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Structure and properties of $La(Zn_{1/2}Ti_{1/2})O_3$

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Abstract

$(La,Nd)(Zn,Mg)_{0.5}Ti_{0.5}O_3$ compounds are of great interest for microwave dielectric applications, although the structure of some of these complex perovskites is still uncertain. The perovskite tolerance factors in this family of compounds range from 0.916 to 0.952, suggesting a very high degree of tilting in the oxygen octahedra for compositions throughout the system. The effects of this tilting in $La(Zn_{0.5}Ti_{0.5})O_3$, for example, have been observed in this study by transmission electron microscopy in the form of $1/2\{3\,1\,1\}_c$ and $1/2\{1\,3\,1\}$ α superlattice reflections and $1/2(2\,3\,1)_c$ γ reflections corresponding to anti-phase and in-phase tilting, respectively. Systematic La^{+3} displacement was also detected by the appearance of $\{h+1/2, k, l\}_c$ (β) reflections. Reflections of the type $1/2\{1\,1\,1\}_c$ in neutron diffraction patterns indicate 1:1 cation ordering on the B-site. Electrical tests show no piezoelectricity in $La(Zn_{0.5}Ti_{0.5})O_3$, indicating a centrosymmetric point group. Rietveld refinements of neutron diffraction patterns indicate that the space group is $P2_1/n$, with lattice constants $a = 7.8943$ Å, $b = 5.5959$ Å, $c = 5.5805$ Å, and $\beta = 90.0291°$.

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1. Introduction

Microwave resonators are used extensively in telecommunications equipment, including cellular telephones and satellite links, and are at the heart of a multi-billion pound market. Oxide ceramics are critical elements in these devices, and three properties are important in determining their usefulness as a dielectric resonator. First, the material must have a high dielectric constant (ε_r) to enable size reduction. Second, a high quality factor Q (low $\tan\delta$) means fine frequency tunability and better filters. Third, these ceramics compensate for frequency drift because of their low temperature coefficients of resonant frequency (τ_f), permittivity (τ_ε), and capacitance (τ_C).

The basic principles for tuning τ_f in complex perovskites have already been established. Colla et al.[1,2] and Reaney et al.[3] have shown that τ_ε in Ba- and Sr-based complex perovskites is fundamentally related to the onset and degree of octahedral tilting. Moreover, it can be tuned through $\pm 300\,\mathrm{m\,K^{-1}}$ without significantly altering Q or ε_r by manipulating the perovskite tolerance factor, t,

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)} \tag{1}$$

from 1.01 to 0.93, where R_A, R_B, and R_O are the radii of the ions in the perovskite (ABO_3) structure. Reducing t results in the onset of octahedral tilt transitions. The relationship between τ_ε and τ_f is:

$$\tau_f = -\left(\frac{\tau_\varepsilon}{2} + \alpha_L\right) \tag{2}$$

where α_L is the coefficient of linear thermal expansion ($\approx 10\,\mathrm{m\,K^{-1}}$ for perovskites).

The structure of $La(Mg_{0.5}Ti_{0.5})O_3$ was first published[4] as cubic, space group $Pa3$, with a lattice constant of 7.868 Å. Several years later, Negas et al.[5] found it to be orthorhombic, and Meden and Ceh[6] refined its structure in space group $Pbnm$; however, Harshé et al.[7] failed to find any orthorhombic peak splitting and again suggested a cubic unit cell, but with a lattice constant of 3.9195 Å. Neither of the previous studies by German et al.[4] nor Meden and Ceh[6] were cited in that work. Recently, Lee et al.[8] have reported that $La(Mg_{0.5}Ti_{0.5})O_3$ is monoclinic in its ordered state ($P2_1/n$), although it becomes disordered and orthorhombic upon doping with small amounts of

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$SrTiO_3$[8,9] or $BaTiO_3$.[10] In its pure, ordered form it has[8] $\varepsilon_r = 28$, $Q_f = 63{,}100$, and $\tau_f \approx -77\ \mathrm{m\,K^{-1}}$, although Seabra et al.[11] have reported $Q_f = 114{,}000$ and $\tau_f = -81\ \mathrm{m\,K^{-1}}$ and Negas et al.[5] found $\varepsilon_r = 33$, $Q_f = 40{,}000$, and $\tau_f \approx -100\ \mathrm{m\,K^{-1}}$.

