



Sr₄Nd₂Ti₄Nb₆O₃₀ tungsten bronze thick films prepared by electrophoretic deposition as a temperature-stable dielectric



Xiaoli Zhu^{a,b}, Paula M. Vilarinho^{a,*}

^a Department of Materials and Ceramics Engineering, Centre for Research in Ceramics and Composite Materials, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

^b Laboratory of Dielectric Materials, Department of Materials Science and Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China

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ABSTRACT

Temperature stable dielectrics of tungsten bronze Sr₄Nd₂Ti₄Nb₆O₃₀ (SNTN) with maximized dielectric performance are achieved with thick films prepared by electrophoretic deposition. 30 μm thick SNTN films sintered at 1300 °C, exhibit permittivity $\epsilon > 375$, loss tangent $\tan\delta < 0.01$ and stable to $\pm 7.5\%$ of the room temperature value in the temperature range of -95°C to 280°C . This permittivity is $\sim 34\%$ higher than that for bulk ceramics (~ 280) processed under the same conditions. Contrary to the microstructure of ceramics, SNTN thick films exhibit anisotropy of the grain growth with increasing sintering temperature. It is proposed that the observed anisotropy is responsible for the maximization of the dielectric properties and is due to the anisotropic crystal structure of SNTN and to the sintering under constraint. The main contribution of the *c* axis vibration to the dielectric constant in tungsten bronze SNTN is confirmed. These results are relevant because via tailoring the substrate constraint and sintering conditions the grain anisotropy of SNTN thick films can be controlled and thus the dielectric properties.

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1. Introduction

Tungsten bronze (TTB) oxides are the largest dielectric family just after perovskites, and their interesting dielectric and ferroelectric properties have attracted systematic research activities towards gathering understanding on their structural and physical properties. The main promising applications for TTBS include nonlinear optics [1], thermoelectrics [2], electrocalorics for refrigeration applications [3], temperature stable multilayer capacitors (MLCC) [4], among others.

The tetragonal tungsten bronze structure consists of layers of distorted BO₆ octahedra sharing corners in such a way that three different types of interstices (pentagonal A1, square A2 and trigonal C) are available for cation occupancy (A1)₄(A2)₂(C)₄(B1)₂(B2)₈O₃₀ [5]. Research has been devoted to the characterization of single crystals and ceramics [5,6]. So far, no studies have been carried out on tungsten bronze thick films. However, the layered and anisotropic structure of tungsten bronzes and our previous knowledge on the role of constrained sintering on the development of anisotropic microstructure in thick films [7], allows us to predict behavioural differences between ceramics and thick films of TTBS

and possible ways to tailor properties for specific applications. Therefore, preparation and characterization of TTBS films is important both for applications and for physical understanding of the dielectric behaviour of this family of materials.

The crystal structure, sintering characteristics and dielectric properties of Sr₄Nd₂Ti₄Nb₆O₃₀ (SNTN) tungsten bronze ceramics have been previously studied by Zhu et al. [8] SNTN belongs to filled tungsten bronze, with full filled A and B sites. Dense ceramics can be obtained after sintering at 1300 °C for 3 h. A temperature stable permittivity region ~ 280 can be observed in SNTN ceramics between two dielectric anomalies (from -50°C to 250°C). The temperature stability is of prime importance in the manufacture of multilayer ceramic capacitors (MLCCs) used in consumer electrical products. Two strategies are currently being used to obtain temperature-stable materials: (i) combining two or more end members with positive and negative temperature coefficients of permittivity to obtain a solid solution with a flattened temperature dependence and (ii) using dopants to create a distribution of ferroelectric (FE) – paraelectric (PE) phase transitions across room temperature, thereby creating a relatively temperature stable material, like in BaTiO₃-based capacitors.[9] Currently, BaTiO₃-based compounds satisfy what is commonly called the X7R criteria [4,10] and are stable up to $\pm 15\%$ of the room temperature permittivity from -55°C to $+125^\circ\text{C}$ with a dielectric loss < 0.02 at 1 MHz but, unless PbTiO₃ ($T_c = 495^\circ\text{C}$) is added, their maximum operating temperature is

