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Synthesis and crystallization pathway of $Na_{0.5}Bi_{0.5}TiO_3$ thin film obtained by a modified sol–gel route

Fabien Rémondière [a], Barbara Malič [b], Marija Kosec [b], Jean-Pierre Mercurio [a,*]

[a] *Science des Procédés Céramiques et de Traitements de Surface, UMR CNRS 6638, Université de Limoges, 123 Avenue Albert Thomas, 87060 Limoges, France*
[b] *Institut Jožef Stefan, Ceramics Department, Jamova 39, 1000 Ljubljana, Slovenija*

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Abstract

As a lead-free candidate for electronic application, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) thin films were produced by a 2-methoxyethanol sol–gel route and CSD method. Thermal decomposition and crystallization pathway of the alkoxide-based precursor have been studied by thermal analysis and X-ray diffraction (XRD) techniques. No transitory nanocrystalline phase was detected during the crystallization process of NBT. As a consequence, the nucleation of the stable perovskite phase occurred at low temperature (<500 °C). The parameters of the post-coating steps, i.e. drying and pyrolysis temperatures were chosen according to thermogravimetric data. Studies of the thermal annealing for crystallization are presented and discussed in terms of microstructure features from field-emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) observations.

Keywords: Films; Sol–gel processes; Perovskites; Ferroelectric properties; $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)

1. Introduction

Originally discovered by Smolenski et al. in 1961,[1] $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is a ferroelectric compound with a complex perovskite-type structure. NBT and NBT-based lead-free piezoelectric material have been studied as bulk ceramics, single crystals and since a decade as thin film capacitors. The phase transition exploration of this A-site substituted ABO_3 perovskite by XRD and Raman spectroscopy has brought a controversy in the phenomena interpretation but everyone agreed with the non-centrosymmetric rhombohedral symmetry at room temperature, a remnant polarization of 38 $\mu C\,cm^{-2}$ and a very high coercive field of 74 $kV\,cm^{-1}$.[2–5]

To make them valuable candidates for the substitution of PZT, NBT films processing must avoid a high temperature annealing due to sodium and bismuth volatility in order to keep a satisfied compatibility and integration in the silicon technology. Oriented toward reliability and low temperature processing, we have used the 2-methoxyethanol-based sol–gel route developed by Gurkovich and Blum and Budd et al. for PZT thin films.[6,7] Precursor solutions were produced by inorganic polymerization and, then, reaction of the titanium alkoxide $Ti(OR)_4$ with sodium and bismuth acetates in 2-methoxyethanol medium. The reaction between a transition metal alkoxide and an acetate salt can proceed by either ester-elimination and/or addition leading to the formation of oxo- or aceto-bridges between the different cations.[8]

The CSD method is divided in several steps: solution synthesis, coating on a substrate like a platinized silicon wafer, drying, pyrolysis and subsequent crystallization treatments. Compared to the physical methods, solution-based synthesis of a heterometallic precursor enables a higher homogeneity at molecular level and markedly lower nucleation temperature.[9] In the case of thin film processing, the evaporation, pyrolysis and crystallization temperatures are further reduced due to the specific geometry of the deposited film offering a very large surface/volume ratio.

The aim of the present study is to prove the ability to prepare NBT thin films at a temperature as low as 460 °C with the strategic use of a reactive solvent and a sol–gel procedure. The polymerization degree of the precursor solution was followed by the measurement of the ester content in the distillates using a saponification mechanism and acid-base reaction. Crystalline structure of both xerogel and thin film were investigated by XRD

* Corresponding author. Tel.: +33 5 5545 7427; fax: +33 5 5545 7270.
E-mail address: jpmercurio@unilim.fr (J.-P. Mercurio).

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(Siemens D5000 Bragg-Brentano), FESEM (GEOL 7400) and AFM (Picoscan Molecular imaging).

2. Solution synthesis

The solution for coating is obtained by the dissolution, according to the stoichiometric ratio, of the subsequent quantities of titanium *n*-butoxide, sodium and bismuth acetates altogether in 120 mL of 2-methoxyethanol. The mixture is then slowly heated to the refluxing point of 2-methoxyethanol for 2 h and, then, 60 mL of by-products are distilled of for 30 min in order to get, after dilution in 2-methoxyethanol, a 0.4 mol L^{-1} clear yellowish precursor solution. Four-volume percent formamide is added as a bridging reagent to adjust the coating properties of the solution.[10] All the experiments are conducted in a dried N_2 flow.

The ester distilled during the distillation step is fully transformed into carboxylate species by refluxing the distillate with excess potassium hydroxide for 1h30 (cf. saponification mechanism, Fig. 1a).

The ester content is titrated by a coupled colorimetric/pHmetric method following the acido-basic reaction between the excess of potassium hydroxide and a molar solution of hydrochloric acid (a few drops of phenolphthalein is used as acido-basic indicator).

