

Control of $0.2\text{CaTiO}_3\text{-}0.8\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ microwave dielectric ceramics by additions of $\text{Bi}_2\text{Ti}_2\text{O}_7$

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Abstract Ceramics of $0.2\text{CaTiO}_3\text{-}0.8\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ have been prepared by the mixed oxide route using additions of $\text{Bi}_2\text{O}_3\text{-}2\text{TiO}_2$ (up to 15 wt%). Powders were calcined 1100°C ; cylindrical specimens were fired at temperatures in the range $1250\text{--}1325^\circ\text{C}$. Sintered products were typically 95% dense. The microstructures were dominated by angular grains $1\text{--}2\ \mu\text{m}$ in size. With increasing levels of $\text{Bi}_2\text{O}_3\text{-}2\text{TiO}_2$ additions, needle and lath shaped second phases developed. For $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions up to 5 wt%, the relative permittivity increased from 95 to 131, the product of dielectric Q value and measurement frequency increased from 2150 to 2450 GHz and the temperature coefficient of resonant frequency (τ_f) increased from $-28\text{pp}/^\circ\text{C}$ to $+22\text{pp}/^\circ\text{C}$. A product with temperature stable τ_f could be obtained at ~ 2 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions. For high levels of additives, there is minimal change in relative permittivity, the Q values degrade and τ_f becomes increasingly negative.

Keywords Perovskite · CaTiO_3 · Microwave dielectric · Electron BackScatter Diffraction (EBSD)

Introduction

The demand by the telecommunications industry for the miniaturization of microwave components [1] can be achieved by increasing the relative permittivity (ϵ_r) since the size of microwave components is inversely proportional to the square root of the relative permittivity. Additional requirements are that the microwave losses should be minimized (or the Q value maximized) and the dielectric properties

be temperature stable such that the temperature coefficient of resonant frequency (τ_f) is close to zero ($\pm 5\ \text{ppm}/^\circ\text{C}$). A number of materials that have similar crystal structures but opposite τ_f can be combined to produce a ceramic with microwave properties that can be tailored to specific applications. One such combination of ceramics is the system $\text{CaTiO}_3\text{-Li}_x\text{Ln}_{1-x}\text{TiO}_3$ ($\text{Ln} = \text{Sm}, \text{Nd}$) that has attracted interest [2–6] because of its high ϵ_r . Both end members in the system are distorted perovskites with high, but opposite, non-zero τ_f values. The $\text{CaTiO}_3\text{-Li}_x\text{Ln}_{1-x}\text{TiO}_3$ ($\text{Ln} = \text{Sm}, \text{Nd}$) system has been shown to exhibit good dielectric properties for compositions having x in the range 2–3 [2, 6], although the Nd analogue exhibits higher relative permittivity [6, 7]. The use of Bi_2O_3 additions has been shown to be beneficial to both $\text{BaO-Nd}_2\text{O}_3\text{-TiO}_2$ [8–10] and $0.4\text{CaTiO}_3\text{-}0.6\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ [6] based ceramics. In this study the effect of $\text{Bi}_2\text{Ti}_2\text{O}_7$ addition to $0.2\text{CaTiO}_3\text{-}0.8\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ (0.2CT-0.8LNT) has been investigated, with a view to producing a temperature stable dielectric material and determining the important structural changes that result from the presence of bismuth.

Experimental

Ceramics of the 0.2CT-0.8LNT were prepared by the mixed oxide route using CaTiO_3 (99%-ALFA AESAR), Li_2CO_3 (99%-Fluka), Nd_2O_3 (99%-Honeywell Electronic Materials) and TiO_2 (98.5%-Tioxide UK Ltd). After mixing, the powders were wet milled in Propan-2-ol for 16 hours, and calcined at 1100°C for four hours. $\text{Bi}_2\text{O}_3\text{-}2\text{TiO}_2$ (BT) was added and the mixture ball milled for a further 16 h. Cylindrical samples were pressed 60 MPa. For firing they were placed on an alumina support covered in the starting material; the pellets were embedded in starting material and covered by an alumina housing to minimize Li loss. Sintering was performed in

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a horizontal tube furnace at temperatures in the range 1250° to 1325°C for three hours. Product densities were determined by weight and dimension measurements.

