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Microwave dielectric ceramics in the system BaO–Li_2O–Nd_2O_3–TiO_2

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Abstract

Ceramics in the system BaO-Li_2O–Nd_2O_3–TiO_2 (BNT–LNT) were prepared by the mixed oxide route. Powders were mixed, milled, calcined and sintered at 1475°C for 4 h. Fired densities decreased steadily along the series from BNT to LNT. The microstructures of samples rich in BNT were dominated by small needle-like grains; the LNT samples comprised larger (6 μm) cubic grains. X-ray diffraction showed that there was a transition from orthorhombic BNT to cubic LNT; small amounts of LNT could be accommodated in BNT, but between 10–20% LNT there was the development of the second phase. Small additions of LNT led to a small increase in relative permittivity, but decreased the dielectric *Q*-value (from the maximum of 1819 at 4 GHz). As BNT and LNT exhibit negative and positive temperature dependencies of permittivity respectively, the addition of 10–20% LNT to BNT should yield samples with zero temperature dependence of ε_r Impedance spectroscopy showed that data could only be acquired at elevated temperatures for BNT rich samples (above 500°C), but at modest temperatures (less than 100°C) for the more conductive LNT. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: BaO–Li_2O–Nd_2O_3–TiO_2; Electron microscopy; Impedance spectroscopy; Microwave dielectric ceramics

1. Introduction

For over 20 years, ceramics based on BaO–(RE oxide)–TiO_2 (where RE = rare earth), particularly those of the system BaO–Nd_2O_3–TiO_2, have been the subject of detailed study because of their suitability for application in microwave resonators.[1–4] Wakino et al.[1] demonstrated that additions of Pb, for example, could overcome the strong negative temperature dependence of permittivity of the undoped end-member, to yield materials suitable for practical exploitation. High relative permittivity, around 90, and moderate $Q \times f$ (product of dielectric *Q*-value and resonant frequency) values ~6000, with temperature dependencies close to zero[1,5] enabled this to become a reality.

The complexity of the large orthorhombic unit cell of BaO–Nd_2O_3–TiO_2 and its analogues have led to ambiguities in details of the crystal structure.[6–9] However, the existence of comparatively large channels within the structure, and the possibility of multiple substitutions, has made the material attractive for tailoring properties by selective doping. Lead–bismuth oxide combinations are now well established[1,5] but many others have been proposed. Takahashi et al.[9] indicated that additions of alkaline earth oxides may be beneficial in certain circumstances.

In this study, microwave ceramics based on BaO–Nd_2O_3–TiO_2 (BNT), and Li_2O–Nd_2O_3–TiO_2 (LNT), both with constituents in 1:1:4 combinations have been investigated. The objective was to assess the potential of Li_2O additions to BNT based dielectric ceramics.

2. Experimental

All samples were prepared by the mixed oxide route. The stock end-member powders, undoped BNT and LNT, were prepared by mixing appropriate amounts of reagent grade (>99%) $BaCO_3$ (Alfa), Nd_2O_3, Li_2CO_3, and TiO_2 (Fluka Chemika) to form 1:1:4 compositions. These were wet milled in propan-2-ol with zirconia media (balls:powder 1:3 by weight) for 22 h, calcined at 1250°C for 4 h, wet milled again for 22 h and dried. To form the mixed compositions, controlled amounts of calcined LNT (2–30 wt.%) were added to calcined BNT (Table 1). The mixed powders were wet milled and dried as described above.

Pellets were formed by uniaxially pressing powders in steels dies (10 or 15 mm diameter) at a pressure of 100 MPa; these were sintered at 1475°C for 4 h in an oxygen atmosphere. The resulting compacts were

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typically 3–4 mm thick. Densities were determined from weight and dimension measurements.

X-ray diffraction was carried out using CuK_α radiation in a Philips X'pert APD system operating at 50 kV. Each sample was scanned over the range 20–60° in steps of 0.05°. For microstructural analysis selected samples were observed in the as-sintered condition; the remainder were ground on 1200 grade SiC, polished on diamond paste to 1 μm and with an oxide powder suspension (OPS), and thermally etched at 1275°C for 12 min. Following optical microscopy, samples were studied by scanning electron microscopy (Philips 505 SEM, equipped with EDS).

