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The Effect of $La_2Ti_3O_9$ Second Phase on the Microstructure and Dielectric Properties of $La_2Ti_2O_7$ Ceramics

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Abstract

Lanthanum dititanate ceramics have been prepared by the mixed oxide route. Up to 6 mol% Nb_2O_5 or 10 mol% excess TiO_2 was added to the starting mixes. Sintered products exhibited densities of ≥ 95% theoretical. $La_2Ti_3O_9$ was present as a second phase in all doped samples. With the addition of increasing amounts of Nb_2O_5 or TiO_2 there was formation of $La_2Ti_3O_9$ within the $La_2Ti_3O_9$ matrix, and the average grain size decreased slightly. Dielectric properties were sensitive to the presence of the second phase: relative permittivity increased from 47 to ~56 with additions; the dielectric loss tangent was independent of the amount of excess titania but increased dramatically when > 3 mol% Nb_2O_5 was added; the temperature coefficient of capacitance (TCC) decreased monotonically from +50 ppm/°C for undoped $La_2Ti_2O_7$ ceramics to —50 ppm/°C for specimens containing ~10 mol% additions. Material with zero TCC can be achieved with the addition of ~5 mol%, Nb_2O_5 or excess TiO_2.

1 Introduction

Lanthanum dititanate, ($La_2Ti_2O_7$) is an important member of the ferroelectric family, having the general formula $A_2B_2O_7$ and a layered perovskite structure. Investigations of the electrical properties of $La_2Ti_2O_7$ ceramics commenced over 30 years ago,[1,2] but more recent studies of single crystals revealed that lanthanum dititanate has a very high Curie temperature (1500°C)[3] and exhibits strong piezoelectric and electro-optic effects.[4] The room temperature structure of $La_2Ti_2O_7$ is essentially monoclinic, although two modifications have been proposed; one with symmetry $P2_1$[5,6] and one with symmetry $Pbn2_1$.[7] The structure changes to orthorhombic ($Cmc2_1$) at approximately 780°C, and at 1500°C it transforms into the paraelectric phase.[8] The layered perovskite (or perovskite - slab) structure contains slabs of four distorted TiO_6 octahedra linked by La atoms.[5] The structural anisotropy is expected to lead to anisotropy in dielectric and electrical properties.[9]

With its unusually high Curie temperature and temperature-stable dielectric properties, $La_2Ti_2O_7$ is a candidate for high temperature piezoelectric and electro-optic devices,[9] and microwave frequency components.[10]

Ceramics of $La_2Ti_2O_7$ have mainly been prepared by the classical mixed oxide route,[1,2] although Fuierer and Newnham[9] employed Evaporative Decomposition of Solutions (EDS) and molten salt synthesis routes. Takahashi and Kageyama[11] used a coprecipitation method to prepare ceramics of mixed phases of $La_2Ti_2O_7$ and $La_2Sn_2O_7$. Most studies to date have focussed on the microstructure and properties of the end member $La_2Ti_2O_7$, or solid solutions involving this compound.[11,12] The primary objectives of the present study were to assess the effect of (i) excess TiO_2, and (ii) additions of Nb_2O_5 on the behaviour of $La_2Ti_2O_7$ prepared by the mixed oxide route. Specific attention was paid to the role and effect of second phase $La_2Ti_3O_9$.

2 Experimental

Two series of samples were prepared by the standard mixed oxide route: (A) $x\mathrm{TiO_2}.(1\text{-}x)\mathrm{La_2Ti_2O_7}$ where x = 0, 0·02, 0·04, 0·06, 0·08 and 0·10; (B) $y\mathrm{Nb_2O_5}.(1\text{-}y)\mathrm{La_2Ti_2O_7}$, where y = 0, 0·005, 0·015, 0·03 and 0·06.

Hence $x = y = 0$ represents the undoped, $La_2Ti_2O_7$ reference composition.

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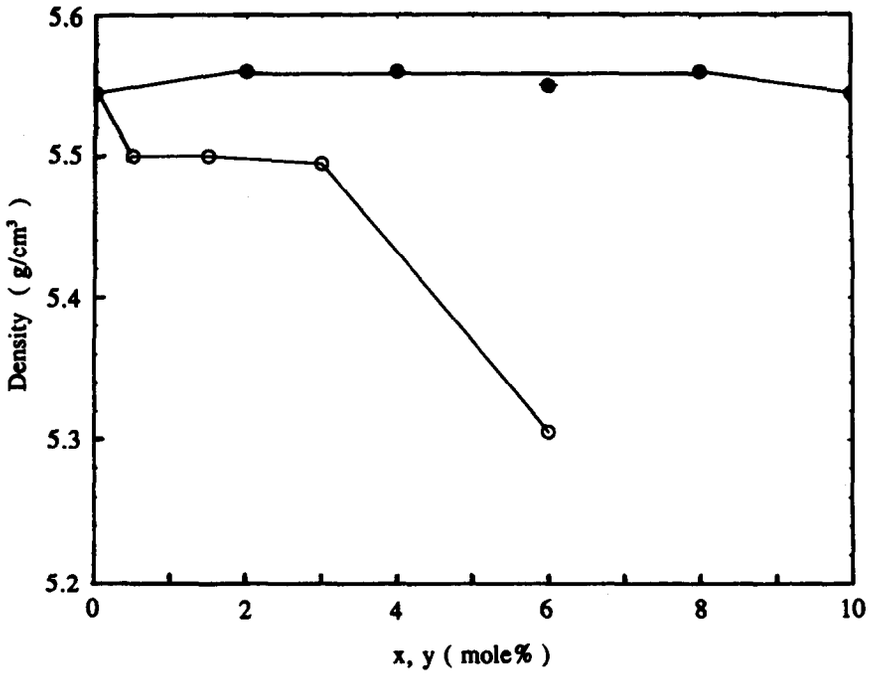


Fig. 1. Specimen densities as a function of additive content: ○ Nb_2O_5; ● TiO_2.