According to the experiment (quality of the reagents and the equipment precision), 31% (±1%) of the total acetate groups have been removed from the precursor solution.

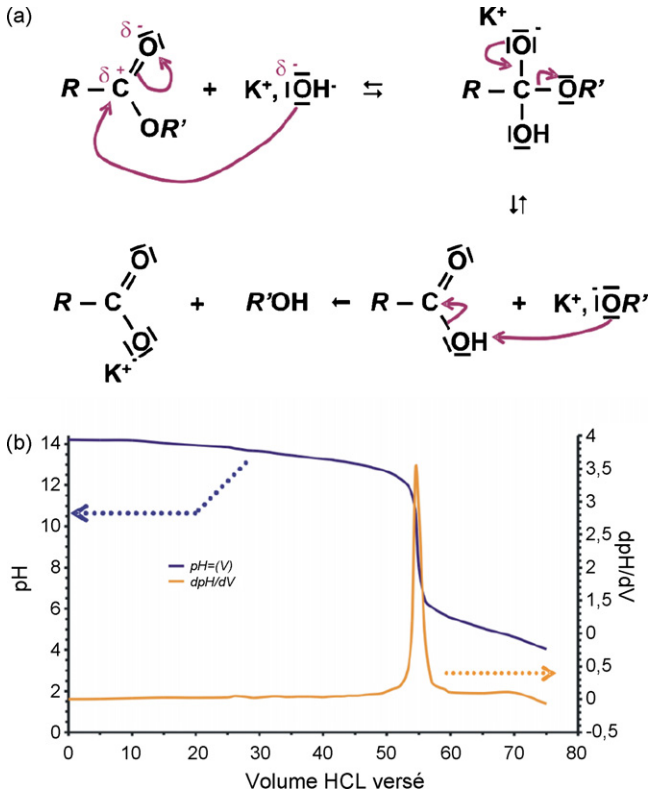

Fig. 1. (a) Mechanism of ester saponification by reaction with potassium hydroxide and (b) pH = $f(V_{HCl})$ and first derivative for the determination of excess potassium hydroxide after reflux.

3. Xerogel study

The thermal decomposition of the sol, dried at 80 °C for 1 h was followed by thermal analysis and coupled gas analysis (mass spectroscopy). From the TG/DTG/DTA curves (Fig. 2), four main steps were observed for a total weight loss of 22%. The first step (6.25% weight loss) is predominantly connected with adsorbed water exhaust. Between 150 and 250 °C, some water, carbon dioxide and acetone issued from the solvent evaporation and organic decomposition were detected in the products of oxidation of the second weight loss. Between 250 and 400 °C, essentially water and carbon dioxide were removed and finally, around 500 °C, a last 0.5% weight loss of carbon dioxide was eliminated upon heating. The crystallization of NBT correlated with the last small weight loss is thought to begin at 492 °C (dynamic DTA acquisition). Previous FTIR study has shown the formation of sodium carbonate at 400–430 °C. Sodium carbonate is the stable product of decomposition of sodium acetate and is thought to be issued from a fraction of solvated sodium acetate in our precursor solution due to the high solubility of sodium acetate in 2-methoxyethanol.

No transitory nanocrystalline phase was observed at intermediate temperature in the XRD patterns of the annealed xerogel (Fig. 3a). Only one small and sharp peak around 27.8° could be interpreted as some β-Bi_2O_3 heterogeneities. One can observe that the nucleation of NBT crystals is initiated below 400 °C and that the powder annealed at higher temperature is pure at XRD resolution. Fig. 3b shows the pseudo-cubic shape and size (∼700 nm) of the crystalline particles in the case of a powder annealed by rapid thermal annealing at 700 °C. The nucleation temperature for NBT produced by the 2-methoxyethanol route is far lower than the one found by Kim et al. in the case of a sol–gel route using nitric acid[11] and Hao et al. with a stearic acid gel method.[12]

As a conclusion for the thermal decomposition experiment, 97.5% of the organic groups are eliminated at $T < 380$ °C. Drying and pyrolysis temperatures (respectively 240 and 380 °C) were chosen to minimize stress in the compliant metalorganic film during the coating application and other heat treatments.

