Synthesis and Dielectric Properties of Thin-Layered (La,Nd)TiO_2N Perovskites

J. Aechawarattaworn^1, D.P. Thompson^2*, F. Azough^2, R. Freer^2

^1School of Chemical Engineering and Advanced Materials, University of Newcastle, Newcastle upon Tyne, NE1 7RU, U.K.
^2School of Materials, University of Manchester, Manchester M13 9PL, U.K.

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Abstract

Dielectric measurements made on thin layers of oxynitride of composition (La,Nd)TiO_2N deposited on substrates of the equivalent pure oxides gave high and variables 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)yTiIV_2-xTiIII_xO_7-x/2 and La,Nd_1-yTiIV_1-yTiIII_yO_2-y/2N respectively. It is well established that the presence of Ti^{3+} 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.

I. Introduction

Previous work on oxynitrides^1 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 work^2 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 ABO_2N, 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 BaTaO_2N, SrTaO_2N and CaTaO_2N, considering them to be potentially high relative permittivity materials. However, Gouin et al.^3 compared the infrared spectra of BaTiO_3 and BaTaO_2N, 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 SrTaO_2N and BaTaO_2N respectively at room temperature, but CaTaO_2N was found to have a much lower relative permittivity (k = 30). These researchers also observed metallic conductivity for BaNbO_2N, 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 LnTiO_2N 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_2N by RF sputtering using a nitrogen/argon plasma with increasing levels of nitrogen. Approximately stoichiometric LaTiO_2N 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 δ = 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
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 LnTiO2N oxynitrides (Ln = 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 Ln2Ti2O7 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.

II. Experimental

(1) Preparation and characterisation of oxynitride-coated La2Ti2O7 samples

Powder samples of La2Ti2O7 were prepared by mixing together and grinding appropriate weights of La2O3 (Sigma–Aldrich 99.9 %; < 0.1 % of mainly rare earth oxide impurities) and TiO2 (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 pelleting, heated at 1350 °C for 16 h to achieve a single-phase La2Ti2O7 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 La2Ti2O7 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 La2Ti2O7-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 nitried for 4, 8 and 12 h, x-ray diffraction revealed mainly the oxynitride peaks of LaTiO2N with very weak peaks of unreacted La2Ti2O7 also present. For longer reaction times (16, 20 and 24 h), x-ray diffraction showed only the peaks of pure, single-phase LaTiO2N, as shown in Fig. 2.

Table 1: Densities of sintered La2Ti2O7 powder samples. Values are quoted to an accuracy of typically ± 2 %.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>1Theoretical density (q) (g/cm³)</th>
<th>Experimental density (q) (g/cm³)</th>
<th>% ϕc</th>
</tr>
</thead>
<tbody>
<tr>
<td>La2Ti2O7</td>
<td>5.78</td>
<td>5.25</td>
<td>90%</td>
</tr>
<tr>
<td>La2Ti2O7+PVA</td>
<td>5.78</td>
<td>5.41</td>
<td>94%</td>
</tr>
</tbody>
</table>

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

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 LaTiO2N had been produced. Below this, it was expected that the starting La2Ti2O7 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 $\theta$ or smaller $d$-spacings) compared with their normal La$_2$Ti$_2$O$_7$ positions. It was also noted that whereas La$_2$Ti$_2$O$_7$ is white or cream and LaTiO$_2$N 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 La$_2$Ti$_2$O$_7$ peaks returning to their normal positions. Clearly, there is an intermediate interfacial region of modified composition between the La-TiO$_2$N surface layer and the un-nitrided La$_2$Ti$_2$O$_7$ underneath.

(2) Preparation and characterisation of oxynitride-coated Nd$_2$Ti$_2$O$_7$ samples