The starting materials were La_2O_3, TiO_2 (Fluka, purity of 99·98, and 99% respectively) and Nb_2O_5, (BDH, purity 99·5%). Prior to weighing the lanthanum oxide was dried by heating at 700°C for 4 h. Powders of La_2O_3 and TiO_2, in the molar ratio of 1 : 2, were mixed and vibration-milled in propan-2-ol with zirconia balls for 6 h. The dried mixtures were then calcined at 1100°C for 4 h. The required amounts of excess TiO_2 or Nb_2O_5 were added to batches to form compositions in the series (A) and (B). The powders were then remilled in propan-2-ol for 8 h. Pellets 16 mm in diameter and 8 mm high were pressed uniaxially at 900 kg/cm^2 without binder and then sintered at temperatures in the range 1300–1400°C for 4 h. Specimens for electrical measurements, diameter ~12·4 mm and thickness typically 1·4 mm, were cut from the sintered pellets. Specimens for microstructural studies were ground to 1200 grade SiC, polished with diamond paste down to 1/4 μm and then thermally etched at a temperature of approximately 1150°C.

X-ray diffraction analysis was carried out using Cu K_α radiation with a Philips PW1710 diffractometer and horizontal goniometer. Microstructures were studied by optical microscopy and scanning electron microscopy, Philips SEM 505 with energy

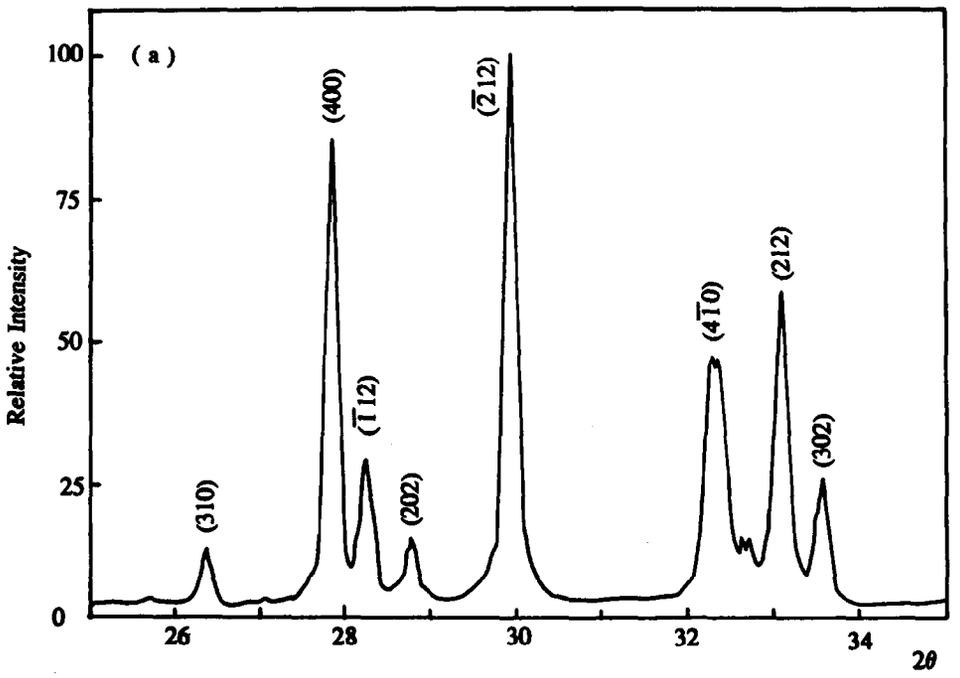


Fig. 2. X-ray diffraction spectra for ceramic specimens prepared from starting mixes $(y)Nb_2O_5.(1\text{-}y)La_2Ti_2O_7$, (a) $y = 0$; (b) $y = 0{\cdot}015$; (c) $y = 0{\cdot}06$. $LT_2 = La_2Ti_2O_7$; $LT_3 = La_2Ti_3O_9$.

dispersive X-ray analyser EDAX, model 9100. For each specimen, 5–8 grains of each type were analysed and the average composition determined. Area fractions of each phase, based upon contrast differences, were determined manually, after applying fine mesh grids to SEM micrographs for each specimen. The average grain sizes were obtained by the mean linear intercept method.

A Hewlett Packard 4284A precision LCR meter was used to determine relative permittivity (via capacitance measurements) and loss factor as a function of temperature from 15 to 120°C at frequencies up to 1 MHz. Values for the temperature coefficient of capacitance (TCC) were determined from data obtained in the range 15–85°C.

3 Results and Discussion

3.1 Specimen density

Figure 1 shows the densities for specimens of the two series as a function of composition. The theoretical density for $La_2Ti_2O_7$ is 5·782 gm cm^{-3} [13] and that of the related phase $La_2Ti_3O_9$, 5·325 gm cm^{-3}.[14] The presence of extra titania (Series A) did not have any significant effect on density. For all samples, density was approximately 96% theoretical. For the niobia-doped samples, densities were around 95% theoretical at low doping levels, but much lower in the specimens doped with 6 mol% Nb_2O_5.

