

Topotactical growth of thick perovskite oxynitride layers by nitridation of single crystalline oxides

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Dedicated to Prof. Dr. Hermann Schmalzried on the occasion of this 75th birthday.

Abstract

Thick films of the perovskite-related oxynitrides LaTiO_2N , NdTiO_2N , SrNbO_2N and SrTaO_2N were synthesised by nitridation of single crystals of the corresponding oxides with general composition $\text{ABO}_{3.5}$. The oxide crystals were obtained by optical floating zone growth. They correspond to $n = 4$ member of the $A_nB_nO_{3n+2}$ family of layered perovskites and were reacted at temperatures between 900 °C and 1050 °C to form the oxynitrides. Electron probe microanalysis proved the presence of nitrogen in a surface layer of a few micrometer thickness. Cross-section SEM revealed additional thin stripes of oxynitride within the bulk of the crystals, indicating that nitrogen is incorporated preferably parallel to the perovskite-type layers, which in turn are connected in a zipper-type mechanism. The formation of the desired perovskite-type oxynitrides was confirmed by X-ray diffraction. Pole figure measurements proved an epitaxial orientation ABO_2N (110)[001] || $\text{ABO}_{3.5}$ (001)[100]. The mosaicity of the oxynitrides both in polar and azimuthal direction was very small ($<2^\circ$) indicating a nearly single crystalline quality of the surface layer. The nitridation of the crystals results in a dramatic change in colour. Optical spectroscopy revealed shifts of the absorption edge by more than 200 nm to longer wavelengths with respect to the parent oxides, corresponding to a reduction of the band gap energies by 1.4–1.8 eV. © 2007 Elsevier Masson SAS. All rights reserved.

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1. Introduction

The classical way of modifying the structures and physical properties of perovskite-related oxides is to perform substitutions on the cationic sites. The anionic composition is most often only considered with respect to non-stoichiometries like vacancies, which in many cases strongly affect both the physical and chemical properties of the corresponding compounds.

Anion substitutions — the replacement of oxygen by other simple anions like N^{3-} (nitride) or F^- (fluoride) — are by far

less examined. Substitutions within the anionic framework can, on the other hand, strongly alter the material properties of perovskites due to the different charge and differences in the ionicity of the metal–anion bond. Especially the oxynitride perovskites have been identified within the last two decades as a highly fascinating class of new materials. A review of early reports on these materials is given in [1]. The usual preparation technique for oxynitrides is the reaction with ammonia gas at temperatures around 1000 °C, usually called ammonolysis. As starting materials either mixtures of binary oxides and/or carbonates or complex oxides adopting perovskite-related structures can serve. Numerous other methods have been reported in the literature but these are mostly restricted to special materials and none of them is as widely applicable as the ammonolysis.

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Oxynitride perovskites are known for some main group metals like aluminium and for the early transition metals Ti, V, Zr, Nb, Ta, Mo and W. At the preparation temperatures the late transition metal cations are reduced to the corresponding metals. In fact the reducing potential of ammonia, which can partly be explained by the decomposition to nitrogen and hydrogen, is a serious problem in many cases. By using wet ammonia the reducing strength can be considerably decreased.

Most of the oxynitride perovskites possess (distorted) cubic structures. In addition, some Ruddlesden–Popper type oxynitrides are also known. Examples of the $A_2B(O,N)_4$ structure type ($A_{n+1}B_nO_{3n+1}$ with $n = 1$) are $A/B = \text{Sr/Ta, Ba/Ta, Sr/Nb}$ and Nd/Al [2–4]. To the best of our knowledge the only known $n = 2$ oxynitrides are $\text{Sr}_3\text{Nb}_2\text{O}_5\text{N}_2$ [5] and $\text{Li}_2\text{LaTa}_2\text{O}_6\text{N}$ [6].

Besides the academic interest, oxynitride perovskites are attractive for several potential technical applications. While oxide perovskites are generally either black or colourless, oxynitrides often exhibit bright colours. In addition, oxynitrides are usually very stable towards chemicals like acids and they can be heated in air up to several hundred degrees Celsius before they start to decompose. The intense colour of oxynitride perovskites together with their chemical and thermal stability has led to the suggestion to use these materials as inorganic pigments [7,8]. The solid solution of CaTaO_2N and LaTaO_2N was found to exhibit colours from yellow to red. To date cadmium-based pigments are usually used for such colours. Although these pigments are not toxic due to their very low solubility, their use has lately been strongly restricted in the European Union. These restrictions are based on the precautionary principle, taking into account that the toxic cadmium may become bio-available for instance during waste combustion. For these reasons there exists an increasing demand for new, non-toxic pigments. Although oxynitrides based on tantalum are too expensive for mass-produced articles, the above-mentioned $\text{Ca}_{1-x}\text{La}_x\text{TaO}_{2-x}\text{N}_{1+x}$ compounds clearly show the feasibility of this approach.