Relative permittivity and dielectric Q-values were determined at 4 GHz using the Hakki and Coleman[11] dielectric resonator method. To examine the temperature dependence of permittivity, the capacitance was measured at 1 MHz at temperatures from 30 to 110°C using an impedance analyser (HP 4192A) to yield τ_{ε_r} values.

Table 1
Samples, designations and BNT/LNT content

Sample	(wt.%) LNT added	LNT content (mol%)	Ba/Li (atomic ratio)
BNT	–	0	–
B/2LNT	2.0	2.2	20.67
B/5LNT	5.0	5.5	8.03
B/8LNT	8.0	8.8	4.87
B/10LNT	10.0	11.0	3.82
B/20LNT	20.0	21.7	1.69
B/30LNT	30.0	32.2	0.99
LNT	–	100	–

Preliminary impedance spectroscopy of selected samples (BNT, B/8LNT, LNT) was undertaken. Discs, approximately 8 mm diameter, were reduced in thickness to 0.5 mm and gold coated. The samples were connected to the impedance analyser (HP 4192A) with Pt wires, and examined at temperatures from 120 to 600°C at frequencies from 5 Hz to 1.3 MHz.

3. Results and discussion

3.1. Physical properties

The densities of the sintered ceramics are shown in Fig. 1. Addition of LNT to BNT causes a marked reduction in density. This in part reflects the relative molar masses of Ba and Li, but may also reflect a possible change in the sintering mechanism.

X-ray diffraction spectra for BNT and LNT ceramics are presented in Fig. 2. These are in good agreement with the results of Gens et al.[12] and Takahashi et al.[10] for undoped BNT and undoped LNT (having the 1:1:4 composition) respectively. The X-ray diffraction spectra of these end member compositions are compared with those for specimens doped with 2–30 wt.% LNT in Fig. 3. When the LNT content is less than 10% the differences between the spectra are very limited. However, for ceramics containing 20% or more LNT there are significant changes in the shape and position of the spectral peaks (including, for example, the disappearance of the shoulder to the peak at 2θ~47.5°) suggesting the transformation from the complex orthorhombic structure of BNT to the cubic structure of LNT.[8]

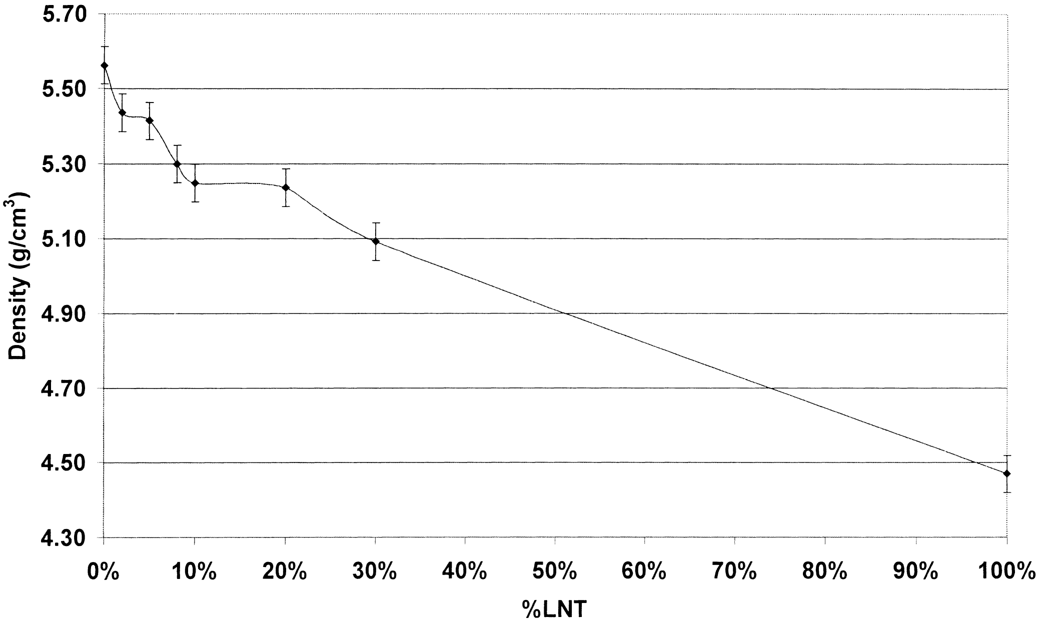

Fig. 1. Density of samples as a function of LNT content.