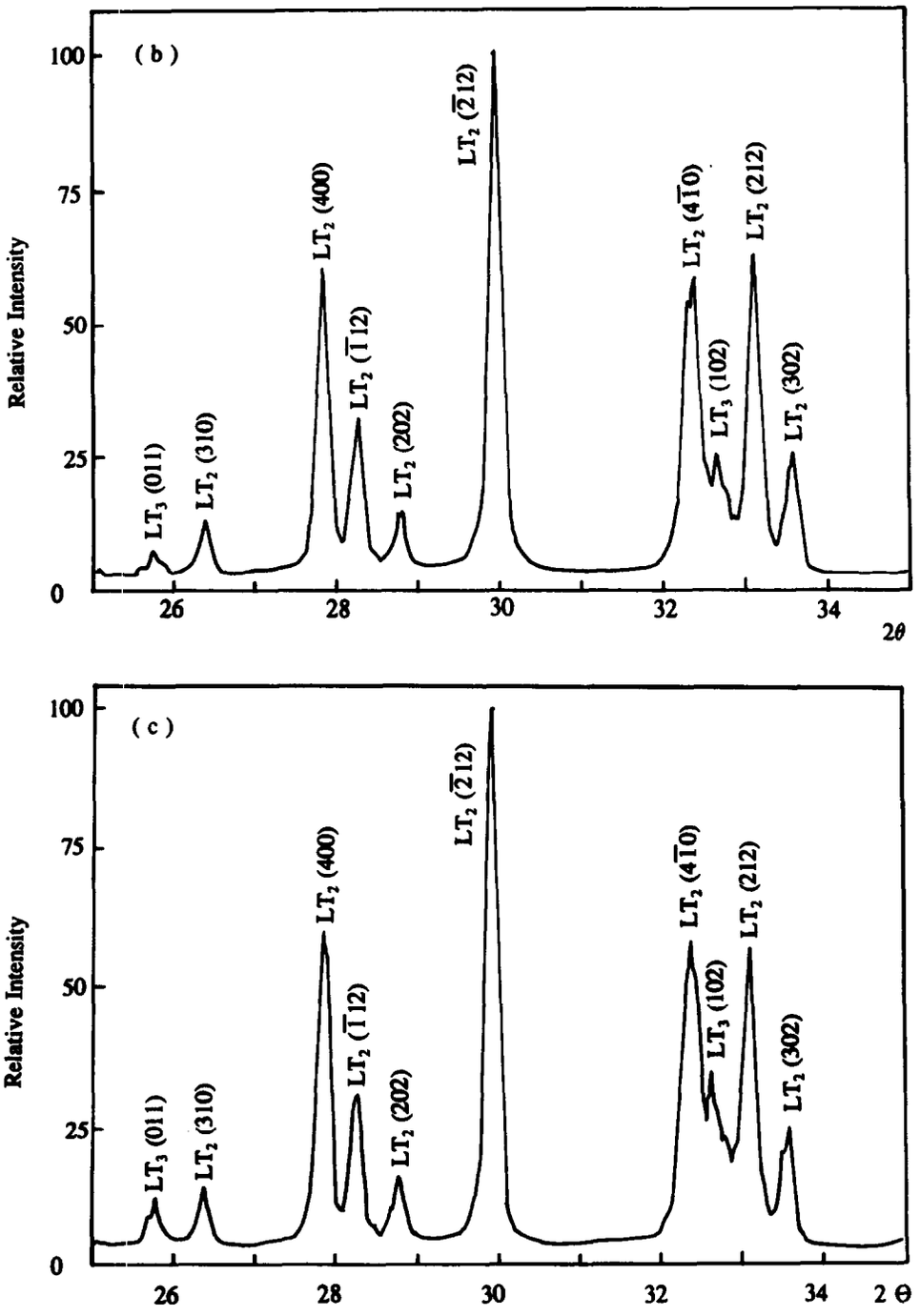


Fig. 2. — continued.

3.2 Phase analysis

Figure 2 shows parts of the X-ray diffraction spectra obtained for selected specimens. The major peaks for all the samples containing up to 6 mol% Nb_2O_5 (i.e. $y \leq 0{\cdot}06$) and up to 10 mol% excess TiO_2 (i.e. $x \leq 0{\cdot}10$) can be indexed to monoclinic $La_2Ti_2O_7$ with the space group as $P2_1$.[1] The positions and intensities of the peaks are in satisfactory agreement with published data.[13] In the X-ray diffraction spectra specimens, a number of extra reflections are present, e.g. near 25·8 and 32·7° 2θ (Figs 2(b) and (c)). None of the extra peaks could be assigned to the phase $La_4Ti_9O_{24}$, which is expected to be the nearest compound to $La_2Ti_2O_7$ on the TiO_2-excess side of $La_2Ti_2O_7$ in the phase diagram of the La_2O_3–TiO_2 system.[2] However, the positions and intensities of the extra peaks were found to represent $La_2Ti_3O_9$.[14] The peaks corresponding to the (011), (102) and (111) reflections of the $La_2Ti_3O_9$ phase grew in intensity as x and y increased. (NB: the peak for (111) occurs at 2θ angle of 40·50 which is outside the range covered by Fig. 2.)

3.3 Microstructures

Undoped $La_2Ti_2O_7$ specimens are single phase with a near homogeneous microstructure (Fig. 3). The grains, ranging in size from 10 to 30 microns, are somewhat elongated, but not to the degree reported by Fuierer[9] where the grains appeared as highly anisotropic platelets. For the specimens prepared with excess TiO_2, or Nb_2O_5 additions, a second phase is visible in SEM micrographs (e.g. Fig. 4) as clusters of grains much smaller than those of the major phase. These small grains look darker than the matrix, indicating lower average atomic number.

Quantitative EDAX analyses for the specimens prepared with excess titania gave a La:Ti ratio of approximately 50 : 50 for the large grains of the major phase (Table 1), irrespective of the level of TiO_2 added, and a La:Ti ratio of approximately 40 : 60 for the dark second phase grains (Table 2). These analyses confirm that the second phase in $La_2Ti_2O_7$ specimens prepared with excess TiO_2 is $La_2Ti_3O_9$.

