

Synthesis and Dielectric Properties of Thin-Layered (La,Nd)TiO₂N Perovskites

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Abstract

Dielectric measurements made on thin layers of oxynitride of composition (La,Nd)TiO₂N deposited on substrates of the equivalent pure oxides gave high and variable values for the relative permittivity, and very high values of dielectric loss, showing that the samples were significantly conducting. This is believed to be due to reduction taking place during the nitridation step, the use of ammonia (by far the most convenient and effective nitriding agent for this purpose) resulting in the simultaneous production of active atomic hydrogen which easily diffuses through both the surface oxide and the simultaneously forming layer of oxynitride to give compositions of the type (La,Nd)₂Ti^{IV}_{2-x}Ti^{III}_xO_{7-x/2} and La_xNd_{1-x}Ti⁴⁺_{1-y}Ti³⁺_yO_{2-y/2}N respectively. It is well established that the presence of Ti³⁺ in titanium oxides and oxynitrides readily promotes conductivity. These results explain the diverse dielectric property measurements reported by previous researchers working on oxynitride materials, and show that alternative nitridation methods are needed in order to determine correct values of dielectric properties of pure oxynitride materials.

Keywords: Oxynitrides, perovskites, XRD characterisation, dielectric properties.

1. Introduction

Previous work on oxynitrides¹ has mainly focused on materials at the nitrogen-rich end of the spectrum because of their good mechanical properties, especially at high temperatures. Even though some of the early work² considered the possibility of selected members of this group finding application as dielectrics, synthesis was only possible in the form of powders, and subsequent densification into dense solids proved impossible. Early studies concentrated on perovskite compounds of the type ABO₂N, where either A was a Group II element combined with a B metal of Ta or Nb, or A was a lanthanide element, in which case the B metal was Ti or Zr. Thus for example, Marchand *et al.*² synthesised BaTaO₂N, SrTaO₂N and CaTaO₂N, considering them to be potentially high relative permittivity materials. However, Gouin *et al.*³ compared the infrared spectra of BaTiO₃ and BaTaO₂N, and showed that the latter did not have a soft polar mode, and therefore the relative permittivity should be smaller. Later work by Kim *et al.*⁴, using powder samples cold isostatically compressed to 55 % of theoretical density, reported high relative permittivity (k) of 2900 and 4900 for SrTaO₂N and BaTaO₂N respectively at room temperature, but CaTaO₂N was found to have a much lower relative permittivity ($k \approx 30$). These researchers also observed metallic conductivity for BaNbO₂N, most likely resulting from partial reduction of niobium from oxidation state +5 to +3, thereby leading to the introduction of charge

carriers in the conduction band. Lanthanide-based perovskite oxynitrides of the type LnTiO₂N were first synthesised by ammonolysis of mixed ternary oxide powders at a temperature of 950 °C by Marchand *et al.*⁵; later work by Clarke *et al.*⁶ extended this work, looking also at compounds with Zr as the B cation. In many cases, repeated ammonolysis with intermediate regrinding was needed to produce a pure product. No dielectric data were reported for these compounds. Ziani *et al.*⁷ deposited thin films of perovskite-type LaTiO_xN_y by RF sputtering using a nitrogen/argon plasma with increasing levels of nitrogen. Approximately stoichiometric LaTiO₂N was achieved using 71 % of nitrogen in the plasma, for which the relative permittivity was measured as 290; however, quite a high dielectric loss ($\tan \delta = 0.18$) was reported.

The comprehensive review by Ebbinghaus *et al.*⁸ summarising synthesis and properties of perovskite oxynitrides demonstrated the considerable level of synthesis and characterisation activity in this field, but showed that not many researchers had actually reported dielectric data, and (as seen from the data quoted above) their results showed wide inconsistencies. A very recent study by Masubuchi *et al.*⁹ has discussed improved preparation procedures for oxynitride perovskites.

Making reliable dielectric measurements on nitride and oxynitride materials is complicated by the difficulties of preparing the materials themselves. The synthesis route currently employed involves nitridation of either mixed binary oxides or pre-prepared ternary oxides with gaseous

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ammonia at approximately 950 °C. This method relies on the very active nitrogen generated by the decomposition of ammonia on the surface of the powder grains. The resulting product is therefore also in the form of a powder. Conversion of this into a dense polycrystalline solid by conventional ceramic sintering techniques requires temperatures of the order of 1500–1600 °C, well above the decomposition temperature of most perovskite oxynitrides. If a sintering additive is used to aid densification and reduce the sintering temperature, it is still difficult to achieve full density prior to decomposition; moreover, after sintering, the grain boundaries contain a dispersion of a second phase, which can significantly contribute to the overall dielectric performance and make accurate measurement of the dielectric properties of the primary phase difficult. Clearly, there is scope for developing improved procedures for producing samples of perovskite oxynitrides in a form suitable for dielectric property measurement. The present paper describes attempts made to deposit thin layers of LnTiO_2N oxynitrides ($\text{Ln} = \text{La}$, Nd and mixtures of the two) on oxide substrates, and then using measurements on the pure and coated substrate to determine the dielectric properties of the oxynitride phase.

The oxynitride layers were deposited on dense cylindrical pellets of sintered $\text{La}_2\text{Ti}_2\text{O}_7$ by nitriding in ammonia. This resulted in a surface layer being formed all round the oxide sample (Fig. 1); unscrambling dielectric data from samples in this form is complicated by the presence of the thin layer along the sides as well as on the top and bottom surfaces. The side layer was therefore carefully removed by grinding, leaving the coating only on the top and bottom surfaces, making interpretation of dielectric results simpler.