X-ray diffraction was undertaken using a Philips X'PERT system (*PW 3710*) over the 2θ range 10° to 100° with a step size of 0.04°. Lattice parameters were determined using CELLREF software. For microstructural analysis all specimens were ground on 1200 grade SiC and then successively polished on 6 μm , 1 μm and 0.25 μm diamond paste followed by OPS (colloidal Silica suspension) for five hours. The samples were investigated in detail by scanning electron microscopy (Philips SEM525 equipped with an EDAX DX4 system). Additional studies were carried out under electron backscatter diffraction (EBSD) conditions using a Philips XL30 FEG SEM. Charging of the sample surface during EBSD was prevented by applying a thin carbon layer that was overlain by a mesh network of metallic silver. The relative permittivity was measured by the Hakki and Coleman parallel plate [11] method whilst the dielectric Q value (reported as product of Qxf , where f is the measurement frequency) by the cavity method; τ_f was determined between -20° and $+60^\circ\text{C}$.

Results and discussion

Undoped ceramics of 0.2CT-0.8LNT achieved 95% theoretical density after firing at the optimum temperature of 1325°C. The addition of bismuth titanate to 0.2CT-0.8LNT reduced the optimum sintering temperature of the solid solution, by up to 75°C in the case of 15 wt% additions (Fig. 1). X-ray diffraction analysis confirmed that products exhibited an orthorhombic perovskite structure. All the spectra were very similar to that for CaTiO_3 [6] and could be indexed on the basis of Pbnm (No. 62), indicating in-phase and anti-phase tilting ($a^+b^-b^-$) with A-site cation ion displacement, according to Glazers classification [12]. The

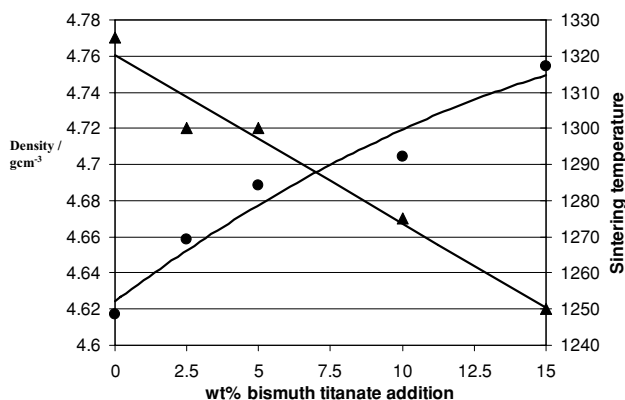


Fig. 1 Sintered density and optimum sintering temperature ($^\circ\text{C}$) for 0.2CT-0.8LNT as a function of bismuth titanate additions: Density (\blacktriangle) and sintering temperature (\bullet)

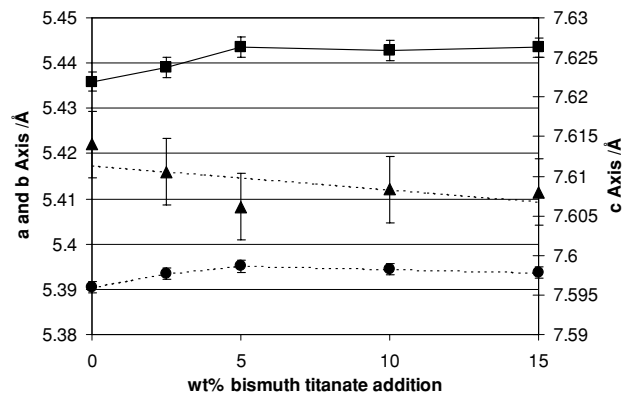


Fig. 2 Lattice parameters for 0.2CT-0.8LNT ceramics as a function of bismuth titanate additions: a -axis (\bullet), b -axis (\blacksquare) and c -axis (\blacktriangle)

tilting mechanisms of 0.2CT-0.8LNT do not appear to be affected by the addition of bismuth titanate. This is similar to the findings of Lowe et al [6] for the behaviour of 0.4CT-0.6LNT ceramics. Figure 2 shows the lattice parameters for 0.2CT-0.8LNT as a function of bismuth titanate additions. With the addition of 5 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$ to 0.2CT-0.8LNT, the a and b axes increase from 5.390 Å and 5.436 Å to 5.394 Å and 5.443 Å respectively. Further additions of bismuth titanate to 0.2CT-0.8LNT do not have a significant effect on the lengths of the a and b axes. In contrast the length of the c axis exhibited minimal variation with composition, although there is a suggestion of a slight reduction with increasing $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions. On the basis of ionic radii, it is anticipated that Bi (coordination 6, ionic radius 1.17 Å [13]) is incorporated into the perovskite structure on the A site. The fact that the cell parameters increase only for samples prepared with up to 5 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions suggests that the solubility limit for Bi is reached between 5 and 10%.