For the Nb-doped materials, the elemental distribution is more complicated, because the Nb dopant atoms are incorporated into both the major and the second phases. EDAX analyses again gave a La:Ti atomic ratio of approximately

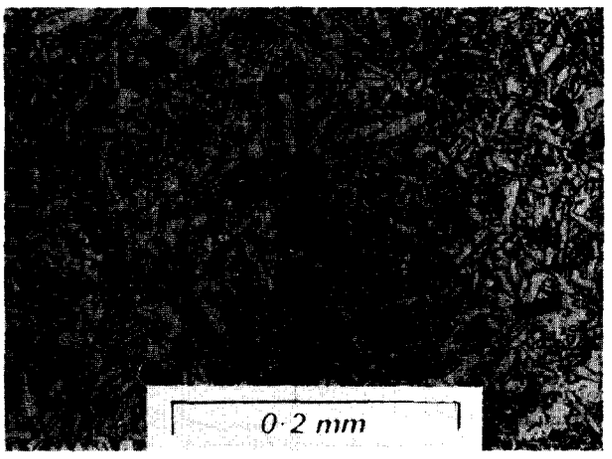
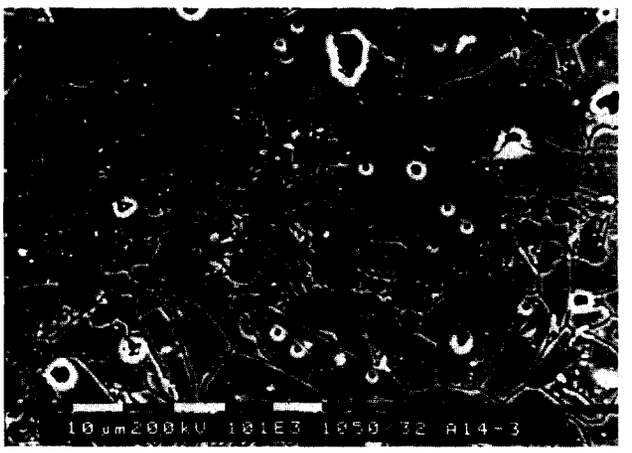
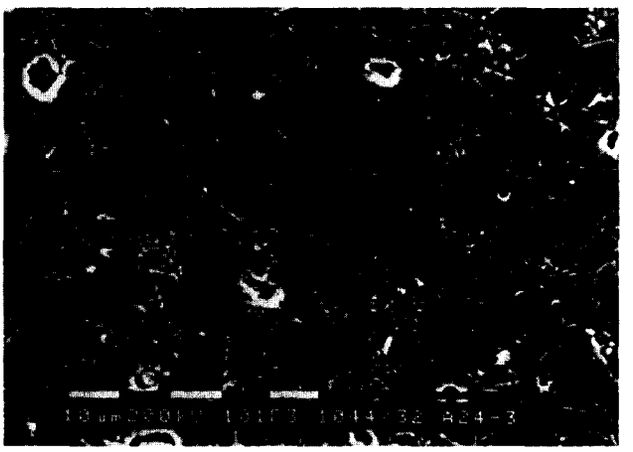


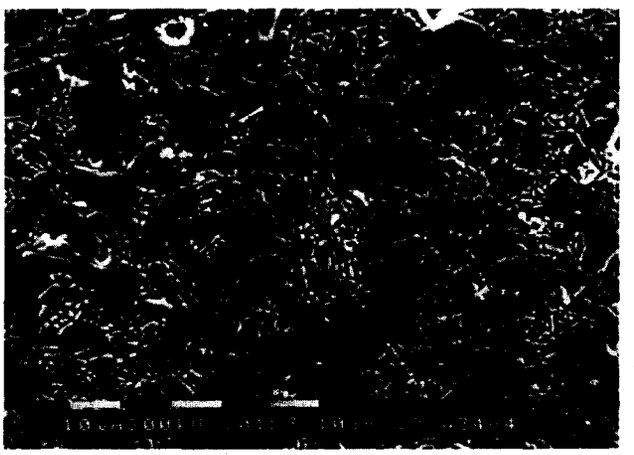
Fig. 3. Optical micrograph of polished and thermally etched $La_2Ti_2O_7$ ceramic.



(a)



(b)



(c)

Fig. 4. SEM micrographs of polished and thermally etched $La_2Ti_2O_7$-based specimens: prepared with (a) 0·5 mol% Nb_2O_5, (b) 3 mol% Nb_2O_5 and (c) 6 mol% Nb_2O_5.

Table 1. Elemental concentrations (atomic %) detected in the major phases of ceramics prepared from starting mixes $y Nb_2O_5.(1-y)La_2Ti_2O_7$ and $xTiO_2.(1-x)La_2Ti_2O_7$

	Mol% Nb_2O_5 additions (y)					*Mol% TiO_2 excess (x)*
	0	0·5	1·5	3·0	6·0	2·0,10·0
Nb	0	0·8	2·3	3·7	5·9	—
Ti	50·2	50·2	48·8	47·8	45·3	50·3
La	49·8	49·0	49·9	48·5	48·8	49·7
σ^a	0·45	0·83	0·74	0·60	0·90	1·0

[a] The maximum standard deviation for all the elements present in the specimen.

Table 2. Elemental concentrations (atomic %) detected in the minor phase of ceramics prepared from starting mixes $y Nb_2O_5.(1-y)La_2Ti_2O_7$ and $xTiO_2.(1-x)La_2Ti_2O_7$

	Mol% Nb_2O_5 additions (y)					*Mol% TiO_2 excess (x)*
	0	0·5	1·5	3·0	6·0	2·0,10·0
Nb	—	2·2	3·5	5·9	8·6	—
Ti	—	58·2	56·7	54·2	52·6	59·5
La	—	39·6	39·8	39·9	38·8	40·5
σ^a	—	0·71	0·82	0·54	0·87	0·83

[a] The maximum standard deviation for all the elements present in the specimen.