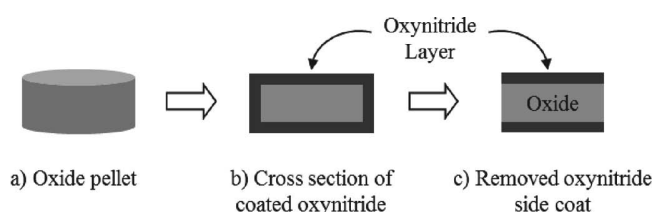


Fig. 1: Coating with a thin surface layer of oxynitride.

II. Experimental

(1) Preparation and characterisation of oxynitride-coated $\text{La}_2\text{Ti}_2\text{O}_7$ samples

Powder samples of $\text{La}_2\text{Ti}_2\text{O}_7$ were prepared by mixing together and grinding appropriate weights of La_2O_3 (Sigma-Aldrich 99.9 %; < 0.1 % of mainly rare earth oxide impurities) and TiO_2 (Merck, BDH Analar 99 %; loss on ignition 0.5 %; metal oxide impurities all < 0.005 %) powders in iso-propanol and compacting into pellets. The pellets were initially calcined in air at 1200 °C for 5 h and then, after regrinding and pelletising, heated at 1350 °C for 16 h to achieve a single-phase $\text{La}_2\text{Ti}_2\text{O}_7$ product. 90%-dense oxide pellets were then produced in a subsequent pressureless sintering step at 1500 °C for 3 h (Table 1). In order to improve powder compaction, adding a few drops of 15 % polyvinyl alcohol (PVA) solution was explored as a binder

(Wang *et al.* ¹⁰). Powder compacts were heated at 550 °C for 2 h to evaporate the PVA, prior to pressureless sintering at 1500 °C for 3 h. This procedure slightly improved the density (94 %). However, x-ray diffraction showed that the $\text{La}_2\text{Ti}_2\text{O}_7$ peaks had shifted to smaller d -spacings (accompanied by a few extra weak reflections). This was believed to be due to residual carbon from the PVA reducing the oxide to a composition of the type $\text{La}_2\text{Ti}_2\text{O}_{7-x}$. Use of the PVA binder was therefore discontinued. Thereafter, sintered pellets were nitrided in flowing ammonia at 950 °C for increasing reaction times. For samples nitrided for 4, 8 and 12 h, x-ray diffraction revealed mainly the oxynitride peaks of LaTiO_2N with very weak peaks of unreacted $\text{La}_2\text{Ti}_2\text{O}_7$ also present. For longer reaction times (16, 20 and 24 h), x-ray diffraction showed only the peaks of pure, single-phase LaTiO_2N , as shown in Fig. 2.

Table 1: Densities of sintered $\text{La}_2\text{Ti}_2\text{O}_7$ powder samples. Values are quoted to an accuracy of typically ± 2 %.

Oxide	¹ Theoretical density (ρ_c) (g/cm ³)	Experimental density (ρ) (g/cm ³)	% ρ_c
$\text{La}_2\text{Ti}_2\text{O}_7$	5.78	5.25	90%
$\text{La}_2\text{Ti}_2\text{O}_7$ +PVA	5.78	5.41	94%

¹ X-ray diffraction database ICDD number: 00–028–00517

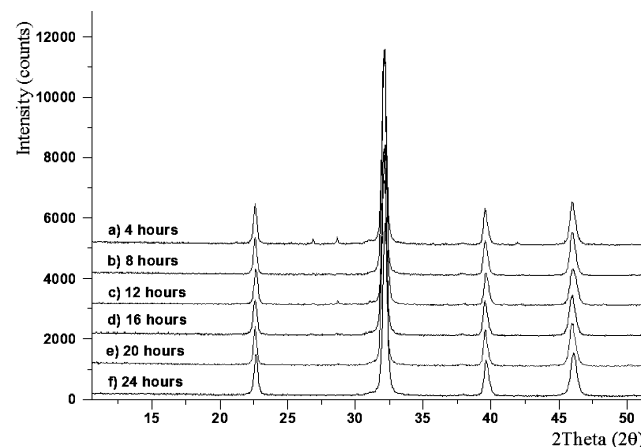


Fig. 2: X-ray diffraction patterns of LaTiO_2N formed as a surface layer on 90 % dense $\text{La}_2\text{Ti}_2\text{O}_7$ by ammonia nitridation for increasing lengths of time at 950 °C.

The surface microstructure (Fig. 3) showed a dense interlocking mesh of elongated rectangular grains of length up to 20 μm and breadth up to 10 μm . Clearly, the procedure of depositing the oxynitride layer on top of a dense oxide substrate successfully produces an acceptably dense surface layer of the oxynitride. Scanning electron micrographs of the cross-section of nitrided pellets confirmed the sandwich-like structure of oxynitride layers on the top and bottom of the sample with unreacted oxide remaining in the middle, as shown in Fig. 4, so that after 16 hours of nitridation, an approximately 4- μm -thick film of LaTiO_2N had been produced. Below this, it was expected that the starting $\text{La}_2\text{Ti}_2\text{O}_7$ would be unchanged. However, the x-ray diffraction pattern of this region (Fig. 5)

showed that the peaks had shifted slightly to the right (i.e. to higher θ or smaller d -spacings) compared with their normal La₂Ti₂O₇ positions. It was also noted that whereas La₂Ti₂O₇ is white or cream and LaTiO₂N is reddish brown to dark brown, after nitridation, the whole of the sample appeared dark grey. Further removal of material by grinding resulted in the La₂Ti₂O₇ peaks returning to their normal positions. Clearly, there is an intermediate interfacial region of modified composition between the LaTiO₂N surface layer and the un-nitrided La₂Ti₂O₇ underneath.