Another possible application for oxynitrides is their use as photocatalysts. It has, for example, been shown that LaTiO_2N can be used in photocatalytic water-splitting reactions [9,10]. Although the activity of the so far investigated compounds is very low, it seems likely that a systematic screening may recover more active oxynitrides. Especially the fact that their electronic structure and by that their colour can easily be tuned by suitable substitutions makes perovskite-based oxynitrides highly interesting for such applications. For example, we found that the optical band gap widths in the system $\text{La}_{1-x}\text{Ca}_x\text{TiO}_{2+x}\text{N}_{1-x}$ can be varied in the range 2.23 eV–3.72 eV [11]. Finally, the dielectric properties of oxynitrides have lately been investigated and were found to be unusually high, opening the possibility to use these materials in capacitors or other electronic components [12].

For applications like coloured surface coatings or photoelectric cells, thin films of perovskite oxynitrides are required. To prepare such films, e.g. RF-sputtering has been used [13,14]. Lately, we reported on thin films prepared by spin coating [15]. Since the direct preparation of oxynitride films was not feasible, oxide films were first grown and nitridated in

a subsequent reaction step. The spin coating technique was found to be very convenient and led to porous films of nanoscopic particles with random orientation. Another possibility to grow thin films of perovskite-type oxynitrides is pulsed laser deposition (PLD). As nitrogen source, NH_3 in the PLD chamber can serve (as in the case of $\text{SrMo}(\text{O,N})_3$ films [16]) or the films are directly ablated from the respective oxynitride as for example reported for BaTaO_2N [17]. Recently, we demonstrated that it is also possible to first ablate oxide films and afterwards ammonolyse them to the corresponding oxynitrides [18]. One advantage of the PLD method is that the films usually show a good crystallinity and grow epitaxially on single crystalline substrates of suitable lattice parameters. The big disadvantages of PLD are that it requires an expensive set-up, the obtained films are rather thin and appropriate (commercial) substrates are often not available or very costly.

In this paper we describe a new complementary approach to obtain thicker oxynitride films of excellent crystallinity and epitaxial orientation. The basic idea is not to grow the oxynitrides on the surface of an inert single crystalline substrate but to use the single crystal itself as reactant. The advantages are obvious: the lattice mismatch is minimal and the correct cationic composition is already fixed. As we will show in the following the nitridation of oxide single crystals leads to oxynitride films with a thickness in the micrometer range. These films possess a very small mosaic spread, a fixed epitaxial relationship to the oxide material and are well suited for measurements of physical properties like optical absorption. The controlled partial nitridation also sheds some light onto the hitherto poorly known mobility and reactivity of nitride anions in oxide matrices.

2. Experimental

Polycrystalline samples of $\text{LaTiO}_{3.5}$, $\text{NdTiO}_{3.5}$, $\text{SrNbO}_{3.5}$, and $\text{SrTaO}_{3.5}$ were prepared by conventional solid state reactions in air using SrCO_3 , TiO_2 , Nb_2O_5 , Ta_2O_5 , and pre-dried Ln_2O_3 ($\text{Ln} = \text{La, Nd}$) as starting reagents. The purity of the obtained samples was checked by X-ray powder diffraction. The resulting powders were pressed in bars of $85 \times 5 \times 5 \text{ mm}^3$ and $15 \times 3 \times 3 \text{ mm}^3$, respectively, which served as feed and seed rods for the crystal growth experiment. The bars were sintered at $1300 \text{ }^\circ\text{C}$ for 24 h to increase their density and mechanical stability. Crystals were grown by the floating zone technique. The applied growth furnace (model GERO SPO) is equipped with two 1000 W halogen lamps, the radiation of which is focussed by gold-coated ellipsoidal mirrors. During the crystal growth seed and feed rods were counter rotated with a speed of 30 rpm and 15 rpm, respectively. A constant flow of synthetic air (0.2 l/min) was used as gas atmosphere. The growth rate was fixed to 7.5 mm/h. The resulting crystal boules were transparent (violet in the case of $\text{Nd}_2\text{Ti}_2\text{O}_7$ and colourless for the other samples) with typical lengths of at least 1 cm and 3–6 mm diameter. The boules were cleaved into thin slices of some hundred micrometer thickness and several square millimetres area. These slices were ammonolyse in a tube furnace at temperatures between $900 \text{ }^\circ\text{C}$ and $1050 \text{ }^\circ\text{C}$ for several hours

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