3.2. Microstructure

SEM micrographs of the as sintered surfaces of BNT and LNT are shown in Fig. 4. Major differences between the microstructures are apparent; BNT is characterised by needle like grains with an average grain size of 2 μm, whilst LNT consists of much larger grains (typical size 6 μm), with a quasi-rectangular shape. This difference reflects the crystal structures of the two end members (orthorhombic and cubic respectively).

All the specimens were examined in detail after polishing and etching. Table 2 summarises the grain sizes of specimens as a function of composition. There is very little change in grain size for specimens containing up to

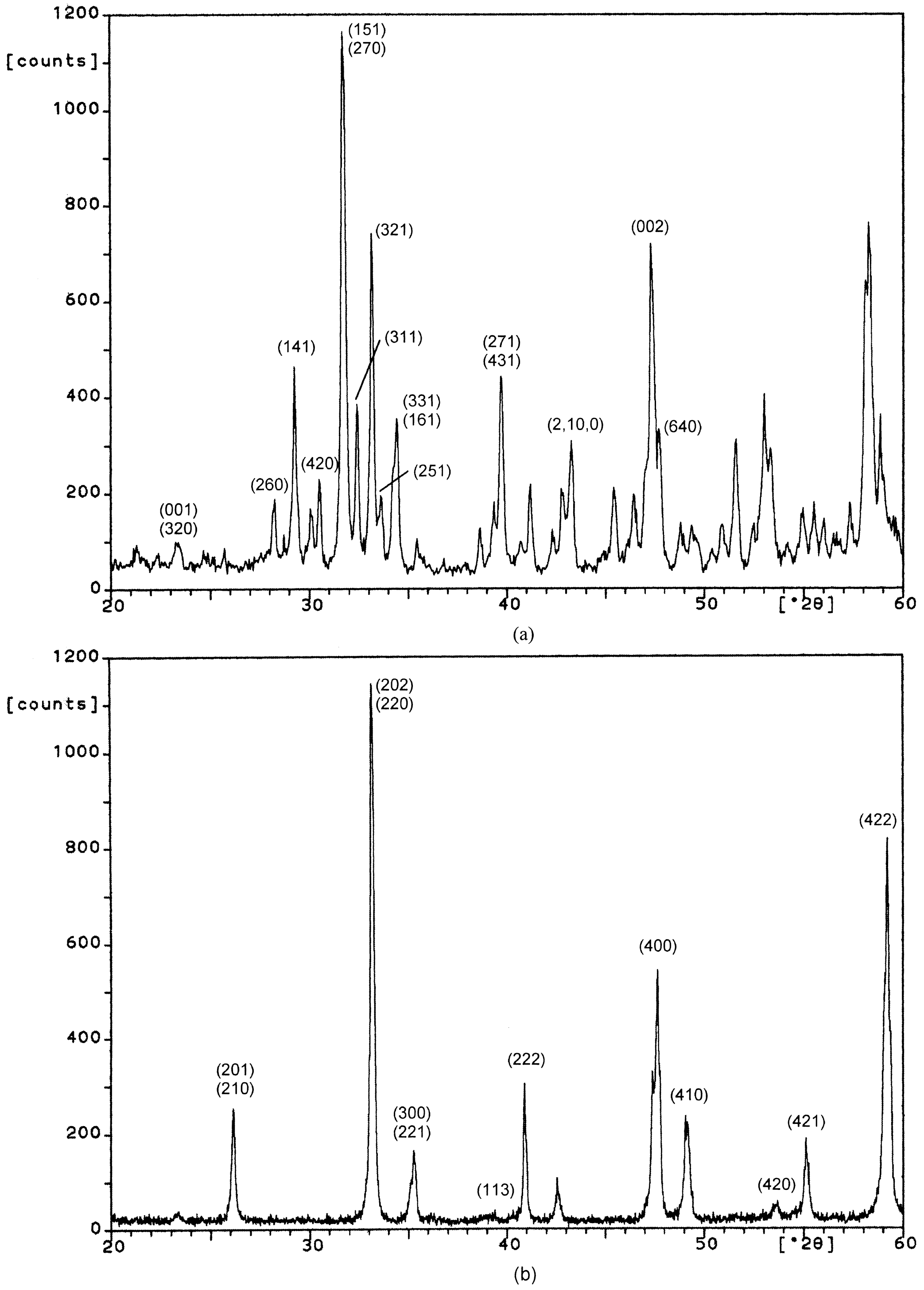

Fig. 2. X-ray diffraction spectra of (a) BNT and (b) LNT.