The same procedure was used to generate thin layers of NdTiO$_2$N on a Nd$_2$Ti$_2$O$_7$ 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 La$_2$Ti$_2$O$_7$. X-ray diffraction traces (Fig. 6) showed that even after 72 hours of nitridation, the rate of formation of the NdTiO$_2$N layer was significantly slower than in the lanthanum case. The top surface and a cross-section of the NdTiO$_2$N film on the Nd$_2$Ti$_2$O$_7$ substrate are shown in the optical micrograph of Fig. 7. The cross-sectional image shows the thickness of the NdTiO$_2$N layer to be approximately 2.3 – 2.7 $\mu$m, and such a thin layer would be expected to allow the x-ray beam to pass through to the oxide underneath. The grains of NdTiO$_2$N can be seen as being irregular and angular. As with LaTiO$_2$N, the top surface of the nitried Nd$_2$Ti$_2$O$_7$ was mixed in colour, consisting of the normal dark brown of NdTiO$_2$N, 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 Nd$_2$Ti$_2$O$_7$ peaks had shifted to smaller $d$-spacings, but after further polishing, the Nd$_2$Ti$_2$O$_7$ peaks returned to their initial positions before nitriding (see Fig. 8).

Thin films of La$_x$Nd$_{1-x}$TiO$_2$N solid solutions were also produced by reacting pre-prepared (La$_x$Nd$_{1-x}$)$_2$Ti$_2$O$_7$ pellets with ammonia in the same way as described previously for La$_2$Ti$_2$O$_7$ and Nd$_2$Ti$_2$O$_7$. 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$_{0.5}$TiO$_2$N layers (Fig. 11) indicated
a thickness of \( \approx 3 \) μm. In contrast to the LaTiO\(_2\)N samples, all Nd-containing samples have the advantage that the NdTiO\(_2\)N and La\(_x\)Nd\(_{1-x}\)TiO\(_2\)N layers can be distinguished from the original oxides on the basis of colour. Before nitriding, both Nd\(_2\)Ti\(_2\)O\(_7\) and the complete range of (La\(_x\)Nd\(_{1-x}\))\(_2\)Ti\(_2\)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\(_2\)N film on a Nd\(_2\)Ti\(_2\)O\(_7\) substrate.

Fig. 8: X-ray diffraction spectra of Nd\(_2\)Ti\(_2\)O\(_7\) underneath the NdTiO\(_2\)N film.

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

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

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

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

Gold electrodes were sputtered on both sides of \( \approx 10\) 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 ±5%. Initially, the dielectric properties of La$_2$Ti$_2$O$_7$, Nd$_2$Ti$_2$O$_7$ and (La$_x$Nd$_{1-x}$)Ti$_2$O$_7$ 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.

Previous researchers have reported a value of 49 for the relative permittivity of La$_2$Ti$_2$O$_7$ (Paul & Robert 11) and 36 for the relative permittivity of Nd$_2$Ti$_2$O$_7$ (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 La$_2$Ti$_2$O$_7$ with high density (≈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.

Dielectric measurements were then made on La$_2$Ti$_2$O$_7$ samples coated with LaTiO$_2$N, 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-nitried 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-nitried 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 nitrided samples clearly indicates increased conductivity in these materials.

Fig. 16: Relative permittivity of 70–90-%-dense La_xNd_{1-x}Ti_2O_7 samples entirely coated with oxynitride layers.

Fig. 17: Dielectric loss of 70–90-%-dense La_xNd_{1-x}Ti_2O_7 samples entirely coated with oxynitride layers.

IV. Discussion

The dielectric measurements reported above clearly show that coatings of oxynitride on (La,Nd)_2Ti_2O_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 (La,Nd)_2Ti^{IV}_{2-x}Ti^{III}_{x}O_{7+2x/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 atmosphere, and is accompanied by a change in colour from white to grey and in the present case, it was noted that the nitried 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 La_xNd_{1-x}Ti^{4+}_{1-y}Ti^{3+}_{y}O_{2+y/2}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 conductivity, and this would give rise to the high values of relative permittivity and dielectric loss observed in the present case.

Ebbinghaus and co-workers also explored oxynitride coating but used single crystal instead of polycrystalline oxide substrates. Films of the perovskite oxynitrides La-TiO_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 unnitried oxides. With longer reaction times, thicker oxynitride layers were formed. Whereas the relative permittivity of SrNbO_3.5 is 1000 at 100 K, falling to below 100 at room temperature, 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 unnitried crystals. 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 nitridation 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., 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 SrTaO$_2$N, these authors found that post-annealing of samples could be used to restore the composition to its intended stoichiometry, thereby reducing the reducing the titanium from Ti$^{4+}$ to Ti$^{3+}$. It is well established that the presence of Ti$^{3+}$ 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 ABO$_2$N 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.

References