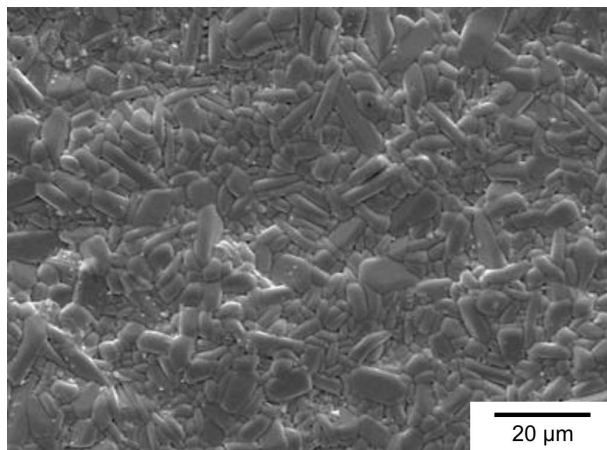


Fig. 3: SEM image of the top surface of an La₂Ti₂O₇ pellet nitrided at 950 °C for 16 h.

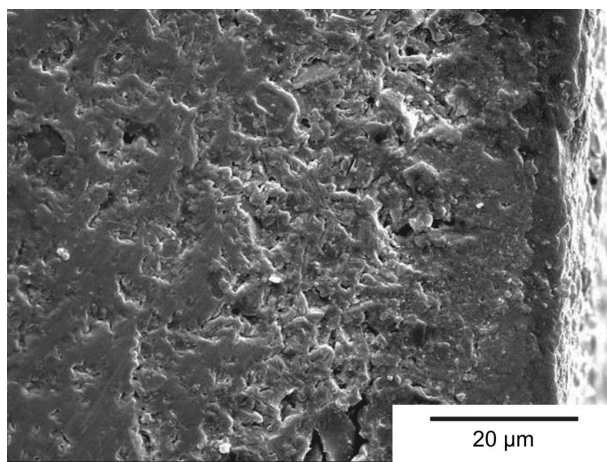


Fig. 4: SEM image of a cross-section of an La₂Ti₂O₇ pellet nitrided at 950 °C for 16 h (x 1500).

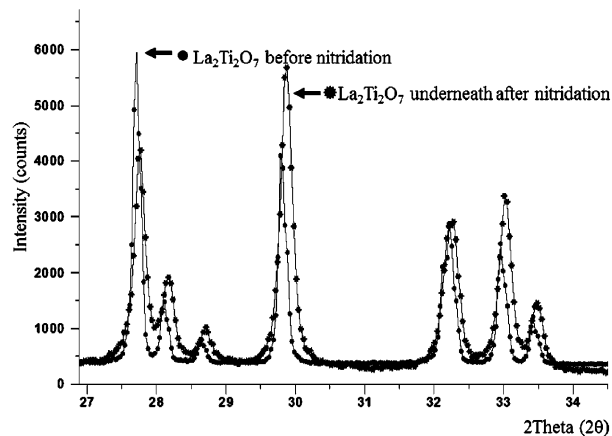


Fig. 5: X-ray diffraction pattern of the La₂Ti₂O₇ underneath the LaTiO₂N film.

(2) Preparation and characterisation of oxynitride-coated Nd₂Ti₂O₇ samples

The same procedure was used to generate thin layers of NdTiO₂N on a Nd₂Ti₂O₇ substrate. Approximately 85 % of theoretical density was achieved for the oxide after sintering, and these samples were then nitrided in ammonia for increasing lengths of time as described previously for La₂Ti₂O₇. X-ray diffraction traces (Fig. 6) showed that even after 72 hours of nitridation, the rate of formation of the NdTiO₂N layer was significantly slower than in the lanthanum case. The top surface and a cross-section of the NdTiO₂N film on the Nd₂Ti₂O₇ substrate are shown in the optical micrograph of Fig. 7. The cross-sectional image shows the thickness of the NdTiO₂N layer to be approximately 2.3–2.7 µm, and such a thin layer would be expected to allow the x-ray beam to pass through to the oxide underneath. The grains of NdTiO₂N can be seen as being irregular and angular. As with LaTiO₂N, the top surface of the nitrided Nd₂Ti₂O₇ was mixed in colour, consisting of the normal dark brown of NdTiO₂N, but with the whole sample now much darker than expected. Also, as in the lanthanum case, when the oxynitride layer was polished off, x-ray diffraction showed that the Nd₂Ti₂O₇ peaks had shifted to smaller d -spacings, but after further polishing, the Nd₂Ti₂O₇ peaks returned to their initial positions before nitriding (see Fig. 8).

