Journal of the European Ceramic Society 21 (2001) 2613–2616

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Order–disorder phase transition in $Ba(Zn_{1/3}Ta_{2/3})O_3$

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Abstract

The order–disorder transition temperature in $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics has been investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Samples were quenched into water after annealing at different temperatures ranging from 1550 to 1625 °C/15 h. XRD showed maximum ordering for samples annealed and quenched from 1600 °C accompanied by an order of magnitude increase in the size of ordered domains from that observed in as-sintered samples (20 nm). Although XRD revealed complete disorder for samples quenched from 1625 °C, ⟨110⟩ zone axis electron diffraction patterns revealed the presence of short range 1:1 and 1:2 ordering. XRD indicated that samples furnace cooled from 1625 °C were also disordered but could be re-ordered by annealing at 1500 °C.

Keywords: Complex perovskite; Dielectric properties; Electron microscopy

1. Introduction

$Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT), a 1:2 complex perovskite, is an important microwave ceramic and is currently used as a dielectric resonator in mobile phone base stations. BZT possesses a good combination of the desired properties for a resonator: a temperature coefficient of resonance frequency (TCF) tunable through zero with dopants such as Sr^{2+} on the A- site and/or Zr^{4+} on the B-site, a dielectric constant of 29 and a microwave dielectric quality factor Q of 50–60,000 at 1 GHz.[1] When disordered (Zn and Ta ions arranged randomly on the B-site), BZT, has a cubic perovskite structure in which corner shared, BO_6 octahedra describe a cubo-octahedral A-site interstice.[2] The ordered compound in which Zn and Ta ions occupy alternate (111)-planes of the pseudocubic structure in a 1:2 ratio, adopts trigonal symmetry (Fig. 1). The ordering sequence was initially described by Galasso[2] for the $Ba(Sr_{1/3}Ta_{2/3})O_3$ structure.[3]

Previous X-ray diffraction (XRD) studies on BZT have indicated an increase in the degree of B-site order on annealing between 1400 and 1500 °C.[4] Several authors have suggested that increasing the degree of order improves Q[4,5] but the temperature of the order disorder phase transition, and, therefore, the maximum temperature at which a sample can be annealed to induce ordering, is not known. In this work a series of experiments were performed to investigate the degree of B-site ordering in samples quenched from various temperatures and to ascertain the approximate temperature at which BZT orders prior to disordering.

2. Experimental

To synthesize BZT ceramics, appropriate proportions of $BaCO_3$, ZnO and Ta_2O_5 (all >99.9% purity) were processed by a conventional mixed oxide route. Starting powders were wet milled for 8 h, calcined for 2 h at 1100 °C and remilled for 8 h with 2 wt.% PEG binder. Pellets (30 mm diameter) were uniaxially pressed at 125 MPa into discs and sintered for 2 h at 1475 °C in enclosed crucibles containing a small amount of ZnO powder to minimize ZnO volatilization.

Samples were heat treated at 1550, 1575, 1600 and 1625 °C for 15 h in a muffle furnace. Again, enclosed crucibles were used with a small quantity of ZnO powder present to minimize weight loss due to ZnO volatilization. Pellets were removed from the furnace at the above temperatures and quenched directly into water. One sample was furnace cooled from 1625 °C to room temperature. This sample was subsequently re-annealed at 1500 °C for 15 h.

A Philips X-ray diffractometer was used to characterise powdered samples. X-ray patterns were recorded at 2θ values between 10 and 80° at a scanning rate of $2°2\theta$/min using CuK_α radiation. Samples for TEM were pre-

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0955-2219/01/$ - see front matter
PII: S0955-2219(01)00325-9

pared by conventional grinding and polishing techniques followed by ion beam thinning using a Gatan Duo Mill operating at a combined beam current of 0.6 mA, an accelerating voltage of 6 kV and incidence angle of 15°. Samples were examined using Jeol 3010 and Philips EM420 electron microscopes.

3. Results and discussion

3.1. X-ray diffraction

Fig. 2 shows XRD patterns from samples annealed at 1575, 1600, 1625 and as-sintered sample (1475 °C). The intensity of superlattice reflections (arrowed) reaches a maximum at 1600 °C. The absolute change in the degree of order between 1475 and 1600 °C is difficult to assess since the low symmetry of the trigonal space group gives rise to many superlattice peaks compared with fcc ordering in 1/2:1/2 compounds. However, the intensity of the (1/3:2/3:1/3) peak relative to (110) increases from 2 to 4. Unlike samples quenched from 1600 °C, those quenched from 1625 °C exhibit no superlattice reflections, suggesting that an order-disorder transition (T_c) occurs between these two temperatures.