50:50 for the major phase, and approximately 40:60 for the minor phase (Tables 1 and 2). The concentrations of Nb atom in the two phases are shown as a function of the amount of dopant in Fig. 5. More niobium atoms enter the minor phase than the major phase. Since the ionic radii for Nb^{5+} and Ti^{4+} ions are very similar (0·78 and 0·745 Å respectively),[15] it is possible that Nb^{5+} ions enter the Ti^{4+} sites. The higher TiO_2 content in $La_2Ti_3O_9$ (75%) than in $La_2Ti_2O_7$ (67%), and therefore the availability for exchange with the dopant, may account for the uneven distribution of Nb between the two phases.

Kestigian and Ward[16] reported the preparation of $La_2Ti_3O_9$ in the presence of trivalent Ti^{3+} ions. Later, Marzullo and Bunting,[1] as part of a larger study concerned with TiO_2–Rare Earth Oxide compounds, reported the dielectric properties of $La_2Ti_3O_9$ produced by conventional ceramic methods. This intermediate phase was not shown in the phase diagram of the La_2O_3–TiO_2 system presented by MacChesney and Sauer.[2] Subsequently, several authors described the preparation (and some of the electric properties) of $La_2Ti_3O_9$ ceramics, e.g. prepared with a slight oxygen deficiency,[14,17] stabilized by 2+ or 1+ ions,[18–22] and prepared from coprecipitated powder.[23,24] For example, Nenasheva *et al.*[21] obtained similar results to those of MacChesney and Sauer[2] but noted that $La_2Ti_3O_9$ is unstable because there are vacancies on 1/3 of the sites in the *A* sublattice (i.e. $La_{2/3}\square_{1/3}TiO_3$, where $\square$ is a vacancy in the *A* sublattice of the perovskite structure compound $ATiO_3$); $La_2Ti_3O_9$ on its own decomposes into $La_2Ti_2O_7$ and rutile (TiO_2). Indeed, attempts by Nenasheva *et al.*[21] to synthesise $La_2Ti_3O_9$ by the mixed oxide route yielded only 80% of the desired perovskite structured phase with the remainder as $2La_2O_3.9TiO_2$. They confirmed that additions of $CaTiO_3$, $SrTiO_3$ or $PbTiO_3$ to a mixture of

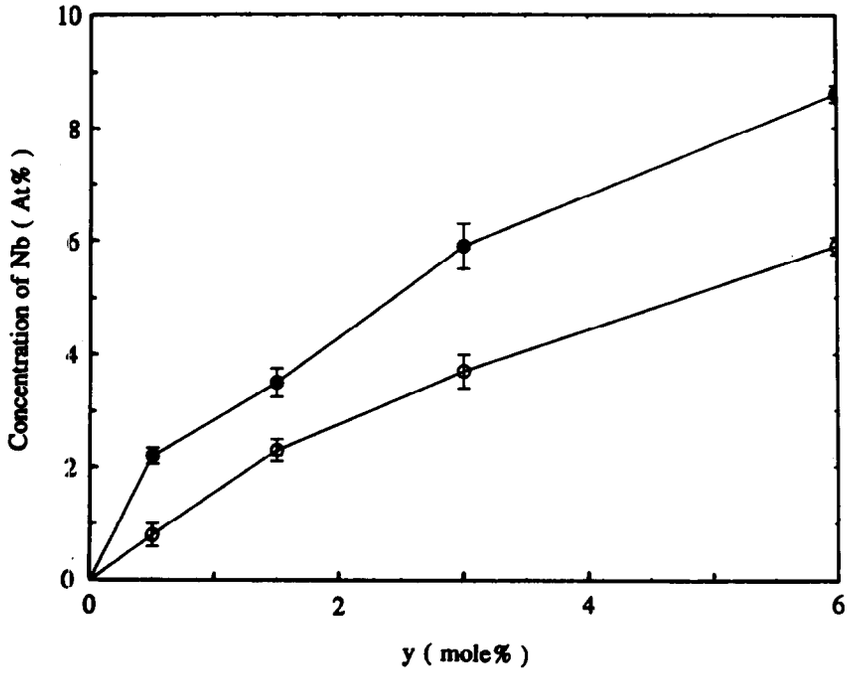


Fig. 5. Niobium (Nb) content of the major ($La_2Ti_2O_7$) phase (O) and minor ($La_2Ti_3O_9$) phase (●) of $La_2Ti_2O_7$ based-ceramics as a function of Nb_2O_5 content (y) of the starting mixture.

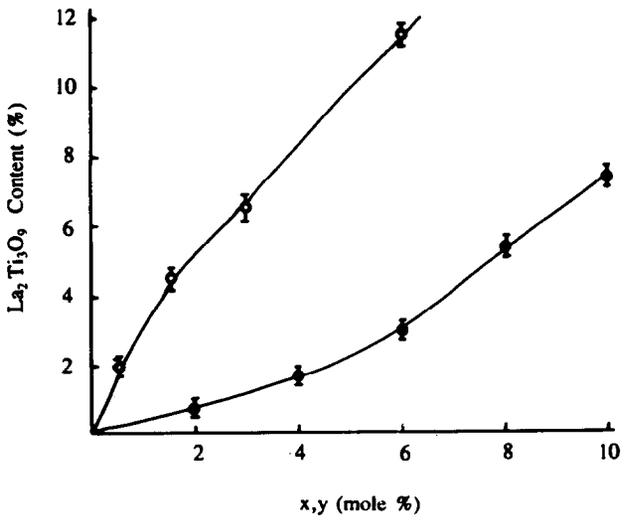


Fig. 6. Fraction of minor phase ($La_2Ti_3O_9$) in $La_2Ti_2O_7$ ceramics prepared with excess TiO_2 (●) and Nb^2O_5 (○) additions.

