. The maximum dielectric constant was found near the temperature of the formation of the multicell cubic state, which was approximately 30°C above the transformation into the long-range antiferroelectric state.

The nature of the multicell cubic state, and the transformation path between the simple cubic and antiferroelectric phases, is presently unknown. No macroscopic symmetry changes characteristic of the multicell cubic state have yet been identified, and no superstructures or distortions have been detected to date. In addition, no detailed structural study has yet been carried out as a function of temperature through the antiferroelectric - multicell cubic - simple cubic phase transformation sequence. In this investigation we report hot-stage transmission electron microscopy and selected area electron diffraction results which have revealed interesting information about the nature of the multicell cubic state, and the details of the structural features.
associated with the simple cubic - multicell cubic and multicell cubic - antiferroelectric transformations. Experimental details of this work can be found in a previous publications5.

EXPERIMENTAL PROCEDURE

Several PZST specimens were examined in a transmission electron microscopy (TEM) equipped with a hot-stage. The composition chosen for study was 42/4/(1., and was prepared by a hybrid coprecipitation-mixed oxide method3. TEM specimens were prepared by ultrasonically drilling 3-mm discs which were mechanically polished to -100μm. The center portions of the discs were further thinned by a dimpler to -15μm, and argon ion-milled to perforation. Specimens were coated with carbon before examination. TEM studies were carried out in a Phillips EM420 microscope operating at an accelerating voltage of 120 kV, using both double tilt and single tilt hot-stages. Electron diffraction patterns were obtained along a number of zone axes as a function of temperature. Precise temperature measurements were difficult, since the TEM specimen heated in the electron beam. However, the values of temperature reported can be used as relative indications since the TEM experiments were carried out under similar conditions of illumination and specimen thickness. All selected area electron diffraction (SAED) patterns were recorded, developed, and printed under the same conditions in order to compare relative changes in the intensity of the superlattice spots and lattice parameters.

II. RESULTS AND DISCUSSION.

II.1 ROOM TEMPERATURE RESULTS.

A typical microstructure of PZST 42/4/2 at room temperature is illustrated in Figure 1a. Two characteristics are readily apparent which can be seen in grain 1 (as well as most grains examined): (i) a dark region separating two bright regions, and (ii) many fine striations within each dark region. These striations were clearly visible when the grains were tilted close to the [001] direction, and subsequently disappeared when the specimen was heated. Similar striations have also been observed for antiferroelectric lead zirconate (PbZrO3)6 and PZST 20/4/27. Therefore in this study, we consider the presence of these striations as a clear indication of antiferroelectricity. The bright and dark areas within a grain are due to diffraction contrast between regions of different orientation, as shown in the electron diffraction patterns given in Figures 1 b and c (recorded from regions A and B in Figure 1a, respectively). Superlattice spots or structural modulations are observable along both the [110] and [110] directions. These two orientations have a common c-axis and are rotated with respect to each other by an angle of 90° (indicating the presence of 90° domains). Figure 1d shows the SAED pattern from region C, both orientations are clearly evident.

The details of the superlattice spots in the [001] SAED patterns are illustrated in Figure 2a. Six superlattice spots can readily be seen in this simple perovskite unit cell between the [000] and [110] reflections. The superlattice spots correspond to the $\frac{1}{2}[110,220,330 \cdots]$ reflections and are characteristic of the room temperature antiferroelectric phase. These superlattice spots are also responsible for the formation of a periodic image in the bright-field pattern. The lattice image corresponding to the SAED pattern is shown in Figure 2b. Fringes or structural modulation can easily be seen, which are regular arrays of antiphase domain boundaries (APBs). The APBs revealed in Figure 2b are one dimensional arrays with (100) planes passing through two sets of
perpendicularly oriented APBs. The period of the modulation can be estimated by the separation of the superlattice spots from the relevant main reflections, which always coincided with the width of the antiphase domains observed from the bright field images. The modulation wavelength along the [110] direction was approximately 20 Å, and was not always commensurate with the lattice. The occurrence of these antiphase domains can be interpreted as interpenetrating layers of polar moments which reverse at the antiphase boundaries. Figure 3a shows a lattice image taken from region A in Figure 1a, the details of the 90° antiferroelectric domain structure and APBs are more clearly illustrated in this micrograph. A corresponding schematic model of the macroscopic 90° domains and microscopic APBs is illustrated in Figure 3b.