Like its La analogue, $Nd(Mg_{0.5}Ti_{0.5})O_3$ also purportedly[12] forms in the monoclinic $P2_1/n$ system, although earlier work[4] suggested an orthorhombic (*Pbnm*) symmetry. Seabra et al.[11] have measured its microwave properties as $\varepsilon_r = 26$, $Q_f = 151{,}000$, and $\tau_f = -47\ \mathrm{m\,K^{-1}}$, while Kim et al.[13] report $\varepsilon_r = 25$, $Q_f = 60{,}000$, and $\tau_f = -72\ \mathrm{m\,K^{-1}}$. No data currently exist on $Nd(Zn_{1/2}Ti_{1/2})O_3$; however, its tolerance factor of 0.916 is too low for a stable perovskite to be likely. Its structure may instead be similar to that of ilmenite ($R\bar{3}$).

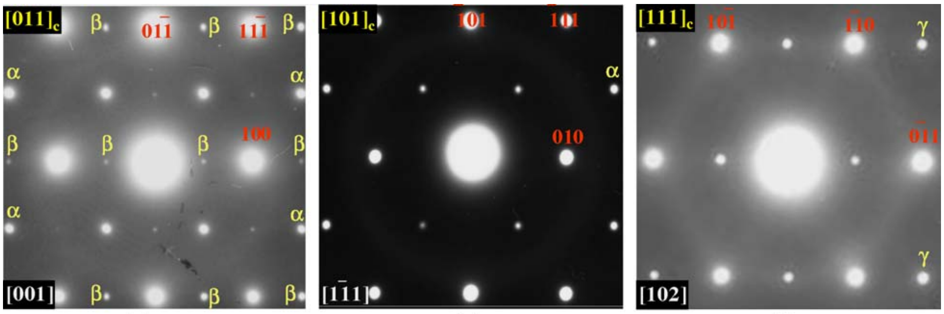
The structure of $La(Zn_{0.5}Ti_{0.5})O_3$ (LZT) published by Kucheiko et al.[14] was orthorhombic, with lattice constants $a = 5.6088$ Å, $b = 7.8986$ Å, and $c = 5.5641$ Å. The microwave properties they measured were $\varepsilon_r = 29$, $Q_f \approx 60{,}000$, and $\tau_f = -71\ \mathrm{m\,K^{-1}}$, but the density of their samples was only about 90% of the theoretical density (ρth). These properties were later re-measured by Cho et al.[15] on samples which were about 97% ρth. They reported $\varepsilon_r = 34$, $Q_f = 59{,}000$, and $\tau_f = -52\ \mathrm{m\,K^{-1}}$.

The average tolerance factor of LZT is $t = 0.947$, which, according to the work of Reaney et al.[3] suggests the presence of both in-phase and anti-phase tilting of oxygen octahedra. The effects of this tilting have been observed[16] by XRD in the form of 1/2(3 1 1) and 1/2(3 1 0) superlattice reflections corresponding to anti-phase and in-phase tilting, respectively. Systematic cation displacement was also detected by the appearance of 1/2(2 1 0) reflections, and 1/2(1 1 1) reflections were observed and ascribed to the doubling of the unit cell caused by the B-site cation ordering. As in its Mg analogue, small amounts of doping with $SrTiO_3$[16,17] or $CaTiO_3$[16,18] are sufficient to disrupt the B-site ordering. Based on the crystallographic evidence, three possible orthorhombic space groups can be derived for the structure (*Pmmn*, *Pnma*, and *Cmcm*), none of which can also account for the B-site ordering. Weissenberg photographs or TEM work combined with neutron diffraction would be required to unambiguously establish the structure, and the results of such work are described here.