$La_2O_3.3TiO_2$ led to the formation of single phase perovskite-type structures ($A_{3/4}\square_{1/4}TiO_3$) although the use of lead titanate caused a tetragonal distorted structure (c/a = 1·004). In the present study, a compound of the formula $La_2Ti_3O_9$-type was formed as a second phase in ceramics in the La_2O_3-TiO_2 system prepared by means of the usual mixed oxide route when excess TiO_2 or Nb_2O_5 was present.

The formation of the phases in samples prepared with excess TiO_2 can be described by:

$$(1 - x)La_2Ti_2O_7 + xTiO_2 \rightarrow (1 - 2x)La_2Ti_2O_7 + xLa_2Ti_3O_9 \quad (1)$$

Thus in the case of specimens prepared with x mol% excess TiO_2, there should be $x/(1\text{-}x)$ mole of $La_2Ti_3O_9$ produced. For the samples doped with Nb_2O_5, the situation is more complex since the niobia enters both the primary $La_2Ti_2O_7$ and secondary $La_2Ti_3O_9$—type phases. However, if it is assumed that the Nb is located only on Ti sites, then we can envisage reactions of the form

$$(1 - y)La_2Ti_2O_7 + yNb_2O_5 \rightarrow (1 - 3y)La_2(Ti,Nb)_2O_7 + 2yLa_2(Ti,Nb)_3O_9 \quad (2)$$

Whilst accepting the approximate nature of eqns (1) and (2), it would appear that doping with niobia (eqn (2)) should generate more $La_2Ti_3O_9$ second phase than 'doping' with excess TiO_2 (eqn(1)). Figure 6, showing the $La_2Ti_3O_9$ content of the ceramics confirms that the niobia-bearing specimens contain typically 2—3 times more second phase than the samples prepared with excess titania.

The actual compositions of the products of the B series ceramics vary with doping level, but when y = 0·03 for example, typical analyses (Tables 1 and 2) indicate that the major and minor phases may be described as $La_2Ti_{1.97}Nb_{0.15}O_{7.3}$ and $La_2Ti_{2.72}Nb_{0.29}O_{9.16}$ respectively, when no allowance is made for any vacancies present.

In specimens of the Nb_2O_5-doped system, there is a tendency for the grain size to decrease as increasing amounts of dopant are employed; in addition, clusters of small grains appear, most of which are the minor phase, ($La_2Ti_3O_9$). SEM micrographs for three specimens in this series are shown in Fig. 4.

3.4 Dielectric properties

3.4.1 Relative permittivity

Figure 7 shows the relative permittivity of lanthanum dititanate ceramics as a function of added excess

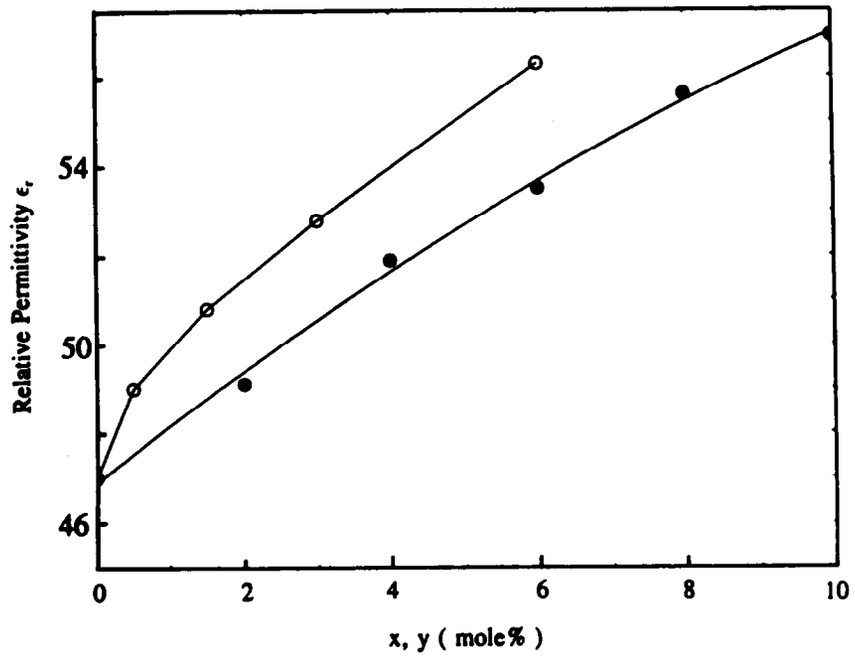


Fig. 7. Relative permittivity of $La_2Ti_2O_7$ ceramics at 1 MHz as a function of added Nb_2O_5 (○) and excess TiO_2 (●).