Typical microstructures for 0.2CT-0.8LNT ceramics are shown in Fig. 3. The grains are angular in shape and tend to decrease in size as the amount of $\text{Bi}_2\text{Ti}_2\text{O}_7$ in the starting formulation increases. In undoped 0.2CT-0.8LNT there is obvious variability in the grain size (Fig. 3(a)), with grains between 1 μm and 5 μm (average 2.6 μm). For 10 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions the grain size reduced to 1.4 μm although there is still extensive twinning, reflecting the effect of the CaTiO_3 component (Fig. 3(b)). At 15 wt% additions there is clear evidence of small lath shaped grains as well as the twinned primary grains (Fig. 3(c)). Energy dispersive spectroscopy (EDS) indicated that the bismuth-rich second phase is $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The brighter rims to the grain boundaries indicates the possibility of segregation of atoms of higher atomic number.

Figure 4 shows the variation in relative permittivity and Qxf value as a function of bismuth titanate additions. Modest additions of $\text{Bi}_2\text{Ti}_2\text{O}_7$ (up to 5 wt%) result in a rapid increase in the relative permittivity from 95 to 131, but there

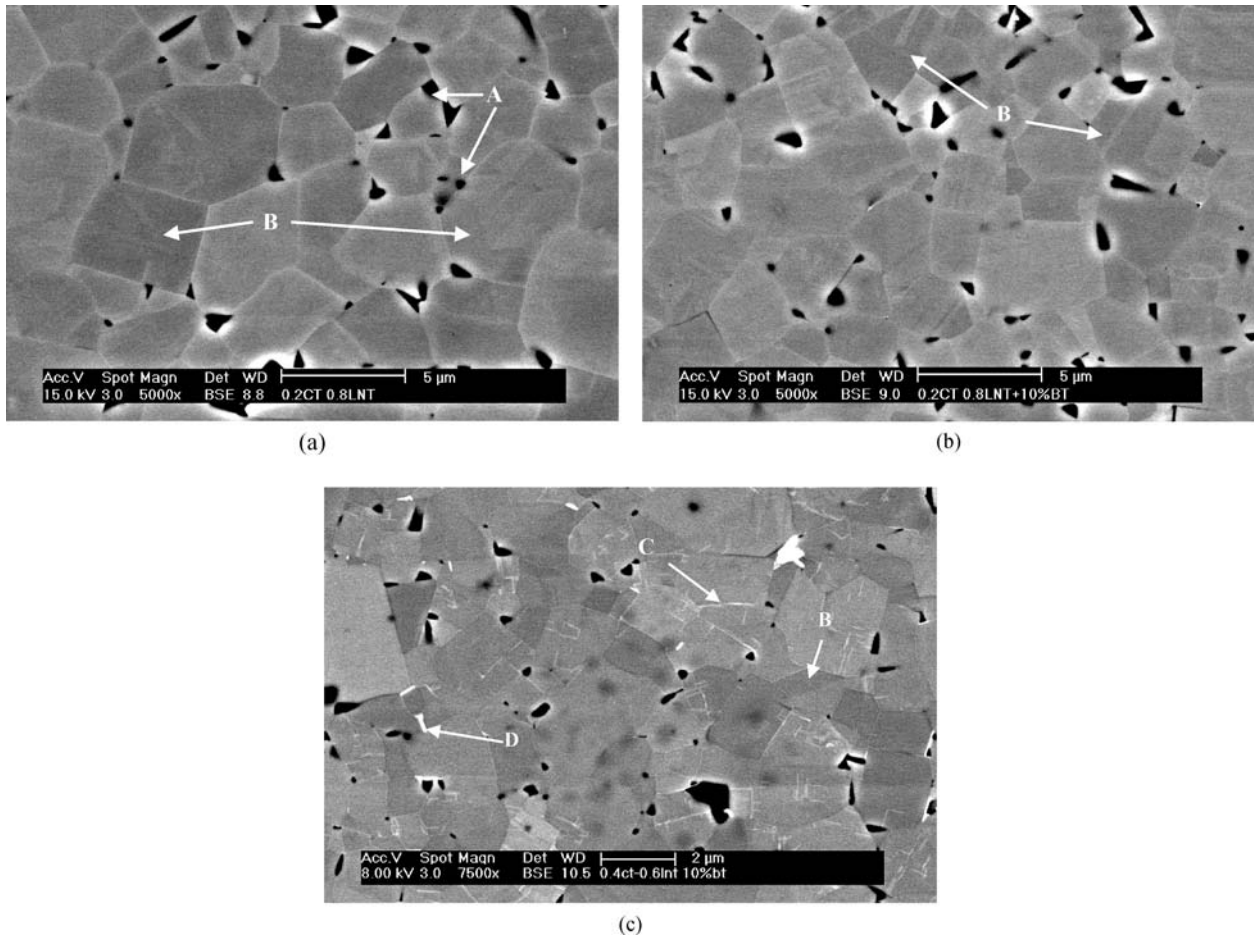


Fig. 3 Electron back scattered images of 0.2CT-0.8LNT ceramics prepared with different amounts of $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions: (a) 0 wt%, (b) 10 wt%, (c) 15 wt%; **A** represents calcium rich regions, **B** indicates the

presence of twinning, **C** indicates bismuth rich laths and **D** indicates bismuth rich second phase

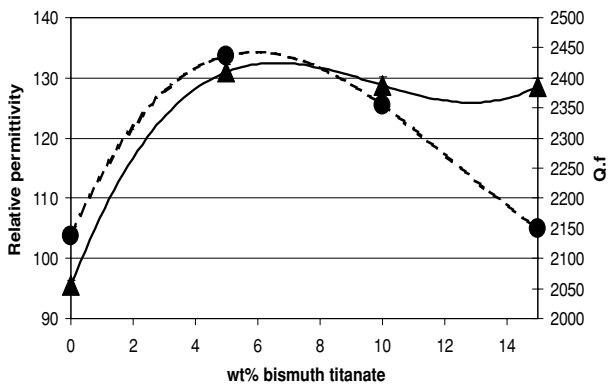


Fig. 4 Relative permittivity (▲) and Qxf (●) for 0.2CT-0.8LNT as a function of bismuth titanate additions