2. Procedure

In this work, conventional mixed oxide powder processing techniques were used. Starting materials included La_2O_3 (99.9% Meldform Rare Earths, UK), TiO_2 (99.9% Alfa Aesar, UK), and ZnO (99.9% Elementis Specialties, UK). Like most rare-earth oxides, La_2O_3 is notoriously hygroscopic and readily hydrates in the atmosphere if unprotected. For this reason, La_2O_3 was first purposely hydrated in distilled water to form $La(OH)_3$. To accomplish this, the oxide powder was first heated to 800 °C for an hour, cooled, then immediately mixed with an excess of distilled water and left to dry. The resultant hydrate was then used in the subsequent processing procedure, which involved milling stoichiometric amounts of powders together in a porcelain millpot partly filled with ZrO_2 media and distilled water for 4 h. A small amount (1 wt.%) of Dispex A40 (Allied Colloids, Bradford, UK) was added as a deflocculant. The slurries were then dried overnight at 80 °C. Dried powders were subsequently granulated with a mortar and pestle and sieved to under 250 μm. Calcination was achieved using a two-stage process. First, powder was heated to 600 °C for 2 h in an open Al_2O_3 crucible to ensure dehydroxylation of the $La(OH)_3$. The completion of the dehydroxylation reaction was monitored by measuring the weight loss upon cooling. Second, this same powder was gently mixed by hand, a lid was placed over the crucible, and it was re-heated to 1200 °C for 2 h. Afterwards, the powder was re-milled for a further 4 h with 2 wt.% PEG 1500 (Whyte Chemicals, London) being added in aqueous solution 5–10 min before completion. These slurries were then dried at 80 °C and subsequently pressed (125 MPa) into cylindrical pellets 10 mm in diameter and 3 mm thick. Sintering was conducted in closed alumina boats for 2 h at 1500 °C.

Phase assemblages were checked by scanning electron microscopy (JSM 6300, Jeol, Tokyo) and X-ray diffraction (D50000, Siemens, Germany), using Cu Kα radiation. Some samples underwent thinning by ion milling (model 600, Gatan, CA, USA) for observation in the transmission electron microscope (JEM 2010, Jeol, Tokyo). Neutron diffraction data were acquired on the D2B instrument at the Institut Max von Laue–Paul Langevin (ILL) (project 5-21-898).



(a) (b) (c)

Fig. 1. Selected area electron diffraction patterns indexed according to the fundamental perovskite pseudocube, $a = 3.9449$ Å. The superlattice reflections are labelled α, β, and γ. The pattern in (a) is the [0 1 1] pseudocubic zone, which corresponds to the [0 0 1] of the revised orthorhombic/monoclinic unit cell. The pattern in (b) is the pseudocubic [1 0 1] or the [1 1 1] of the revised cell. The pattern in (c) is the pseudocubic [1 1 1] or the [1 0 2] of the revised cell. The α reflection in (a) is indexed as $1/2(3\ 1\ \bar{1})$, whereas that in (b) is $1/2(\bar{1}\ 3\ 1)$. The γ reflection in (c) is $1/2(2\ 1\ \bar{3})$.

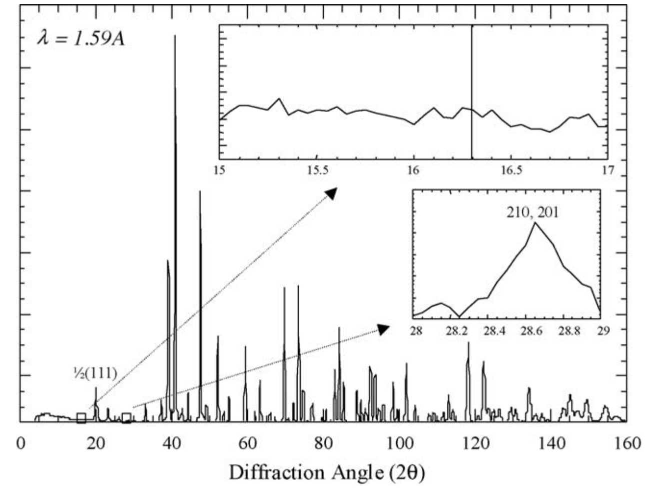


Fig. 2. Neutron diffraction pattern of $La(Zn_{1/2}Ti_{1/2})O_3$ powder, $\lambda = 1.59$ Å.

Measurements of the piezoelectric d_{33} constant of LZT samples pooled at 200 °C with a field strength of 11 kV/mm were made on a quasi-static d_{33} meter (ZJ-3B, CAS), whilst ε_r, Q, and τ_f were measured at Filtronic Comtek (Wolverhampton, UK) on a vector network analyser (model 8753E, Hewlett Packard, USA).