Fig. 3 shows typical XRD patterns from samples furnace cooled from 1625 °C. No ordered superlattice reflections are observed. Subsequently re-annealing

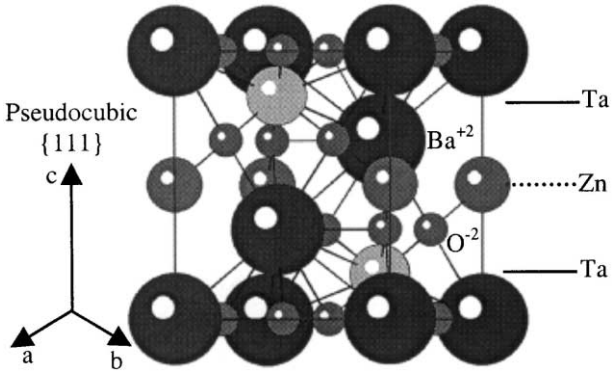

Fig. 1. Diagram illustrating the ordered trigonal (P3ml) of BZT.

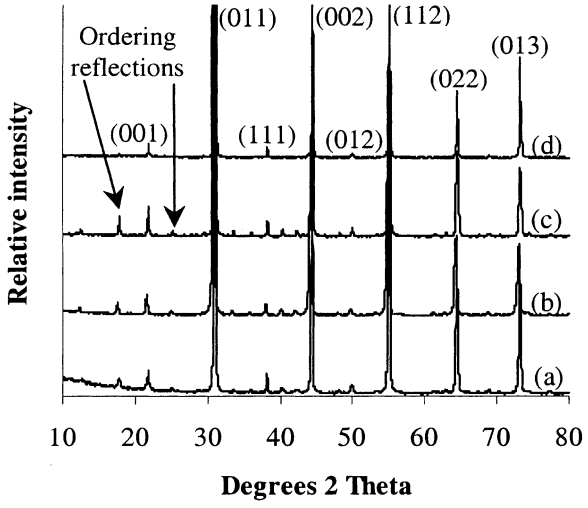

Fig. 2. XRD patterns from BZT (a) sintered at 1475 °C and annealed and quenched from (b) 1575 °C, (c) 1600 °C and (d) 1625 °C. Reflections are indexed according to a pseudocubic setting. The ordered reflections are at $\pm 1/3\{hkl\}$.

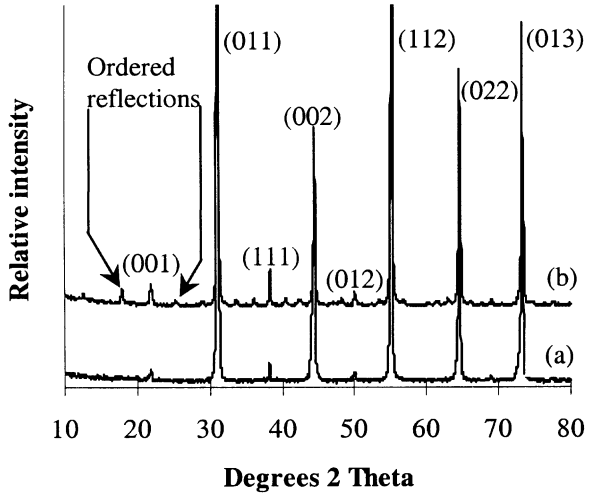

Fig. 3. XRD patterns from a sample (a) slow cooled from 1625 and (b) reannealed at 1500 °C. The ordered reflections are at $\pm 1/3\{hkl\}$.