* Corresponding author. Tel.: +351 234 370354; fax: +351 234 370 204.
E-mail address: paula.vilarinho@ua.pt (P.M. Vilarinho).

only 130 °C [4]. However, the use of PbTiO_3 is undesirable since: (i) due to its hazardous nature its use will be strictly controlled and (ii) under a low $\text{P}(\text{O}_2)$ atmosphere required for manufacturing Ni-MLCCs (Base Metal Electrodes (BE) MLCCs) lead will be reduced [10].

The continuous miniaturization trend together with and increased speed in computer technology has led to a great emphasis on components that sustain optimum performance at high temperatures and in the future capacitors will have to operate successfully up to 150 °C or even 200 °C. For that new materials are required that should have phase transitions between –50 °C and +250 °C, and due to sustainability issues should be PbO and Bi_2O_3 free. $\text{Ag}(\text{Nb,Ta})\text{O}_3$ has been reported as one possible material [11,12]. However, AgO reduction and subsequent Ag migration under low $\text{P}(\text{O}_2)$ atmospheres have hindered its widespread usage. Alternatively, tungsten bronze compounds as potential temperature-stable dielectrics were firstly recently reported by Stennett et al. [10] in mixtures of three Ba-based components. Temperature-stable materials with a single tungsten bronze composition have not been studied yet. Therefore, single phase SNTN tungsten bronze fulfilling the temperature range required for MLCCs, might be a good candidate for MLCC application. Besides, for applications as MLCCs, fabrication and characterization of thick films are necessary.

Electrophoretic deposition (EPD) is used to fabricate the SNTN thick films in this work. The importance of EPD comes from its unique features of high flexibility and simplicity for applications. In addition, EPD enables the fabrication of highly uniform layers with an easy control of layer thickness. The present work addresses the fabrication of SNTN thick films by EPD on Pt foils with $\pm 7.5\%$ temperature stability of permittivity ($\varepsilon > 300$, $\tan\delta < 0.01$ at room temperature) between –50 °C and 250 °C. The dielectric performance of SNTN thick films is evaluated and compared with counterpart bulk ceramics. The impact of the constrained sintering on the anisotropic microstructure development of SNTN films and thereby on the dielectric properties is investigated.

2. Experimental procedure

$\text{Sr}_4\text{Nd}_2\text{Ti}_4\text{Nb}_6\text{O}_{30}$ (SNTN) powders were synthesized by solid-state reaction. Reagent-grade powders of SrCO_3 (SCR, 99.95%), Nd_2O_3 (SCR, 99.9%), TiO_2 (SCR, 99.5%), and Nb_2O_5 (OTIC, 99.99%) were ball-milled for 24 h in Teflon pots with ZrO_2 balls and ethanol according to SNTN stoichiometry. After drying, the mixed powders were calcined at 1200 °C for 3 h. Since a successful EPD fabrication needs a stable suspension in which the charged particles will be well dispersed, as-calcined SNTN powders were ball milled for different times (12–57 h) to reduce the particle size. The particle size distribution was determined by an electrophoretic light-scattering spectrophotometer (COULTER Delsa 440SX ZetaSizer). A powder suspension was then prepared with acetone as the suspension medium and with a concentration of 5 g L^{-1} . 1 ml Triethanolamine (TEA) was added to the solution to optimize the deposition step and reproducibility. Before EPD, the suspension was ultrasonically dispersed and magnetically stirred for 5 and 10 min, respectively, followed by a settling for 5 min in order to sediment coarse particles. 25 μm -thick platinum foils were used as substrates and electrodes and were separated by 2 cm in a glass beaker. Under an external dc electric field (dc voltage source, Glassman High Voltage, Inc.), charged particles moved towards the oppositely charged electrode, and deposited onto the substrate forming a continuous layer. $\sim 45 \mu\text{m}$ thick SNTN films could be deposited under 200 V in 60 s. The as-deposited films were dried at 90 °C for 24 h, pressed under an isostatic pressure of 100 MPa to enhance the green density of the as-prepared green films and then sintered in air between

1250 and 1400 °C for 1 h to attain a high density. The thickness of the sintered films is around 30 μm . SNTN ceramics were sintered at 1300 °C for 3 h for comparison.