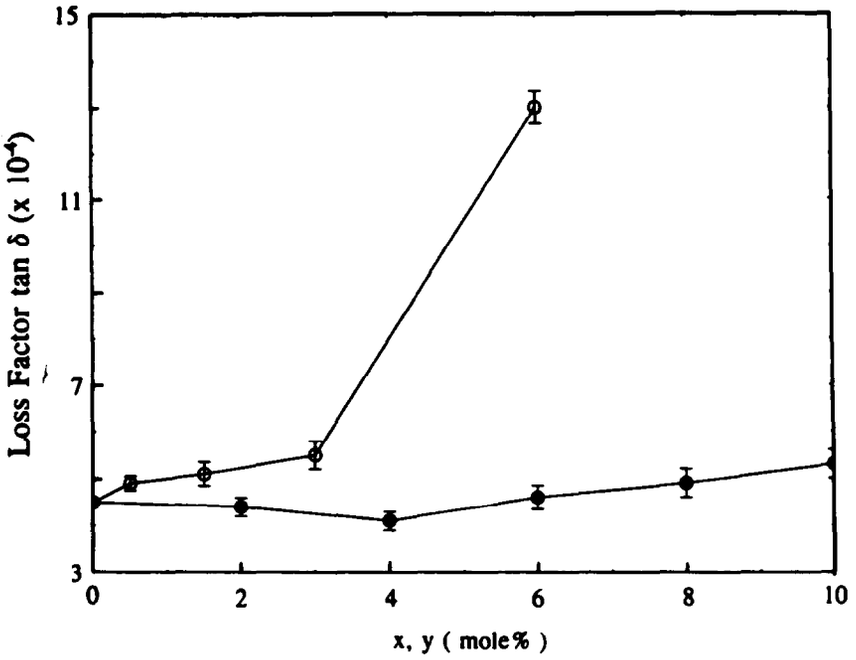


Fig. 8. Dielectric loss factor (tan δ) for $La_2Ti_2O_7$ ceramics at 1 MHz as a function of added Nb_2O_5 (○) and excess TiO_2 (●).

TiO_2 or Nb_2O_5 for the two systems. For the end-member $La_2Ti_2O_7$ the relative permittivity (at 1 MHz ~ 47) was higher than that reported by Mazullo and Bunting[1] (44) and Takahashi and Kageyama[11] (41), but close to that obtained by Fuierer and Newnham[9] for mixed oxide-prepared ceramics (48·8). The last named authors obtained marginally lower values for chemically prepared ceramics and hot forged specimens parallel to the forging direction. The increase in relative permittivity with increasing Nb_2O_5 or TiO_2 (Fig. 7) and the generation of the second phase (Fig. 6) suggests that the $La_2Ti_3O_9$ second phase has a higher relative permittivity than the primary $La_2Ti_2O_7$ phase. For the system with excess titania, extrapolation of the relationship between ε_r and composition (Fig. 7) indicates a relative permittivity of 77 for $La_2Ti_3O_9$. In spite of the long extrapolation this is clearly different from the value of 45 obtained by Marzullo and Bunting[1] (which is in fact lower than recent determinations of ε_r for the $La_2Ti_2O_7$ end member), but in excellent agreement with that reported by Nenasheva *et al.*[21] for $La_2Ti_3O_9$.

3.4.2 *Dielectric loss*

Undoped $La_2Ti_2O_7$ has a comparatively low dielectric loss with the Q value (Q ~ 1/tanδ) ranging from typically 1500 to 3500 at 100 kHz depending on the sintering and processing conditions. Winfield[12] obtained a Q value of 1250 at 1 MHz for mixed oxide prepared $La_2Ti_2O_7$ whilst Fuierer and Newnham[9] at 100 kHz obtained Q values of 900 for Evaporative Decomposition of Solution (EDS) derived material, 5300 for mixed oxide ceramics, 3500 and 4750 for molten salt synthesis products, 2600 and 2950 for hot forged samples. In general, the Q values increased with specimen density. The incorporation of excess titania does not increase the loss significantly (Fig. 8). This is predictable since, as shown in eqn (1), the addition of extra titania induces no defects which may serve as charge carriers and thereby increase conduction. However, a sharp rise in dielectric loss was observed for materials containing more than 2 mol% Nb_2O_5 (Fig. 8).

The substitution of Nb^{5+} into $La_2Ti_2O_7$ and $La_2Ti_3O_9$ requires the operation of some charge compensation mechanism to ensure charge neutrality. For the primary $La_2Ti_2O_7$ phase the situation in the undoped reference material can be described in terms of Kroger-Vink notation[25] by:

$$La_2O_3 + 2TiO_2 \rightarrow 2La_{La}^{x} + 2Ti_{Ti}^{x} + 7O_o^{x} \quad (3)$$

After doping with niobia, charge compensation could be achieved by:

(i) cation vacancies

$$5La_2O_3 + 4Nb_2O_5 \rightarrow 10La_{La}^{x} + 8Nb_{Ti}^{\bullet} + 2V_{Ti}^{''''} + 35O_o^{x} \quad (4)$$

or (ii) electronic defects

$$La_2O_3 + Nb_2O_5 \rightarrow 2La_{La}^{x} + 2Nb_{Ti}^{\bullet} + 7O_o^{x} + \tfrac{1}{2}O_2 + 2e' \quad (5)$$

Although the second phase ($La_2Ti_3O_9$) is much smaller in quantity, similar mechanisms may be envisaged for the incorporation of Nb. Starting with the undoped material:

$$La_2O_3 + 3TiO_2 \rightarrow 2La_{La}^{x} + 3Ti_{Ti}^{x} + 9O_o^{x} \quad (6)$$

After doping, charge compensation could be achieved by:

(i) cation vacancies:

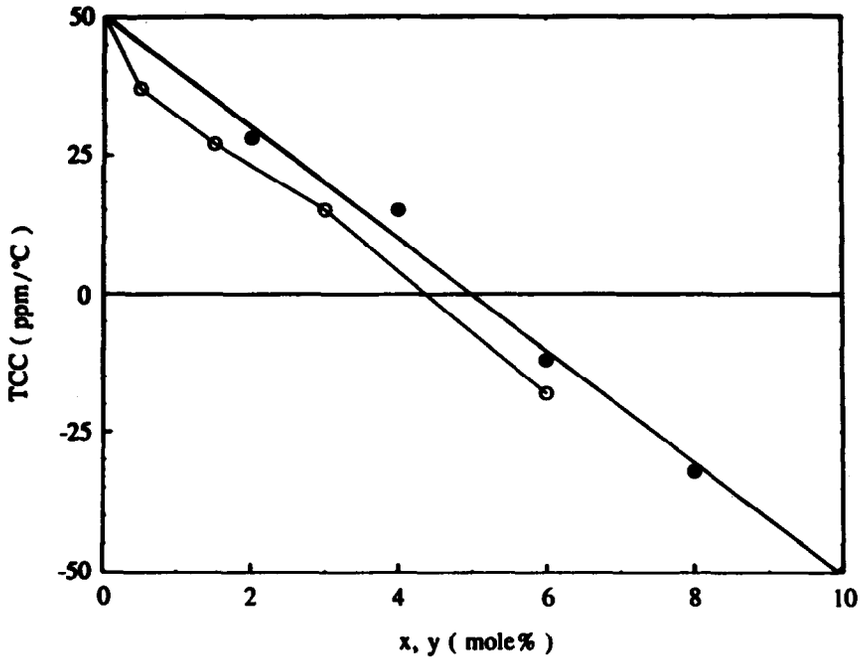


Fig. 9. Temperature coefficient of capacitance (TCC) of $La_2Ti_2O_7$-based ceramics as a function of added Nb_2O_5 (O) and excess TiO_2 (●).

$$5La_2O_3 + 6Nb_2O_5 \rightarrow 10La_{La}^{x} + 12Nb_{Ti}^{\bullet} + 3V_{Ti}'''' + 45O_o^x \quad (7)$$

or (ii) electronic defects

$$2La_2O_3 + 3Nb_2O_5 \rightarrow 4La_{La}^{x} + 6Nb_{Ti}^{\bullet} + 18O_o^x + 1\tfrac{1}{2}O_2 + 6e' \quad (8)$$

Thus, at small doping levels of Nb_2O_5, charge compensation can be achieved by cation vacancies (eqns (4) and (7)); at high doping levels there may be a transition to a compensation mechanism based on electronic defects (eqns (5) and (8)). Dielectric losses are higher in niobia-containing specimens than ceramics prepared with excess TiO_2 (Fig. 8), and losses increase rapidly above 2 mol% Nb_2O_5. It seems probable that charge compensation is by cation vacancies at the low Nb_2O_5 doping levels, but there is insufficient data to confirm whether or not there is any contribution from electronic defects at the higher doping levels.

The intrinsic losses in a material are defined by the lattice vibrational modes,[26] and these will be modified by the presence of significant numbers of defects. It is now established[27] that oxygen vacancies increase losses in $ZrTiO_4$-based dielectrics. In the lanthanum ditanate ceramics of the present study, the niobium atoms incorporated into the structure probably give rise to large numbers of cation vacancies, thereby modifying the lattice vibrational modes and increasing the dielectric losses (Fig. 8).

3.4.3 Temperature coefficient of capacitance (TCC)

It is of interest from a practical point of view to define temperature-stable ceramic compositions, particularly those which exhibit a zero value TCC. One of the standard methods to achieve this property is to prepare a solid solution from components which possess characteristics with negative and positive dependencies on temperature. Marzullo and Bunting[1] were the first to report TCC values for $La_2Ti_2O_7$ and $La_2Ti_3O_9$ of +30 and –60 ppm/°C respectively. This implies that a material with a zero TCC can be prepared if $La_2Ti_3O_9$ is introduced as a minor phase in a $La_2Ti_2O_7$ matrix. This presumption is justified by the temperature-dependence of the 'doped' materials shown in Fig. 9. With increasing Nb_2O_5 or excess titania, the TCC decreases linearly from a value of +50 ppm/°C in the undoped material to approximately –50 ppm/°C for starting compositions containing approximately 10 mol% of additions. The increasing amount of the $La_2Ti_3O_9$ phase appears to be responsible for this phenomenon.

The rate of change of TCC with additive level is greater for the niobium doped specimens than for TiO_2 excess specimens. This corresponds to the difference in the yield of the minor phases produced by equal amounts of additions. The TCC value of the sample prepared with 10 mol% excess titania is unexpectedly high in view of the previously reported value of –60 ppm/°C[1] for pure $La_2Ti_3O_9$. Due to the low level of additions, it is not possible to extrapolate the TCC data to that equivalent to the pure $La_2Ti_3O_9$ phase with any degree of reliability, but it can be anticipated that the value will be much lower than –60 ppm/°C, or even lower than the value of –170 to –200 ppm/°C

reported by Nenasheva *et al.*[21] for $La_2Ti_2O_7$–$La_4Ti_9O_{24}$ mixtures. The most interesting result, however, is that $La_2Ti_2O_7$-based compositions with zero TCC, and thus temperature stable dielectric characteristics, can be obtained by the addition of approximately 4·2 mol% Nb_2O_5 or 5 mol% excess TiO_2 to the starting mixtures. It can be seen that the presence of the second phase $La_2Ti_3O_9$ is responsible for, and therefore favourable to the improvement of the dielectric properties. However, the addition of > 3 mol% Nb_2O_5 leads to a rapid increase in dielectric losses.

4 Conclusions

(1) Good quality lanthanum dititanate ceramics have been prepared using conventional mixed oxide ceramic methods. Modification of the structure and electrical properties were achieved by the additions of up to 10 mol% Nb_2O_5 or excess titania to $La_2Ti_2O_7$.

(2) With increasing amounts of additives there was a growth of $La_2Ti_3O_9$ as a second phase within the $La_2Ti_2O_7$ matrix.

(3) Changes in the dielectric properties of the families of ceramics can be correlated with the presence of the second phase:

(a) relative permittivity increased with the additions;
(b) dielectric loss was independent of the amount of excess titania but increased dramatically when > 3 mol Nb_2O_5 was added;
(c) TCC values for the materials decreased monotonically from +50 ppm/°C for undoped-$La_2Ti_2O_7$ to approximately —50 ppm/°C for materials containing 10 mol% addition. Thus, a material with zero TCC value can easily be obtained.

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