is minimal change thereafter. The dielectric Qxf value shows a similar increase for low levels of additions (from 2150 to 2450 GHz) but beyond the peak at 5 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$ the Qxf value decreases, returning to 2150 GHz at 15 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$.

The initial increase in relative permittivity can be attributed in part to the incorporation of Bi into the perovskite

structure; the stabilisation in ϵ_r at 5–10% $\text{Bi}_2\text{Ti}_2\text{O}_7$ reflects the fact that the solubility limit is reached, with clear evidence of a Bi-rich second phase for samples prepared with 15 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$ (Fig. 3(c)). Whilst polarisability changes resulting from ionic substitutions have a significant impact on relative permittivity, further insight into dielectric behaviour can be gained from consideration of bond valence or bond strength concepts [14]. The bond valences for the A-site and B-site in 0.2CT-0.8LNT have been calculated [14, 15] as a function of $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions (Fig. 5). The addition of bismuth titanate to 0.2CT-0.8LNT results in a linear increase of the A site bond valence while the B site bond valence decreases linearly up to 5 wt%. This suggests that Bi additions cause the A-site to become more constrained, although, according to Park et al. [14] the A site bond valence has little effect upon the relative permittivity. In contrast, the reduction in the B-site bond valence (up to 5 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$) means the highly polarisable Ti ions can be readily be displaced within the structure, leading to enhanced relative permittivity.