30% LNT; in contrast the grain size of the cubic end-member LNT is almost three times that for the other compositions.

Fig. 5 shows SEM micrographs of specimens BNT, B/2LNT and B/30LNT. The interlocking network of needle-like grains in BNT leads to the development of a high-density microstructure (Fig. 5a). There is only limited evidence of porosity. With the addition of only 2% LNT there is significantly more porosity (Fig. 5b) and a reduction in density (Table 1). SEM micrographs and backscattered electron images of samples containing up to 10% LNT showed no evidence of second

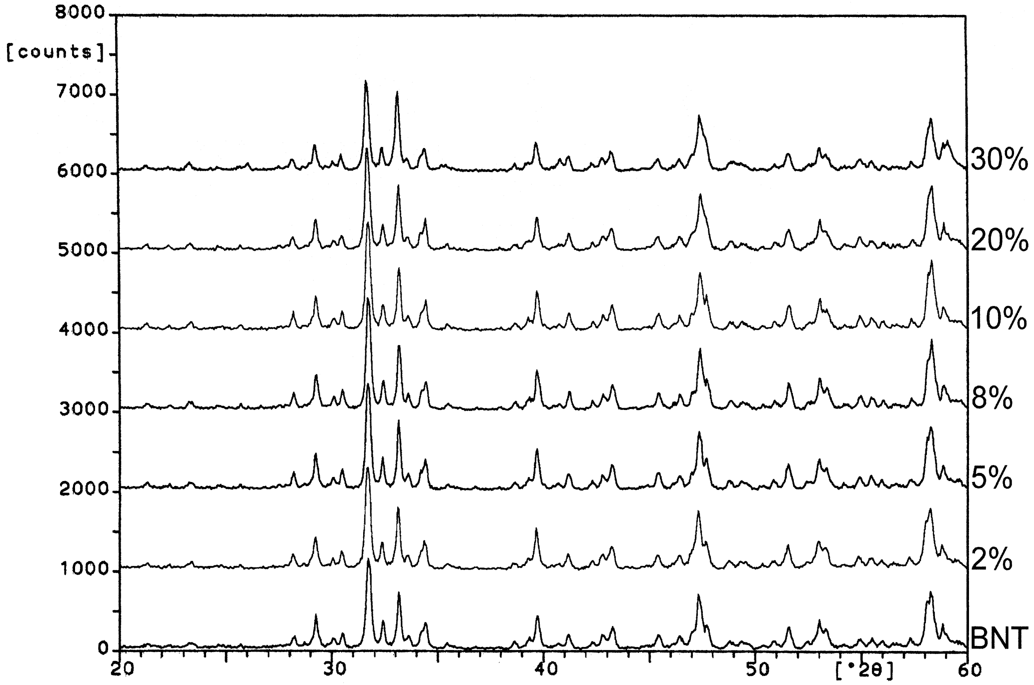

Fig. 3. X-ray diffraction spectra of BNT, B/2LNT, B/5LNT, B/8LNT, B/10LNT, B/20LNT and B/30LNT.