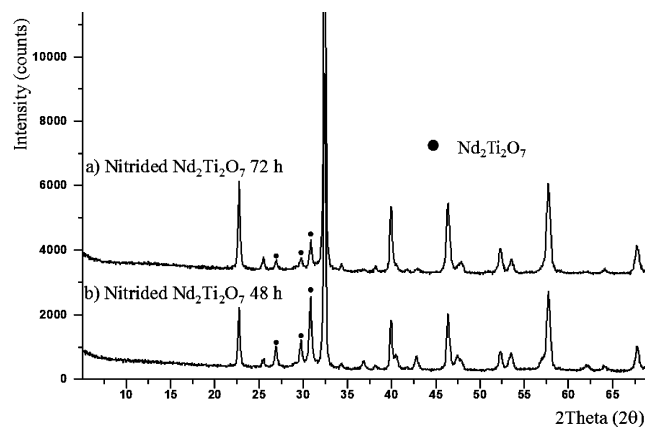


Fig. 6: X-ray diffraction patterns of NdTiO₂N formed as a surface layer on 85 % dense Nd₂Ti₂O₇ after ammonia nitridation for increasing lengths of time at 950 °C.

Thin films of La_xNd_{1-x}TiO₂N solid solutions were also produced by reacting pre-prepared (La_xNd_{1-x})₂Ti₂O₇ pellets with ammonia in the same way as described previously for La₂Ti₂O₇ and Nd₂Ti₂O₇. Compositions were explored at 0.2 increments in x , and the midpoint ($x = 0.5$) was also included. X-ray diffraction traces of the initial oxide samples showed that a solid solution occurred across the whole range and also confirmed the formation of the oxynitride films on these 70–90 %-dense oxide samples after a 24-h ammonia treatment, as shown in Fig. 9 and Fig. 10. Whereas traces of oxide peaks were still just visible in the pure Nd sample ($x = 0$) after this nitriding time, all the rest showed only oxynitride peaks, indicating a several micron thickness of oxynitride layer. Optical micrographs of the La_{0.5}Nd_{0.5}TiO₂N layers (Fig. 11) indicated

a thickness of $\approx 3 \mu\text{m}$. In contrast to the LaTiO_2N samples, all Nd-containing samples have the advantage that the NdTiO_2N and $\text{La}_x\text{Nd}_{1-x}\text{TiO}_2\text{N}$ layers can be distinguished from the original oxides on the basis of colour. Before nitriding, both $\text{Nd}_2\text{Ti}_2\text{O}_7$ and the complete range of $(\text{La}_x\text{Nd}_{1-x})_2\text{Ti}_2\text{O}_7$ samples are purple in colour but after nitriding they turned from purple through brown to dark greyish brown, with a colour variation clearly dependent on the La:Nd ratio.

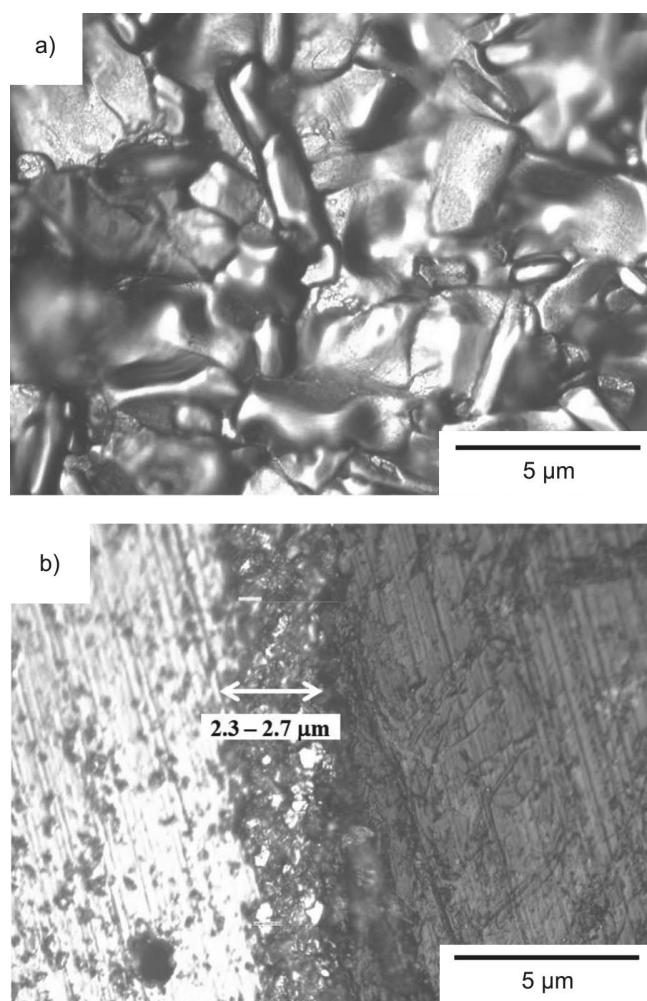


Fig. 7: Optical micrographs of (a) Top-surface and (b) a cross section of the NdTiO_2N film on a $\text{Nd}_2\text{Ti}_2\text{O}_7$ substrate.

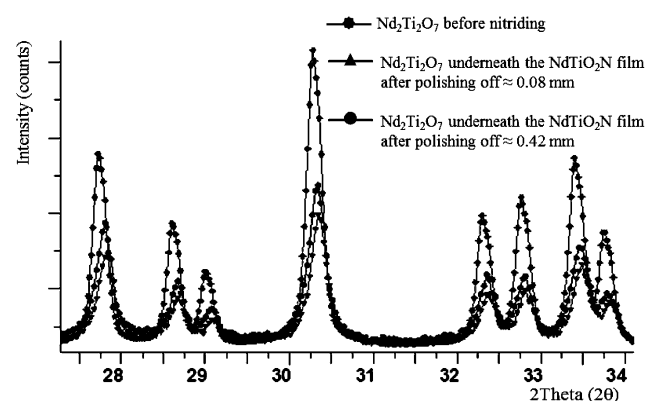


Fig. 8: X-ray diffraction spectra of $\text{Nd}_2\text{Ti}_2\text{O}_7$ underneath the NdTiO_2N film.