3. Results and discussion

3.1. Structure of LZT

Powder X-ray diffraction (XRD) alone is not sufficient to determine the symmetry of tilted perovskites like LZT. Peaks associated with oxygen octahedral tilting, as well as those arising from cation ordering, are very weak in XRD. Electron diffraction of single crystals within a ceramic has some advantages, although the interpretation of patterns is complicated by the fact that LZT readily twins on pseudocubic $\{1\,1\,0\}$. The selected area diffraction patterns (SADPs) in Fig. 1 have been indexed according to the simple pseudocubic perovskite unit cell ($a = 3.9449$ Å) and unambiguously show the presence of two α-type 1/2(*odd*, *odd*, *odd*) superlattice reflections and a single γ-type 1/2(*even*, *odd*, *odd*) reflection. It thus seems clear that the perovskite unit contains an in-phase octahedral tilt axis along *a* and anti-phase tilt axes along both *b* and *c*. What is left unquantified is the relative magnitudes of each of these distortions. The possible tilt systems, according to Glazer's[19] notation, are $a^+b^-c^-$, $a^+a^-c^-$, $a^+b^-b^-$, and $a^+a^-a^-$, corresponding to either $P2_1/m$ ($\alpha \neq 90°$) or *Pmnb* symmetry. In either case the basic perovskite unit is doubled in *a*, *b*, and *c* directions. A new unit cell can be obtained by inscribing within the doubled pseudocubic cell a smaller one with $a = 2a_c$, $b = c = \sqrt{2}a_c$

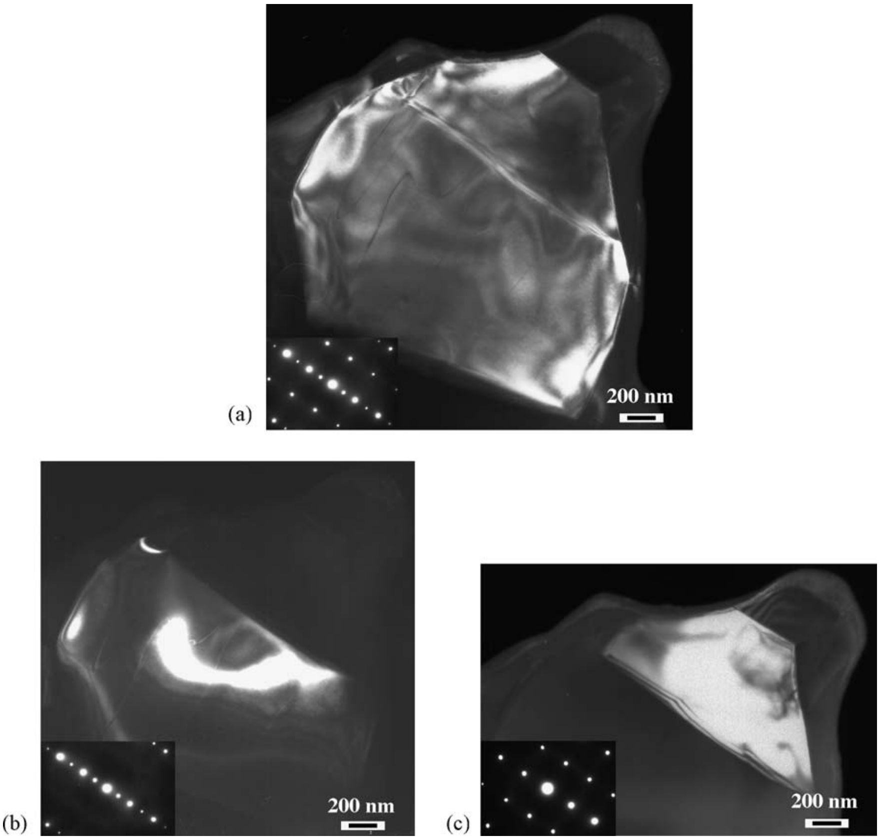


Fig. 3. Dynamical dark field images of twinning in $La(Zn_{1/2}Ti_{1/2})O_3$. The image in (a) includes both variants. The image in (b) was obtained using the second-order Laue zone reflection $\vec{g} = \underline{1}\,\underline{6}\,1\,1$ close to the $[0\,\bar{1}\,3]$ zone axis, while that in (c) was imaged using $\vec{g} = 1\,0\,2$ close to $[2\,\bar{1}\,\bar{1}]$. The twin plane is $(2\,\bar{1}\,1)$, which is not parallel to the beam in this geometry.