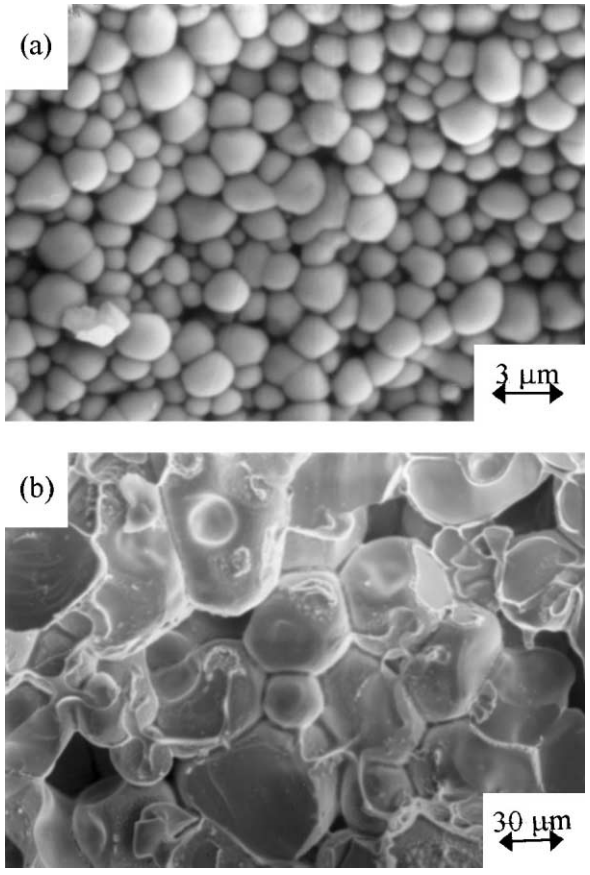

Fig. 4. Secondary electron images of fragments of samples fractured on quenching from (a) 1600 °C and (b) 1625 °C.

these samples at 1500 °C caused the ordering reflections to reappear demonstrating the reversibility of the order–disorder phenomenon in BZT.

3.2. SEM

Fig. 4a and b shows SEM images of samples fractured on quenching from (a) 1600 °C and (b) 1625 °C. Fig. 4a reveals a grain size of approximately 2–3 μm, similar to that in as-sintered samples. In Fig. 4b, the grain size is about 30–40 μm. The mechanism by which grain growth occurs is unclear at present but may be linked to the order–disorder transition. Diffusion distances to rearrange ions into the ordered trigonal structure are greater than to form more symmetrical cubic disordered phases. Therefore, grain growth in the cubic phase may be kinetically favoured. Alternatively, a liquid phase may form between 1600 and 1625 °C that promotes abnormal grain growth. Although no direct evidence of liquid phase has been obtained, a second phase is observed at grain boundaries in SEM images, (Fig. 5).

3.3. Transmission electron microscopy

Fig. 6 shows typical pseudocubic zone axis electron diffraction patterns obtained from the centre of a grain in samples quenched from (a) 1600 °C and (b) 1625 °C. Pseudocubic and superlattice reflections are indexed according to the adjacent schematic. Discrete superlattice reflections (indicative of a coherent ordered structure) at $\pm 1/3\{hkl\}$ positions, expected from a trigonal superlattice, are observed in Fig. 6a. No such reflections were seen in the diffraction pattern obtained from samples quenched from 1625 °C. However, streaking parallel to ⟨111⟩ directions and diffuse intensity (characteristic of short-range order) at $1/2\{hkl\}$ positions are observed (Fig. 6b). From these results it can be concluded that the order–disorder phase transition in BZT occurs at a temperature between 1600 and 1625 °C in agreement with XRD. However, the presence of enhanced intensity at $1/2\{hkl\}$ positions in nominally disordered samples needs to be explained. It is suggested that, during the initial ordering stages an approximate fcc structure forms that is composed of alternate Ta^{5+} rich and deficient layers (with respect to the bulk composition) on {111} planes. This is an intermediate metastable structure frozen-in on quenching. A lapse of a few seconds during the quenching process would have brought the temperature to below that of the order–

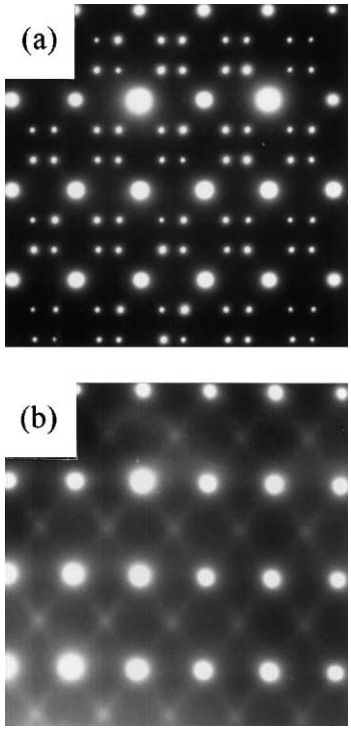

Fig. 6. Electron diffraction patterns with the beam perpendicular to a pseudocubic ⟨110⟩ direction obtained from the centre of a grain in a sample quenched from (a) 1600 °C and (b) 1625 °C. Pseudocubic and superlattice reflections are indexed according to the adjacent schematics.