X-ray diffraction (XRD) analyses, using a Rigaku Geiger flex D/Max-B (Tokyo, Japan) and $\text{Cu K}\alpha$ radiation, were performed to inspect the formed phases. Microstructures of SNTN ceramics were observed with scanning electron microscopy (SEM, Hitachi S-4100). The degree of orientation of the film microstructure was quantified by the aspect ratio, as the quotient between the length and the diameter of each grain. Using an image analysis software (ImageJ 1.46r), lengths and widths of around 100 grains from several SEM micrographs were measured and average values computed. XRD Pole Figures were performed with a Philips Xpert XRD diffractometer, using a $\text{Cu K}\alpha$ X-ray source with a crossed slit incident optic and open receiving slit of 1 mm before the proportional detector and used to investigate crystallographic orientation of the films.

For the assessment of the electrical properties, metal-insulator-metal capacitors with Pt/SNTN/Au structures were fabricated by sputtering Au electrodes with diameter of 0.6 mm. Then SNTN films with top electrodes were post-annealed at 200 °C for 30 min to improve the quality of the interface between the metal and the film. The dielectric permittivity and loss tangent were evaluated using a precision LCR metre (4284A, Hewlett Packard) over a frequency range of 1 kHz to 1 MHz from room temperature up to 350 °C. Low temperature dielectric properties were collected over a frequency range of 1 kHz to 1 MHz and from room temperature cooling down to –260 °C ($\sim 10 \text{ K}$) with an Agilent E4980A Precision LCR metre (Santa Clara, CA, USA) and closed cycle helium cryostat (ARS-2HW Compressor, Advanced Research Systems, Inc., Macungie, PA, USA).

3. Results and discussion

A bimodal distribution of the particle size was observed for SNTN powders after milling for different times (from 12 to 57 h), with peaks centred around 0.2 μm and around 2–3 μm . As expected, the particle size decreased with increasing milling time with an obvious increase of the intensity of the peak of the finer particles (centred near 0.2 μm) at the expenses of the decrease of the peak of the coarser ones (centred between 2 and 3 μm). The mean particle size decreased from 2.25 μm to 1.183 μm after milling for 34 h. After milling for 45 h, as shown in Fig. 1, SNTN powders have an average particle size $< 1 \mu\text{m}$ and were used for the deposition. Adding TEA to the suspension, green films with homogeneous and flat surfaces

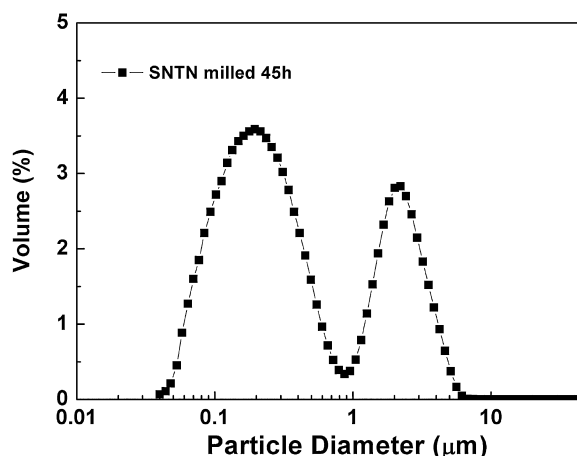


Fig. 1. Particle size distribution of SNTN powders used for deposition, milled for 45 h and dispersed in water. A bimodal distribution is observed, with peaks centred at 0.2 μm and 2.5 μm , respectively. The milled powders have an average particle size of 0.948 μm .

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