It was noted above that the Qxf values initially increase (along with ϵ_r) but subsequently decrease (Fig. 4). The

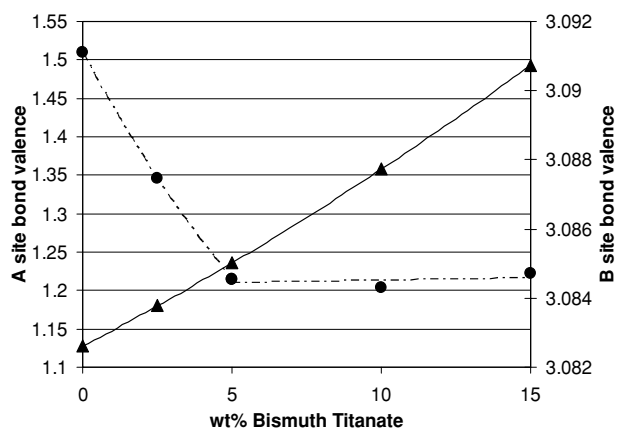


Fig. 5 The A site bond valence (▲) and B site bond valence (●) for 0.2CT-0.8LNT as a function of bismuth titanate additions

decrease in Qxf at higher levels of $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions can be attributed to the appearance of the second phase. Some understanding of the reason for the increase in Qxf for bismuth titanate additions below 5 wt% may be gained by considering the anharmonicity of the system. A crude measure of the change in lattice anharmonicity (μ) with bismuth titanate addition can be achieved through Eq. (1) [16], where k_b is Boltzmann's constant, T is temperature, M is the atomic mass of the unit cell and v is the mean velocity of sound. As no published value for CaTiO_3 could be found, the value for the related material LaAlO_3 (an orthorhombic perovskite), was adopted.

$$\mu = \frac{k_b T}{M v^2} \quad (1)$$

Equation (1) essentially predicts that anharmonicity and Qxf values for 0.2CT-0.8LNT will increase upon addition of bismuth titanate. Clearly the simple relationship fails at high levels of $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions when second phases form and the Qxf values reduce.

The final dielectric parameter for 0.2CT-0.8LNT is the temperature coefficient of resonant frequency (τ_f). As bis-

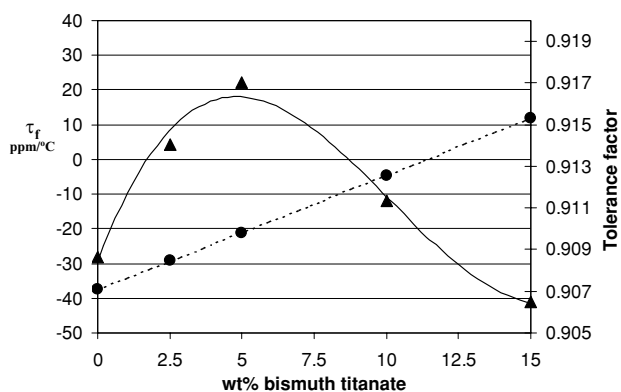


Fig. 6 τ_f (▲) and tolerance factor (●) for 0.2CT-0.8LNT as a function of bismuth titanate additions

mut titanate content increases (Fig. 6), the τ_f value increases from $-28 \text{ ppm}/^\circ\text{C}$ (zero additions) to $4 \text{ ppm}/^\circ\text{C}$ (2.5 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$) to $+22 \text{ ppm}/^\circ\text{C}$ (5 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$). For higher levels of bismuth titanate additions, the τ_f value decreases steadily to $-40 \text{ ppm}/^\circ\text{C}$ (15 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$). The polarity changes in the τ_f value mirror changes in the Qxf values (Fig. 4).

Reaney et al. [17] identified an empirical relationship between the tolerance factor (t_o) and τ_f , for number of different compositions. They showed that for dielectric materials exhibiting in-phase and anti-phase tilting ($t_o < 0.964$), the τ_f would decrease towards zero as the tolerance factor increased. For the present 0.2CT-0.8LNT ceramic system, it is noted (Fig. 6) that both t_o and τ_f increase for $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions up to 5 wt%, but at higher levels τ_f decreases whilst the tolerance factor continues to increase. Thus the simple relationship between t_o and τ_f does not hold for 0.2CT-0.8LNT prepared with $\text{Bi}_2\text{Ti}_2\text{O}_7$ additions. An alternative way of exploring changes in τ_f , is the bond valence approach.