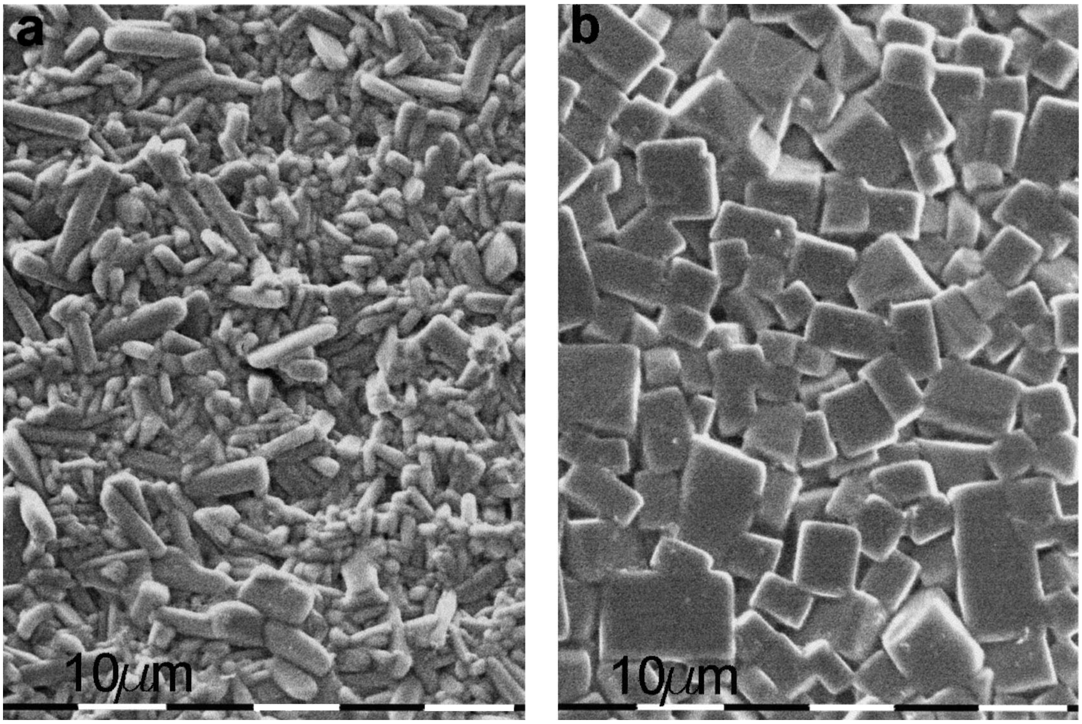

Fig. 4. SEM micrographs of as-sintered (a) BNT and (b) LNT.

phase. This is consistent with the X-ray diffraction spectra which indicated that small additions of LNT cause only a small distortion of the crystal structure of BNT (revealed by the limited displacement of the X-ray peaks) but not the large scale disruption of the BNT structure that would lead to the development and possible precipitation of a different phase.

At higher levels of LNT additions (above 10% or more), there is clear evidence of the formation of a second phase in SEM micrographs and backscattered electron images. Fig. 5c (B/30LNT) shows an example of the formation of a large second phase (indicated by the arrow) with a very distinct shape within the matrix of BNT). The precipitation behaviour appears to depend upon the amount of LNT present. In samples prepared with 20% LNT additions the second phase grains are small and well dispersed within the microstructure; in the 30% LNT samples, the second phases are larger and more localised (e.g. Fig. 5c). The transition from single phase to two phase structure appears to occur at addition levels between 10% and 20% LNT.

Micrographs showed that small additions of LNT (e.g. up to 10%) reduced the effectiveness of the sintering process and led to the development of increasing amounts of porosity (reflected in the reduction in density, Fig. 1). However, at higher levels of LNT (20% and more) there was a marked reduction in the levels of porosity, with a strong suggestion of liquid phase formation during sintering.

Table 2
Grain sizes of BNT–LNT ceramics

Sample	Grain size (μm)
BNT	1.8±0.1
B/2LNT	2.0±0.1
B/5LNT	1.9±0.1
B/8LNT	2.0±0.1
B/10LNT	2.3±0.1
B/20LNT	2.3±0.1
B/30LNT	2.3±0.1
LNT	6.5±0.1

3.3. Dielectric properties

The dielectric properties of ceramics in the system BNT–LNT are shown in Table 3 and Figs. 6 and 7. It is clear that small additions of LNT to BNT lead to a small increase in the relative permittivity, reaching a maximum when the LNT content is 5% ($\varepsilon_r = 89$). Further additions of LNT reverse this trend and progressively reduce the relative permittivity; the reduction in ε_r beyond 5% LNT is almost linear with the change in composition, reaching a minimum at 100% LNT ($\varepsilon_r = 64$).