Piezoelectric tests on LZT pellets showed $d_{33} = 0$ for all testing conditions, indicating that the structure of LZT must be centrosymmetric.

The neutron diffraction pattern in Fig. 2 reveals much of the fine structure of LZT. The peak at 20.10° labelled 1/2(1 1 1) is a superlattice reflection, which corresponds to the (1 0 1) reflection of the orthorhombic/monoclinic unit cell described above. Although this reflection is allowed in both *Pmnb* and $P2_1/m$, neither of which allows $\{1\,1\,1\}$ ordering of B-cations, it has nevertheless usually been associated with such ordering. Indeed, its relative strength seems to strongly suggest that this is the correct interpretation. $P2_1/n$ is a maximal non-isomorphic subgroup of *Pmnb* which does allow cation ordering. The space group $P\bar{1}$, which is a subgroup of $P2_1/m$, would also allow ordering, but would correspond to a tilt system of $a^-b^-c^-$—antiphase tilting about all three pseudocubic axes—whereas the octahedra in LZT are clearly tilted in-phase about one of these axes. The absence of (0 1 0) or (0 0 1) peaks at ≈16.3°, both of which are allowed in $P2_1/m$, seems to eliminate this space group from consideration.

A Rietveld refinement of these neutron diffraction data indicate that the true symmetry is probably $P2_1/n$, with lattice constants $a = 7.8943$ Å, $b = 5.5959$ Å, $c = 5.5805$ Å, and $\beta = 90.0291°$. A high-degree of order exists on the B-site. This structure is essentially very similar to those of $La(Mg_{1/2}Ti_{1/2})O_3$ and $Nd(Mg_{1/2}Ti_{1/2})O_3$ proposed previously.[8,12] It is related to the unit cell published by Kucheiko et al.[14] except that the cation ordering induces tiny atomic displacements away from true orthorhombic symmetry. The unit cell is monoclinic, not due to any large distortions, but principally because the cation ordering cannot be accommodated within the orthorhombic *Pmnb* space group.

Fig. 3a shows an LZT grain containing two twin variants. The variant in Fig. 3b was imaged using the second-order Laue zone reflection $\vec{g} = \underline{1}\,\underline{6}\,1\,1$ close to the $[0\,\bar{1}\,3]$ zone, while the one in Fig. 3c was imaged using $\vec{g} = 1\,0\,2$ close to $[2\,\bar{1}\,\bar{1}]$. The twin plane is $(2\,\bar{1}\,1)$.

3.2. Properties of LZT

Dielectric measurements at microwave frequencies for LZT pellets (95% ρth) have shown some very interesting and potentially useful properties. For LZT, a relative permittivity of $\varepsilon_r = 34$ was measured at 4.35 GHz, in agreement with previous work,[15] but Q_f was only 36,000, significantly lower than previously reported.[14,15] Likewise, τ_f was measured as $-70\,\mathrm{m\,K^{-1}}$, quite different to that reported by Kucheiko et al.,[14] but in good agreement with work by Cho et al.[15] These discrepancies warrant further investigation.

4. Conclusions

$La(Zn_{1/2}Ti_{1/2})O_3$ has been found to have a monoclinic structure, space group $P2_1/n$, with lattice constants $a = 7.8943$ Å, $b = 5.5959$ Å, $c = 5.5805$ Å, and $\beta = 90.0291°$. The Zn^{+2} and Ti^{+4} sites are ordered on $\{1\,1\,0\}$. In addition, many grains show $\{2\,1\,1\}$ twinning.

The microwave properties of $La(Zn_{1/2}Ti_{1/2})O_3$ are $\varepsilon_r = 34$, $Q_f = 36{,}000$, and $\tau_f = -70\,\mathrm{m\,K^{-1}}$. The measured value of Q_f is lower than previously reported.

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