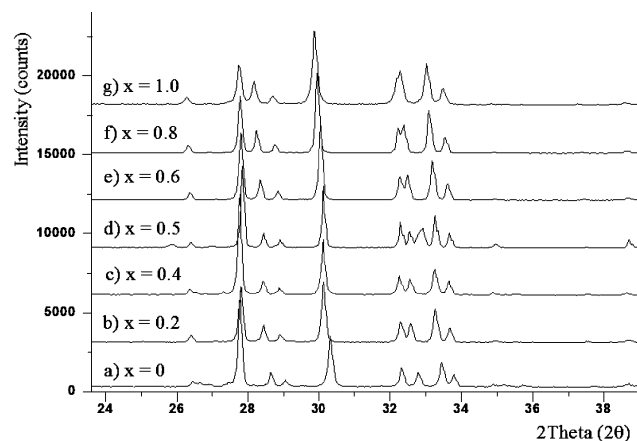


Fig. 9: X-ray diffraction traces of $(\text{La}_x\text{Nd}_{1-x})_2\text{Ti}_2\text{O}_7$ pellets.

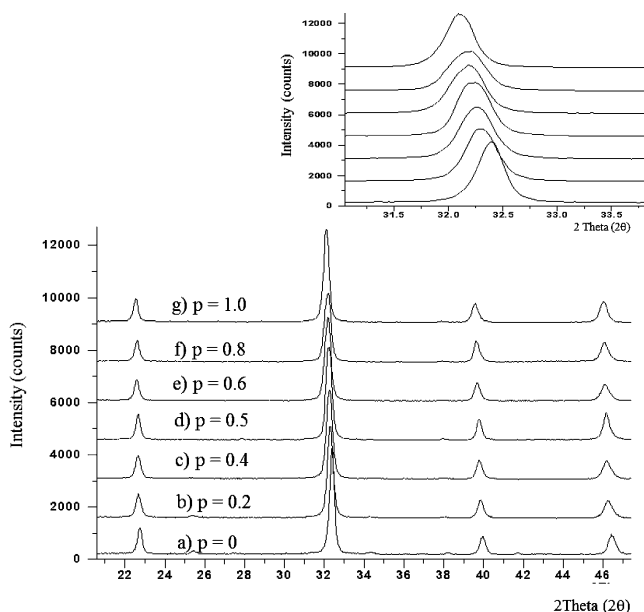


Fig. 10: $\text{La}_x\text{Nd}_{1-x}\text{TiO}_2\text{N}$ solid solutions after ammonia treatment at 950°C for 24 h.

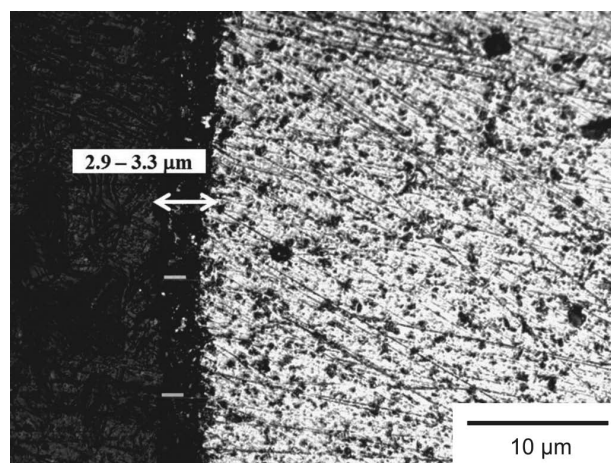


Fig. 11: Cross-sectional optical image of a $\text{La}_{0.5}\text{Nd}_{0.5}\text{TiO}_2\text{N}$ film on a $\text{LaNdTi}_2\text{O}_7$ substrate. The substrate is on the left of the picture.

III. Dielectric Investigations of LnTiO_2N ($\text{Ln} = \text{La}, \text{Nd}$)- and $\text{La}_x\text{Nd}_{1-x}\text{TiO}_2\text{N}$ -Coated Oxides

Gold electrodes were sputtered on both sides of $\approx 10\text{-mm}$ -diameter pellets prepared as described in previous sections. A Hewlett Packard (4284A) LCR bridge was

used to measure capacitance and dielectric loss at room temperature in the frequency range 100 Hz to 1 MHz and values for relative permittivity determined. Errors in final values of both relative permittivity and loss are typically $\pm 5\%$. Initially, the dielectric properties of La₂Ti₂O₇, Nd₂Ti₂O₇ and (La_xNd_{1-x})₂Ti₂O₇ solid solutions, densified to the extent of approximately 70–90 % of theoretical were explored, as shown in Figs. 12 and 13. For most of the frequency range, values for the relative permittivity of each composition remained fairly constant, increasing slightly towards 1 MHz. Across the solid solution, there was a general tendency towards decreasing permittivity with increasing neodymium content.