Dielectric losses exhibit a different trend with composition; even modest additions of LNT (e.g. 2%) to BNT cause a marked reduction to the dielectric Q-value at 4 GHz (from 1819 to 1350). Further additions of LNT (up to 20%) led to a slight recovery in Q-value to 1377 (probably assisted by the change in sintering mechanism and increased densification). Nevertheless, additions of

Table 3
Microwave dielectric properties of ceramics in the BNT–LNT system

Sample	Q (4 GHz)	f_0	ε_r	τ_{ε_r} (ppm/K)
BNT	1819	4.335	86	−121
B/2LNT	1351	4.257	86	−149
B/5LNT	1247	4.231	89	−184
B/8LNT	1272	4.268	88	−191
B/10LNT	1349	4.296	87	−230
B/20LNT	1377	4.400	83	+46
B/30LNT	1032	4.377	82	+419
LNT	478	4.748	64	+1694

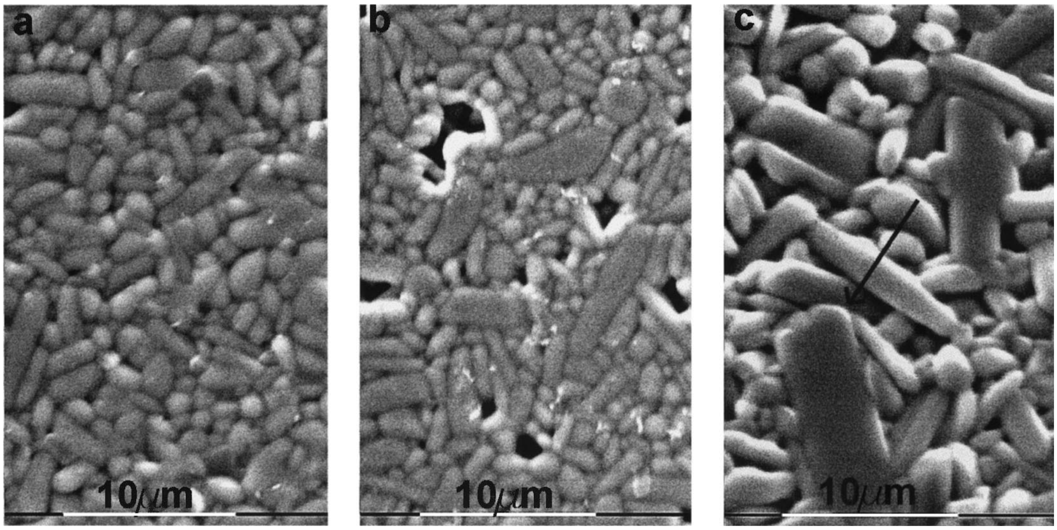

Fig. 5. SEM micrographs of (a) BNT, (b) B/2LNT and (c) B/30LNT after etching.

LNT are detrimental to the *Q*-value of BNT based ceramics, and LNT itself has a very low *Q*-value of 478 (at 4 GHz).

In spite of the deleterious effects of LNT to loss characteristics of BNT ceramics, the potential benefits of such additions are highlighted in Fig. 7. BNT ceramics have a strong negative temperature coefficient of permittivity (τ_{ε_r}).[1,4,5] In contrast, LNT has a strong positive temperature dependence (Fig. 7). As moderate amounts of LNT (less than 10%) are added to BNT, the τ_{ε_r} value becomes increasingly negative. At higher levels of LNT addition there is almost a linear increase in τ_{ε_r} up to the value of +1694 ppm/K for end member LNT. Between 10 and 20% LNT addition there is a strong suggestion that τ_{ε_r} should tend to zero (Fig. 7). This offers another possible way of improving the temperature stability of BNT based ceramics. It is important to note that these results for the temperature dependence of capacitance/permittivity were obtained at low frequency (1 MHz) and detailed verification of the behaviour at microwave frequencies is essential.[13]

Finally, impedance spectroscopy of selected samples was undertaken across the frequency range 5 Hz to 1.3 MHz at a range of temperatures (Fig. 8). For BNT