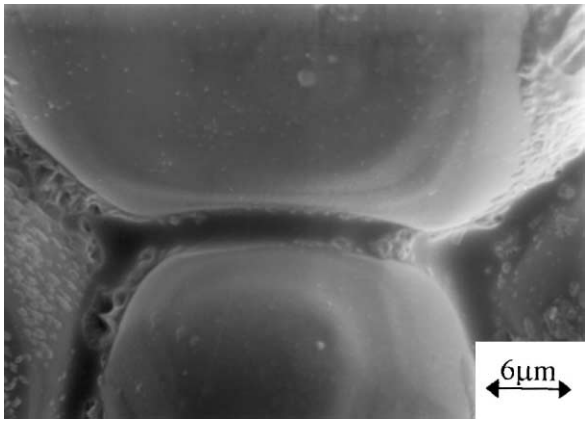

Fig. 5. Secondary electron image of a fragment of a sample quenched from 1625 °C showing a triple junction with rounded grain boundaries.

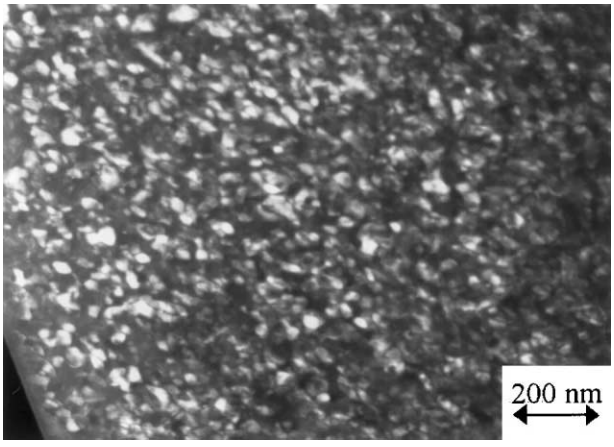

Fig. 7. Dark field TEM image from a grain in as-sintered pellet (1475 °C) sample obtained using one set of $\pm 1/3\{hkl\}$ reflections.

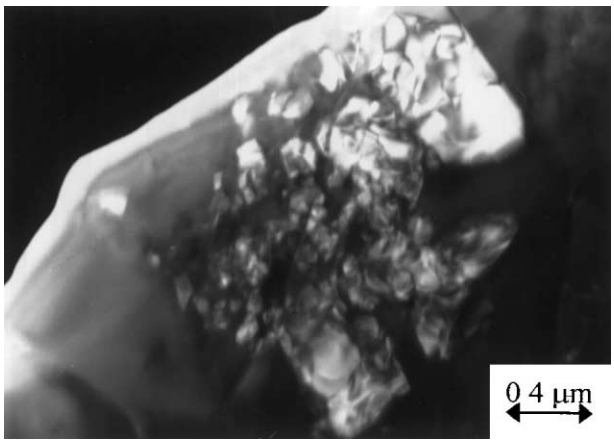

Fig. 8. Dark field TEM image obtained using one set of $\pm 1/3\{hkl\}$ reflections from a grain in the sample quenched from 1600 °C.

disorder, allowing some short-range cation diffusion to occur.

Fig. 7 is a dark-field image from a grain in an as-sintered pellet (1475 °C) using one set of $\pm 1/3\{hkl\}$ reflections. The regions of light contrast are ordered domains, typically 20–40 nm diameter.[6] Dark-field images from samples quenched from 1600 °C reveal domains about 0.4 μm diameter at the grain peripheries and about 0.1 μm diameter at the grain interiors (Fig. 8). It is apparent that the ordered domains have grown by an order of magnitude at 1600 °C (~400 nm) compared to samples sintered at 1475 °C (20–40 nm).

4. Conclusion

A reversible order–disorder phase transition in BZT occurs between 1600 and 1625 °C. The disordered phase exhibits diffuse scatter along ⟨111⟩ directions and diffuse intensity at $1/2\{hkl\}$ positions in electron diffraction patterns arising from a metastable, approximate fcc structure. Ordered domains in samples quenched from 1600 °C (~100–400 nm) are larger than those in as sintered samples (20–40 nm), particularly at the grain periphery.

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