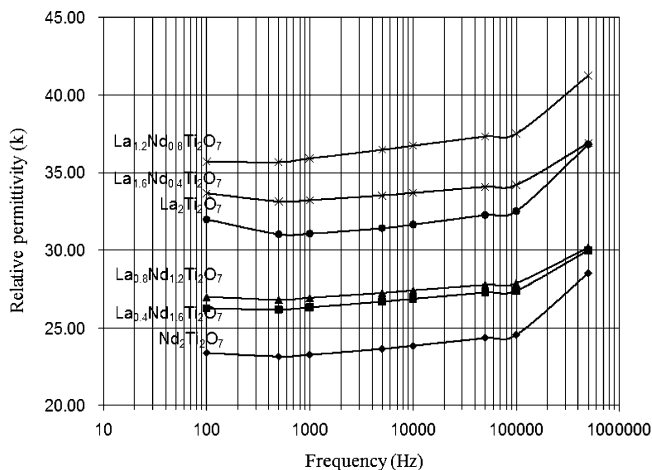


Fig. 12: Relative permittivity of dense (La_xNd_{1-x})₂Ti₂O₇ solid solutions as a function of frequency.

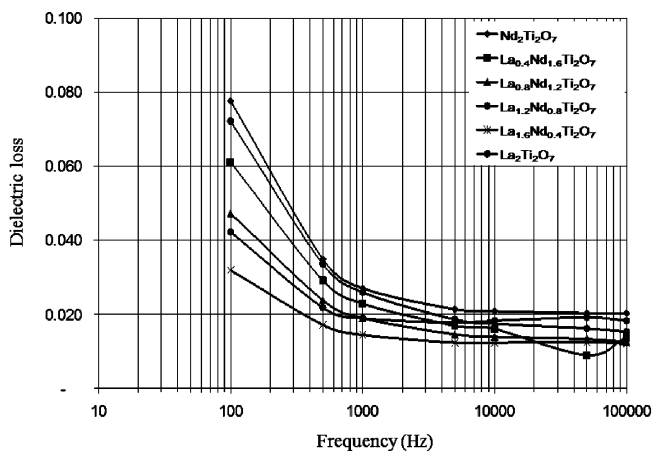


Fig. 13: Dielectric loss of dense (La_xNd_{1-x})₂Ti₂O₇ solid solutions as a function of frequency.

Previous researchers have reported a value of 49 for the relative permittivity of La₂Ti₂O₇ (Paul & Robert¹¹) and 36 for the relative permittivity of Nd₂Ti₂O₇ (Takahashi *et al.*¹²). The data shown in Fig. 12 give lower values than these, probably attributable to the lower densities of the samples used. To explore this effect in more detail, a sample of La₂Ti₂O₇ with high density ($\approx 90\%$ of theoretical density) was measured and a value of 49 obtained for the relative permittivity. The variation in relative permittivity with composition across the solid solution series does not show a linear variation, and this again is thought to be due to the variation in densities of the samples used. The

dielectric loss of La₂Ti₂O₇ and Nd₂Ti₂O₇ and their solid solutions was found to be frequency-independent at all frequencies above 1000 kHz (Fig. 13), consistent with the work of Shao *et al.*¹³, giving values in the range 0.01–0.02. The 90 %-dense sample of La₂Ti₂O₇ examined above was also measured and also gave a value of 0.02 for the dielectric loss.

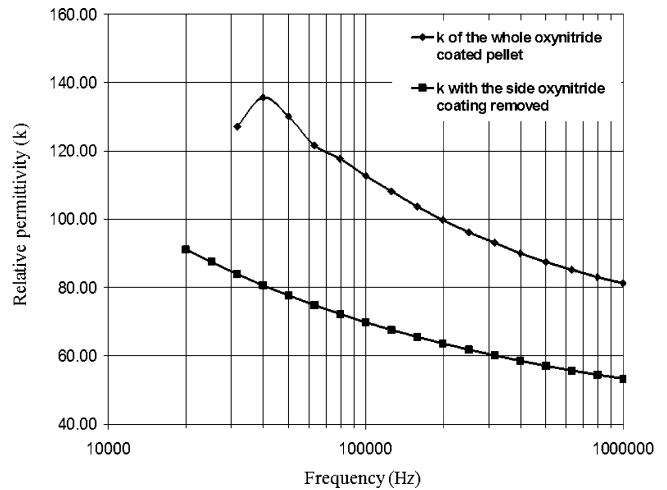


Fig. 14: Relative permittivity of a) LaTiO₂N layer coating the whole La₂Ti₂O₇ pellet, and b) with the LaTiO₂N layer side coating removed.

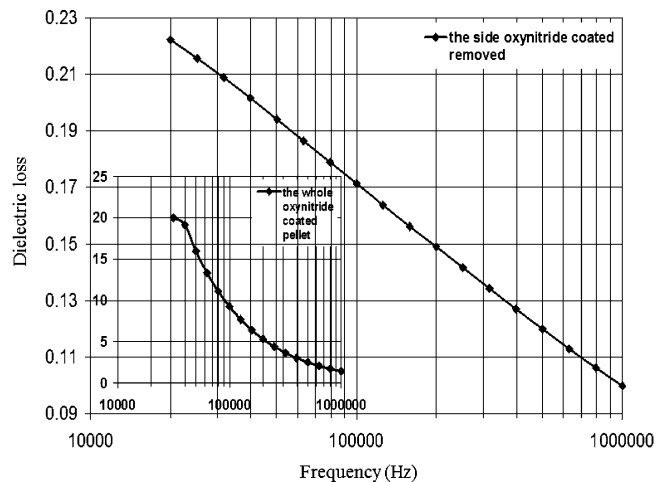


Fig. 15: Dielectric loss of samples with the LaTiO₂N layer side coating removed compared with the completely coated sample (inset).