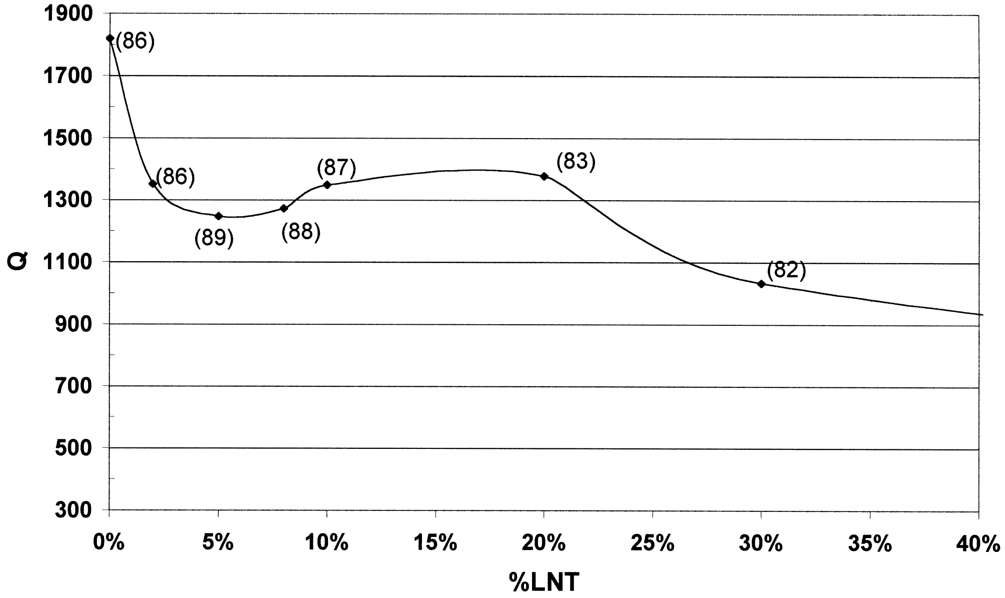

Fig. 6. Dielectric *Q*-value and relative permittivity (values shown in parentheses) at 4 GHz of BNT–LNT ceramics.

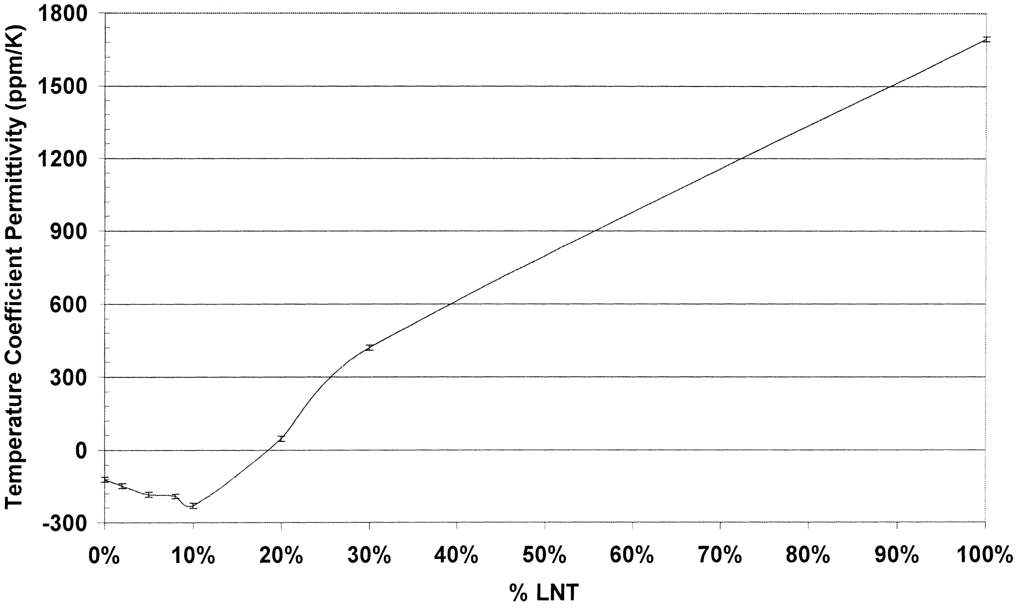

Fig. 7. Temperature coefficient of permittivity at 1 MHz of BNT–LNT ceramics.

and B/8LNT samples, the resistivity data are dominated by a single semicircle (Fig. 8a and b), although there is a suggestion of an additional very small semicircle, at low frequencies. Such data for samples rich in BNT could only be obtained at elevated temperatures, 560°C in this case. In spite of the similarity in the form of the impedance spectroscopy plots for these two samples, it should be noted that the low frequency intercept with the ρ' axis for BNT occurs at approximately 20 000 Ωm, whilst the equivalent intercept for B/8LNT occurs at 80 000 Ωm. This distinction is surprising when it is noted that BNT exhibits a higher dielectric *Q*-value than B/8LNT; it may have been anticipated that samples with higher *Q*-values are associated with higher grain boundary resistance. In contrast to the single semicircies obtained for BNT and B/8LNT in Fig. 8a and b, the results for LNT (Fig. 8c) are characterised by *at least* two semicircies and much lower impedance values. Clearly LNT is much more conductive than BNT-based ceramics, and it should be noted that impedance spectroscopy data for LNT could be acquired at temperatures as low as 90°C, compared to temperatures in excess of 500°C for BNT. The prime purpose of introducing the impedance spectroscopy data in this study is to demonstrate that the technique is sensitive to comparatively small differences in dielectric properties in highly resistive microwave ceramics, and the technique has potential for exploring *local* properties in such materials. A more detailed impedance spectroscopy study of BNT ceramics will appear elsewhere.