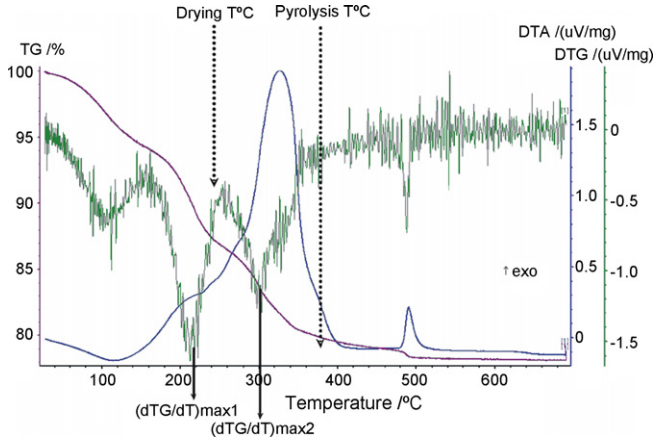

Fig. 2. DTA/TG/DTG curves of NBT xerogel dried at 80 °C (10 °C min^{-1}/in air/Pt–Rh crucible).

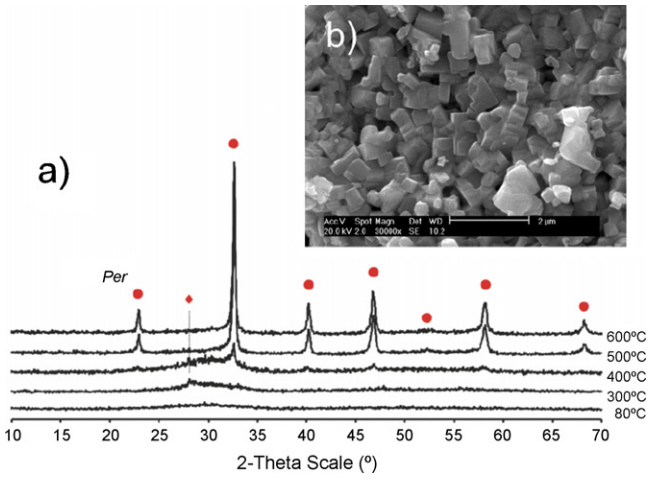

Fig. 3. (a) XRD patterns evolution of NBT xerogel as a function of annealing temperature and (b) SEM micrograph of NBT powder after RTA crystallization at 700 °C.

4. NBT thin films

Figs. 4 and 5 show FESEM micrographs and XRD patterns of NBT thin films deposited onto $Pt/TiO_2/SiO_2/Si$ substrate and composed of six layers dried at 240 °C for 5 min, pyrolyzed at 380 °C for 5 min and finally annealed at 650 and 750 °C.

The XRD patterns reveal that the grown thin films are pure perovskite phase, and randomly oriented polycrystalline material. Nevertheless, the microstructure is composed of numerous homogeneously distributed pores all along the surface. Increasing the annealing temperature up to 750 °C permits to observe some drastic changes in grain size and microstructure. Grain growth and temperature activated diffusion mechanisms are responsible for the coalescence of the porosity at the grain

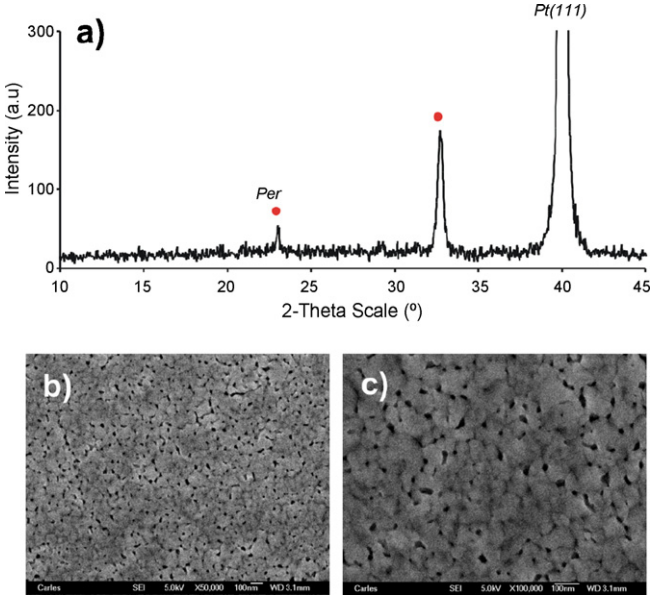

Fig. 4. Six-layer NBT thin films dried 5 min at 240 °C, pyrolyzed 5 min at 380 °C and finally annealed for 30 min at 650 °C/10 °C min^{-1}. (a) XRD pattern; (b) and (c) FESEM micrographs of the top surface.