Dielectric measurements were then made on La₂Ti₂O₇ samples coated with LaTiO₂N, but without any of the oxynitride coating removed (see Figs. 14 and 15). Both relative permittivity and the dielectric loss increased after the ammonia nitriding treatment (950 °C for 20 h), the relative permittivity by a factor of 3–4, but the dielectric loss was now extremely large. After removal of the coating from the sides of the sample, the relative permittivity reduced to values intermediate between those of the as-nitrided and pure oxide samples; the dielectric loss also decreased significantly to a value of only ten times that of the pure oxide substrate. Other oxynitride coated samples with varying La:Nd ratio were studied in the same way and dielectric properties measured in both the as-nitrided and after

side coat removal modes. It was immediately apparent that the relative permittivities of these coated materials, even with the side coat removed, were up to ten times higher than those of their corresponding dense oxides, these results also correlating with higher dielectric loss, as shown in Figs. 16 and 17. Compared with the as-sintered oxides, the higher loss in the nitrified samples clearly indicates increased conductivity in these materials.

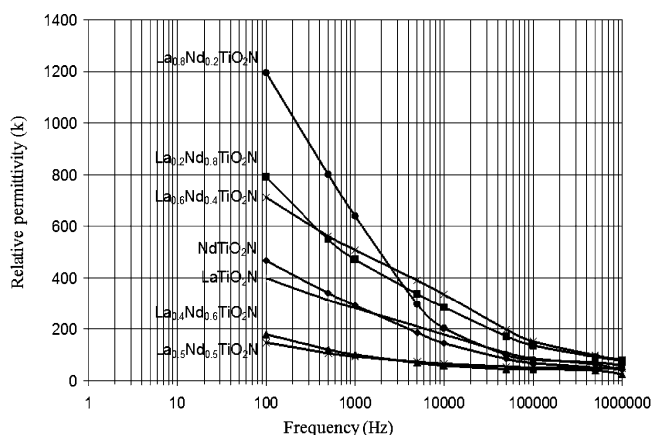


Fig. 16: Relative permittivity of 70–90%-dense $\text{La}_x\text{Nd}_{1-x}\text{Ti}_2\text{O}_7$ samples entirely coated with oxynitride layers.

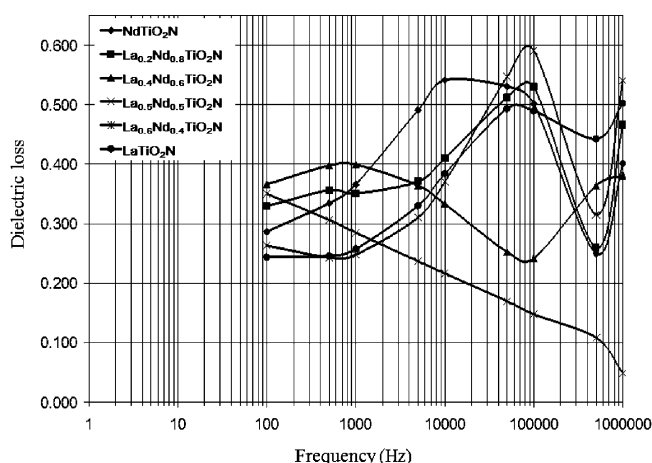


Fig. 17: Dielectric loss of 70–90%-dense $\text{La}_x\text{Nd}_{1-x}\text{Ti}_2\text{O}_7$ samples entirely coated with oxynitride layers.

IV. Discussion

The dielectric measurements reported above clearly show that coatings of oxynitride on $(\text{La},\text{Nd})_2\text{Ti}_2\text{O}_7$ oxides result in a significant increase in both the relative permittivity and the dielectric loss, indicating that the samples have become significantly conducting. Since there is no intrinsic reason why perovskite-type LnTiO_2N oxynitrides should be electrically conducting, other explanations are needed to explain this behaviour. Clues as to the most likely mechanism were provided by the x-ray diffraction patterns of the oxide layers immediately below the oxynitride coating shown in Figs. 5 and 8. Peaks were slightly displaced to lower d-spacings after nitriding, indicating a change in composition, the most likely explanation for which would be reduction of the oxide to give compositions of the type $(\text{La},\text{Nd})_2\text{Ti}^{\text{IV}}_{2-x}\text{Ti}^{\text{III}}_x\text{O}_{7-x/2}$, whereby the loss of oxygen is compensated by a change in oxidation

state of the titanium from +4 to +3. This phenomenon is very common in titanium oxides heated to high temperatures in a reducing atmosphere¹⁴, and is accompanied by a change in colour from white to grey¹⁵ and in the present case, it was noted that the nitrified samples were always darker than the parent oxides. For the same reason, it would be expected that the surface oxynitride would also be reduced from the intended stoichiometric composition to one of the type $\text{La}_x\text{Nd}_{1-x}\text{Ti}^{4+}_{1-y}\text{Ti}^{3+}_y\text{O}_{2-y/2}\text{N}$. The mechanism of this is believed to be due to decomposition of ammonia gas on the surface of the grains of the starting oxide samples. At the nitriding temperatures used (950 °C), this is comfortably above the decomposition temperature of ammonia, but because of the rapid flow rate, the decomposition is delayed until the gas reaches the sample in the hot zone. Decomposition then occurs, with the initial creation not only of the atomic nitrogen required for oxynitride formation, but also significant numbers of hydrogen atoms, which because of their small size and high activity can readily pass through the sample, not only through the oxynitride coating, but also into the oxide layer immediately underneath, picking up oxygen atoms which are converted into water vapour. It is well established that the presence of reduced titanium promotes conductivity¹⁴, and this would give rise to the high values of relative permittivity and dielectric loss observed in the present case.