As bismuth titanate is added to 0.2CT-0.8LNT, the substitution of Ca^{2+} by Bi^{3+} on the A-site results in an increase in the A-site bond valence while the B-site bond valence decreases (Fig. 5). As τ_f increases from $-28 \text{ ppm}/^\circ\text{C}$ (zero additions) towards $\sim 0 \text{ ppm}/^\circ\text{C}$ at ~ 2.0 wt% $\text{Bi}_2\text{Ti}_2\text{O}_7$, the A-site bond valence increases. There is as yet no obvious link for a trend between τ_f and the A site bond valence. However, the B-site bond valence decreases with increasing bismuth titanate content and it has been reported [18] that as B-site bond valence decreases the τ_f approaches zero. As the B-site ions are related directly to the degree of tilting in the structure, then as the B site bond valence decreases (for tilted structures), there is a reduction in the restoring force (term A in the differentiated Clausius Mosotti equation [19]) and this leads to a reduction in τ_f . This implies that the restoring force is reduced to an optimum value, resulting in a temperature stable material when 2.5 wt% bismuth titanate is added to 0.2CT-0.8LNT. However, higher additions cause τ_f to become first positive and then negative once more. Above 5 wt% bismuth titanate the B site bond valence remains constant, indicating that the bismuth titanate does not have any significant effect and other extrinsic factors, including the presence of second phases, become more important.

Conclusions

Good quality ceramics of $0.2\text{CaTiO}_3\text{-}0.8\text{Li}0.5\text{Nd}0.5\text{TiO}_3$ were prepared by the mixed oxide route. Small additions of $\text{Bi}_2\text{Ti}_2\text{O}_7$ resulted in a significant increase in the relative permittivity, a small increase in the Q.f. value and reduction in τ_f towards zero. At higher levels of additions, second phases, rich in bismuth develop as laths with the primary grains. This is accompanied by a small reduction in ϵ_r , a significant reduction in Qxf and τ_f becomes increasingly

negative. Small additions of Bismuth Titanate may be used to tune the microwave properties of 0.2CT-0.9LNT, to yield ceramics with optimum microwave properties.

Acknowledgments The support of the EPSRC through a Doctoral Training Award to T Lowe and grant GR/R72655 is gratefully acknowledged. We gratefully acknowledge the support of Filtronic Comtek with the supply of raw materials and microwave dielectric measurements.

References

1. R. Uvic, I.M. Reaney, and W.E. Lee, *International Materials Reviews*, **43**, 205 (1998).
2. W. S. Kim and K. H. Yoon, *J. Am. Ceram. Soc.*, **83**, 232 (2000).
3. W. S. Kim, K. H. Yoon, and E. S. Kim, *Materials Research Bulletin*, **34**, 2309 (1999).
4. K. H. Yoon, Y. Chang, W. S. Kim, J. B. Kim, and E. S. Kim, *Jpn. J. Appl. Phys.*, **35**, 5145 (1996).
5. J.-S. Kim, C.-I. Cheon, H.-J. Kang, C.-H. Lee, K.-Y. Kim, S. Nam, and J.-D. Byun, *Jpn. J. Appl. Phys.*, **38**, 5633 (1999).
6. T. Lowe, F. Azough, and R. Freer, *J. Korean Ceram Soc.*, **40**, 328 (2003).
7. H. Takashi, Y. Baba, K. Ezaki, and K. Shibata, *Jpn. J. Appl. Phys.*, **35**, 5069 (1996).
8. M. Valant, D. Suvorov, and D. Kolar, *J. Mater. Res.*, **11**, 928, (1996).
9. D. Kolar, S. Gaberscek, Z. Stadler, and D. Suvorov, *Ferroelectrics*, **27**, 269 (1980).
10. J. Durand and J. Boilot, *J. Mater. Sci. Lett.*, **6**, 134 (1987).
11. B. Haki and P. Coleman, *IRE Trans.*, **MTT-8**, 402 (1960).
12. A. Glazer, *Acta Cryst.*, **A31**, 756 (1975).
13. R.D. Shannon, *Acta Crystallogr.*, Sect. A, **32**, 75 (1976).
14. H.S. Park, K.H. Yoon, and E.S. Kim, *J. Am. Ceram. Soc.*, **84**, 99 (2001).
15. T.E. Lowe, Ph.D. thesis, University of Manchester Institute of Science and Technology (2004).
16. V.L. Gurevich and A.K. Tagantsev, *Advances in Physics*, **40**, 719 (1991).
17. I.M. Reaney, E.L. Colla, and N. Setter, *Jpn. J. Appl. Phys.*, **33**, 3984 (1994).
18. K.H. Yoon, E.S. Kim, and J.-S. Jeon, *J. Eur. Ceram. Soc.*, **23**, 2391 (2003).
19. A.J. Bosman and E.E. Havinga, *Phys. Rev.*, **129**, 1593 (1963).