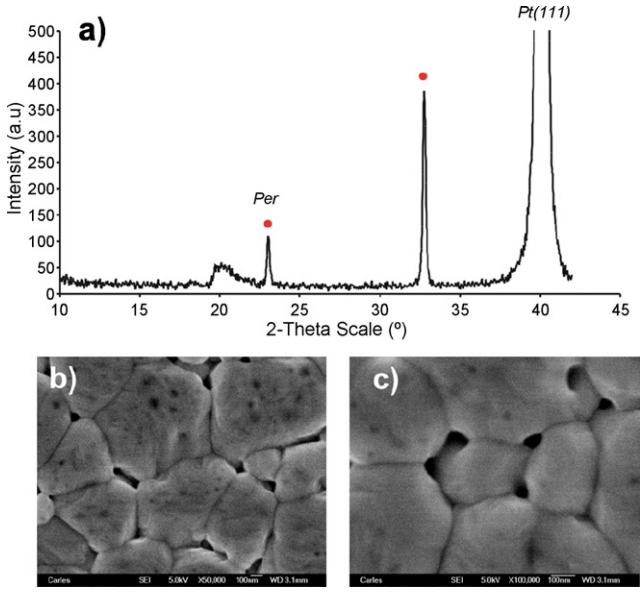

Fig. 5. Six-layer NBT thin films dried 5 min at 240 °C, pyrolyzed 5 min at 380 °C and finally annealed for 30 min at 750 °C/10 °C min^{-1}. (a) XRD pattern; (b) and (c) FESEM micrographs of the top surface.

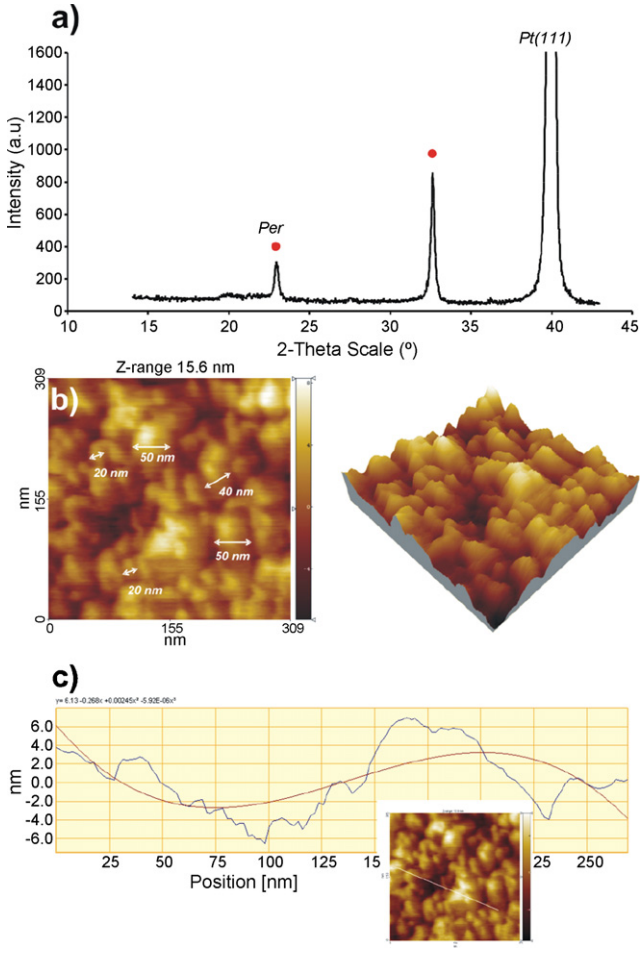

Fig. 6. Six-layer NBT thin films dried at 240 °C for 5 min and pyrolyzed at 460 °C for 5 min. (a) XRD pattern; (b) topographic AFM view; (c) AFM line and profile of the top surface.

boundaries and the presence of very large clusters of coalesced finest grains.

In order to avoid the presence of such voids or pores drawback for electronic application of the film, the pyrolysis temperature was increased up to 460 °C. Knowing that the nucleation temperature of NBT is lower than the new temperature of pyrolysis, the six-layer thin film heat treatment acts as a layer-by-layer crystallization. The final film is pure perovskite (Fig. 6a) and its microstructure homogeneously composed of very fine grains. According to AFM topographic view of the top surface (Fig. 6b), the film shows a quite smooth surface (RMS surface roughness (3 μm × 3 μm) around 2.33 nm). The average grain size is around 40 nm and the maximum amplitude registered on the AFM picture is 15.6 nm. The granular microstructure with random orientation of the crystallites – no texture was observed from glazing angle XRD – typically occurs from homogeneous nucleation in an amorphous matrix.[13]

5. Conclusion

A 2-methoxyethanol sol–gel route was successfully used for the preparation of both NBT xerogel and thin films. According to thermal and XRD analyses, the crystallization is initiated at low temperature ($T < 500$ °C) from homogeneous nuclei in an amorphous matrix. A small weight loss of CO_2 associated with the last exothermic event of DTA curve is believed to originate from the reaction of a fraction of Na_2CO_3 with the surrounding matrix before to be fully transformed into perovskite phase. Adjusting the pyrolysis temperature up to 460 °C permits to obtain a homogeneous grainy thin film without any porosity. To our knowledge, there is no other example of such low temperature processing in the NBT thin film prepared by CSD method.[11,14,15]

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