II.2 TEMPERATURE DEPENDENCE.

In PZST 42/4/2 a phase sequence of antiferroelectric - multicell cubic - simple cubic has been reported on cooling. The antiferroelectric phase is stable below 150°C, the multicell cubic state exists between 150 and 180°C, and at higher temperatures the simple cubic state is stable. The multicell cubic state is characterized by a dielectric maximum, however no macroscopic symmetry changes accompany this anomaly. The transformation into the long-range antiferroelectric state does not occur until approximately 40°C below the dielectric maximum. The nature of the multicell cubic state and the transformation path between the multicell cubic state and the antiferroelectric phase is presently unknown. One of the goals of this study was to investigate these questions using hot stage electron microscopy and diffraction.
Figure 1. a. [001] SAED pattern taken from a single 90° antiferroelectric domain, b. lattice image corresponding to the SAED pattern.

Figure 3. a. Lattice image taken from region A in Figure 1(a), and b. schematic model of the 90° antiferroelectric domain structure and the APBs.
Figures 4a-f illustrate the temperature dependence of the SAED [112] patterns. It is interesting to note that not only the intensity of the $\frac{1}{x}[110]$ superlattice spots decreased with increasing temperature, but also that the distance between these spots and the main reflection decreased. This indicates that the spacing of the lattice fringes (or modulation wavelength length) increased with temperature. The change in the lattice constants was approximately 1% between 25 and 160°C, while the change in the modulation wavelength was nearly 33% from 1.988nm at 25°C to 2.947nm at about 160°C. The implication is that there is no direct correlation between the changes of the lattice parameters and the modulation length, and that the modulation wavelength is incommensurate with the lattice. The $\frac{1}{x}[110]$ superlattice spots disappeared around 160°C (Figure 4d), which coincided with the temperature at which the striations disappeared. A similar temperature dependence of $\frac{1}{x}[110]$ superlattice spots was also observed in the [001] SAED patterns.
In addition to the antiferroelectric superlattice spots, weak $\frac{1}{2}[110]$ superlattice spots were detected, as indicated by the arrows in Figure 4. These spots appeared around 150°C (Figure 4c) and disappeared around 200°C (Figure 4e), which is the same temperature range in which the multicell cubic state was stable. The implication is that unique structural changes occur on forming the multicell cubic state which are responsible for the $\frac{1}{2}[110]$ reflections. Due to the weak nature of these superlattice spots (obtained only after an exposure time of 40 seconds), it is not surprising that this reflection was not previously detected by X-ray diffraction. In addition, the intensity of the reflection was too weak to obtain corresponding information in the bright field image. The presence of $\frac{1}{2}[110]$ reflections has previously been explained by short-range ordering in lead-based perovskites. In PZST, vacancy ordering could give rise to metastable antipolar microregions in the multicell cubic “phase” region leading to the weak $\frac{1}{2}[110]$ superlattice spots. It would appear, at any rate, that minor structural changes occur in the multicell cubic region which are characteristic of this state. The changes are in addition to (or coincident with) the temperature dependent long-wavelength structural modulation.

CONCLUSIONS

Changes in structure with temperature for PZST 42/4 were studied by hot-stage TEM. PZST 42/4 had a phase sequence of antiferroelectric - multicell cubic - simple cubic. The presence of the MCC phase was confirmed for the first time by electron diffraction, and was characterized by the existence of weak $\frac{1}{2}[110]$ superlattice spots in the multicell cubic region. The antiferroelectric phase in both compositions was characterized by the presence of structural modulations along the [110] direction, as observed by $\frac{1}{2}[110]$ superlattice reflections. The modulation wavelength was estimated by measuring the spacing of the lattice fringes and was approximately 2-3 nm, which coincided well with the width of the antiphase domains observed in the bright field images. The modulation wavelength was found to be incommensurate with the lattice and a strong function of temperature (increasing with temperature).

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