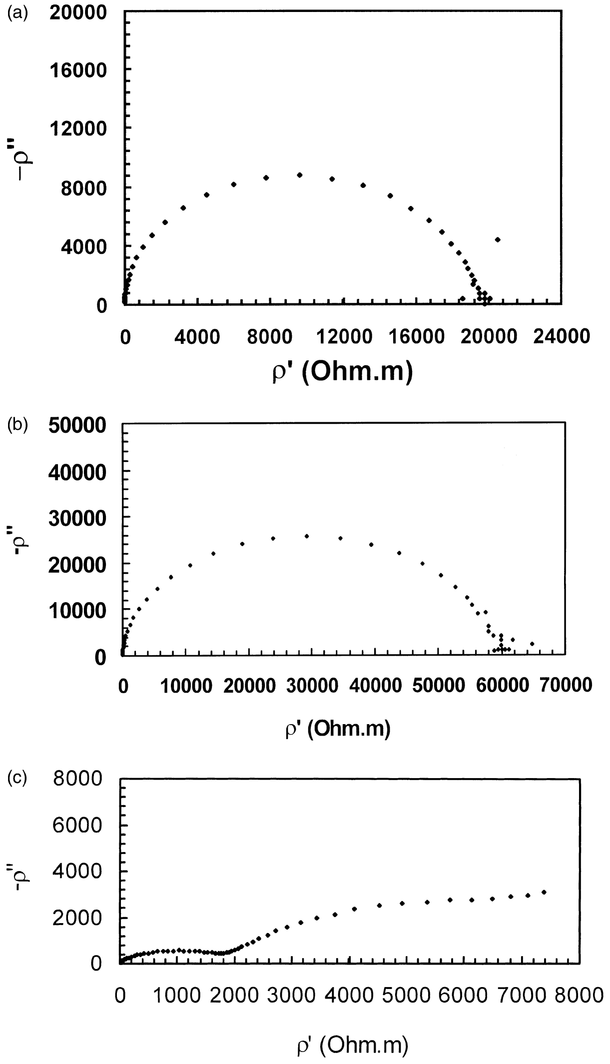

Fig. 8. Impedance spectroscopy (resistivity) data for (a) BNT, measured at 560°C, (b) B/8LNT, measured at 560°C, and (c) LNT, measured at 90°C.

4. Conclusions

Small additions of LNT (up to 10%) to BNT ceramics tend to reduce the effectiveness of the sintering process. Higher amounts of LNT appear to lead to the formation of a liquid-phase during sintering and improvement in densification. Nevertheless, there is a steady reduction density from BNT to LNT.

Small amounts of LNT can be accommodated in the BNT structure, but above 10% substitution of LNT there is the development of a second phase and eventually the transition from the orthorhombic structure of BNT to the cubic structure of LNT.

The relative permittivity of BNT containing small amounts of LNT (up to 10%) is higher than that of undoped BNT (86), reaching a maximum of $\varepsilon_r = 89$ (for LNT content of 5%). Greater additions of LNT cause a steady decrease in ε_r to the minimum of 64 for LNT.

The maximum dielectric *Q*-value in BNT–LNT ceramics is achieved in the BNT end member; even small additions of LNT degrade the *Q*-value.

As BNT and LNT exhibit negative and positive temperature dependencies of τ_{ε_r} respectively, then additions of between 10 and 20% LNT to BNT should yield ceramics with zero temperature dependence of τ_{ε_r}.

Impedance spectroscopy of ceramics in the BNT–LNT system showed marked differences. Data for BNT containing modest amounts of LNT could only be obtained at elevated temperature, reflecting the resistive nature of the ceramics; for the more conductive LNT, data could be acquired at temperatures as low as 90°C.

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