Ebbinghaus and co-workers¹⁶ also explored oxynitride coating but used single crystal instead of polycrystalline oxide substrates. Films of the perovskite oxynitrides LaTiO_2N , NdTiO_2N , SrNbO_2N and SrTaO_2N were deposited as surface layers on single crystals of the relevant ternary oxides by nitriding at temperatures between 900 °C and 1050 °C for several hours in an ammonia flow of 50 ml/min. X-ray diffraction patterns and scanning electron microscopy revealed oxynitride layers a few micrometres in thickness, forming on top of the unnitrified oxides. With longer reaction times, thicker oxynitride layers were formed. Whereas the relative permittivity of $\text{SrNbO}_{3.5}$ is 1000 at 100 K, falling to below 100 at room temperature (Akishige *et al.*¹⁷ and Bobnar *et al.*¹⁸), with only a small dependence on frequency, the relative permittivity of SrNbO_2N was observed to be 5000 at 300 K, at least three orders of magnitude higher than that of the corresponding oxide. Thick films of LaTiO_2N and SrTaO_2N also showed semi-conductive behaviour with considerably higher conductivities than those of the unnitrified crystals¹³. These authors do not comment on whether the transition metals retained their higher valence state (i.e. Ti^{4+} , Ta^{5+} , Nb^{5+}) after nitridation, or whether some reduction to lower valence states had occurred during the long nitriding times, but in view of the very high relative permittivity data reported, this would appear to be very likely. The data reported by Kim *et al.*⁴, giving values of 2900 and 4900 for the relative permittivities of SrTaO_2N and BaTaO_2N respectively are also consistent with the present results, and would suggest that their materials were defect variants of their intended stoichiometric compositions.

It is clear from the above that improved procedures are needed not only for the synthesis of perovskite oxynitrides, but also for preparing them in appropriate shapes and with high density so that reliable dielectric properties can be measured. A number of suggestions for solving these problems have been given by Masubuchi *et al.*⁹. From a number of studies on SrTaO₂N, these authors found that post-annealing of samples could be used to restore the composition to its intended stoichiometry, thereby reducing the conductivity¹⁹. Lowering the nitriding temperature was also found to be beneficial in preventing reduction during the ammonolysis reaction, and this could be achieved by the addition of alkali halides as fluxes²⁰. The use of soft chemistry routes (e.g. co-precipitation or sol-gel methods) were also useful for lowering the nitriding temperature and reducing the nitriding time²¹. Alternative starting materials have also been explored (e.g. using a SrCO₃/Ta₃N₅ starting mix nitride in a CO/CO₂,N₂ gas atmosphere to produce SrTaO₂N²²), with considerable advantage in the purity of the product. Many of these routes have only been explored for Ta-based oxynitrides, but could readily be extended to the Ti-based oxynitrides described in the present study.

V. Conclusions

Surface layers of LaTiO₂N, NdTiO₂N and La_xNd_{1-x}TiO₂N were successfully deposited on bulk samples of the corresponding polycrystalline 70–90 %-dense ternary oxides by means of nitridation in flowing ammonia gas at 950 °C for up to 24 h. X-ray diffraction, scanning electron microscopy and optical microscopy confirmed that the correct phases had been formed, and that the surface layers of oxynitride were dense and typically measured ≈ 3 μm in thickness. Dielectric measurements on the unnitrided oxide samples gave results in satisfactory agreement with accepted literature values, allowing for the reduced densities of the samples used. The presence of oxynitride layers significantly increased the measured relative permittivities of all samples, but very high values of dielectric loss were also observed. These are believed to be due both to non-stoichiometry in the oxynitride layer, giving rise to compositions of the type La_xNd_{1-x}Ti⁴⁺_{1-y}Ti³⁺_yO_{2-y}N, and similar reduction of the oxide material immediately below the oxynitride layer, arising because of the active hydrogen atoms in the nitriding atmosphere, which because of their small size can easily permeate through the oxide and cause removal of oxygen whilst simultaneously reducing the titanium from Ti⁴⁺ to Ti³⁺. It is well established¹⁶ that the presence of Ti³⁺ in oxide titanates promotes increased conduction. Consequently, the dielectric properties of the ammonia-nitrided oxide pellets were determined more by the conducting contribution from non-stoichiometry in both the coating and the underlying reduced oxide layer.

The present results, and probably most of the previous dielectric measurements made on perovskite-type oxynitrides, suggest that these measurements have not been made on fully stoichiometric materials, and therefore the data reported are incorrect, giving much larger values for relative permittivity than would be the case for pure

ABO₂N compositions. Further work on improved nitridation procedures is needed to solve the problem of high dielectric loss, and the recent paper by Masubuchi *et al.*⁹ has suggested some new approaches for tackling this.

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