Sr₄Nd₂Ti₄Nb₆O₃₀ TUNGSTEN BRONZE THICK FILMS PREPARED BY ELECTROPHORETIC DEPOSITION AS A TEMPERATURE-STABLE DIELECTRIC

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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 ~ 280 °C. This permittivity is ~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.

Key Words: Tungsten bronze, Sr₄Nd₂Ti₄Nb₆O₃₀, thick films, electrophoretic deposition, dielectric properties

I. 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 BO_6 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 $(\text{A1})_4(\text{A2})_2(\text{C})_4(\text{B1})_2(\text{B2})_8\text{O}_{30}$. [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 $\text{Sr}_4\text{Nd}_2\text{Ti}_4\text{Nb}_6\text{O}_{30}$ (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 only 130°C . [4] However, the use of PbTiO₃ is undesirable since: (i) due to its hazardous nature its use will be strictly controlled and (ii) under a low P(O₂) atmosphere required for manufacturing Ni-MLCCs (Base Metal Electrodes (BE) MLCCs) lead will be reduced. [10]

The continuous miniaturization trend together with an 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 $+250^{\circ}\text{C}$, and due to sustainability issues should be PbO and Bi₂O₃ free. Ag(Nb,Ta)O₃ has been reported as one possible material [11, 12]. However, AgO reduction and subsequent Ag migration under low P(O₂) 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 ($\epsilon > 300$, $\tan\delta < 0.01$ at room temperature) between $-50\text{ }^{\circ}\text{C}$ and $250\text{ }^{\circ}\text{C}$. 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.

II. 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 $1200\text{ }^{\circ}\text{C}$ 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 gL^{-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. ~ 45 μm 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 Cu K α 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 (Image J 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 Cu K α 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 meter (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 (~10 K) with an Agilent E4980A Precision LCR meter (Santa Clara, CA, USA) and closed cycle helium cryostat (ARS-2HW Compressor, Advanced Research Systems, Inc., Macungie, PA, USA).

III. 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 – 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 Figure 1, SNTN powders have an average particle size < 1 μm and were used for the deposition. Adding TEA to the suspension, green films with homogeneous and flat surfaces were obtained on the negative electrode, which means that SNTN particles in acetone media with TEA are positively charged.

Although the advantages of EPD are apparent, there is no general or universal suspension medium for the EPD of oxides [13]. It is well known that the use of stable suspensions is a critical condition for a successful and optimised EPD. In stable suspensions, particles are kept well dispersed in the liquid medium and can move towards the electrode without influencing or being influenced by other particles [14]. Our previous work have demonstrated that the use of TEA as an additive to acetone based suspension media resulted in uniform, homogeneous and dense microstructure of different functional oxides thick films that exhibit good

dielectric performance [15,16]. It is suggested that TEA molecules become bonded to the surface of the particles in suspension and in all the reported cases TEA addition was beneficial and a high stability of the suspension in spite of the magnitude of the zeta potential was reported. Indeed TEA has unique properties due to the presence of amine and alcohol groups; its basic nitrogen atom with a lone pair accounts for the weak basic character of TEA, whereas its terminal hydroxyl groups may undergo hydrogen bonding with neighbouring OH groups. The known adhesive properties of TEA may also account for the obtained smooth surface of the films. [16] According to the previous work, addition of TEA increases the vol% of small particles, indicating a better performance of the suspension in EPD. [17]

SNTN films were sintered under different sintering conditions and the influence of the sintering temperature on the microstructure evolution was then analysed. SEM images of surfaces and cross sections of SNTN films sintered at different temperatures are depicted in Figure 2 and Figure 3. Films present obvious porosity after sintering at 1250 °C (Figure 2(a)). As the temperature increases, films densify markedly. For samples sintered at 1300 °C a weak random oriented elongated grain growth appears (Figure 2(b)). As the sintering temperature increases elongated grains become very obvious dominating the microstructure of the samples sintered at 1350 °C (Figure 2(c)) and 1400 °C (Figure 2(d)). From these top view images average grain size and grain aspect ratio were measured and calculated using software (Image J), and the results are indicated in Table 1. The aspect ratio increased from 1.18 to 3.49 when the sintering temperature increased from 1250 to 1400 °C, respectively in agreement with the observations. No sign of elongated grain growth was observed for SNTN ceramics sintered from 1250 to 1350 °C. [8] Moreover, this increment is more pronounced for higher sintering

temperatures. The aspect ratio varied from 2.22 to 2.67 for films sintered at 1300 °C and 1350 °C and from 2.67 to 3.49 for films sintered at 1350 °C and 1400 °C, respectively; which clearly indicates the strong dependence of the microstructure anisotropy of SNTN thick films on the sintering temperature. The cross section of the films sintered at 1250 °C (Figure 3(a)) indicates a porous microstructure, consistent with the SEM top view micrographs. From the cross sections of the films sintered between 1300 and 1400 °C (Figure 3(b)-(d)), a high degree of compactness can be seen from these images. In addition, films show uniform thickness ranging from ~40 μm (Figure 3(a)) to ~30 μm (Figure 3(b)-(d)) and good adhesion to the substrate and no particular defects.

The observed microstructure anisotropy of these films can be attributed to two factors: the anisotropic crystal structure of SNTN and the sintering under constraint on Pt foils. SNTN has a tetragonal tungsten bronze structure with the lattice parameter $a = b = 12.27\text{\AA} > c = 3.86\text{\AA}$, [8] therefore the grains of SNTN ceramics tend to grow along the c axis and to have a columnar shape. During the sintering of a green film on a substrate, shrinkage does not take place along the substrate plane. Instead, the film shrinks appreciably in the normal direction but almost not in the plane and the total shrinkage is limited to the film thickness. [18–20] As a result, stresses will be developed in the film, particularly in the film plane that will affect the sintering process (densification mechanisms and grain growth). It was shown that the stresses induced by constraint lead to the development of anisotropic microstructures during sintering [21–22], as observed in the present case of SNTN thick films sintered in Pt foils. For cases where either a non-isotropic strain or non-isotropic stress field is applied to the sintering bodies, directional diffusion fluxes lead to elongated pores and as soon as grain growth sets in to

elongated grains. [23] Thus, in SNTN thick films, both the anisotropic crystal structure and the constraint sintering condition favoured SNTN elongated grains growth along the c axis and parallel to the substrate.

Figure 4 illustrates the X-ray diffraction patterns of SNTN films sintered at various temperatures. The X-ray diffraction pattern of SNTN powders is also depicted for comparison. For every film, all the diffraction peaks were identified as belonging to SNTN (JCPDS card 33-0166, space group $P4/mbm$) and no second phases were detected, within the equipment detection limits. However, some differences are observed in the intensity of some diffraction lines, such as the lines at 2θ of 23.2° (001), 32.4° (420), 32.9° (311) among others, which seems to be linked to the microstructure anisotropy. The intensity of (420) (parallel to the c axis) increases with increasing sintering temperature from 1250 to 1400°C . In contrast, the peak intensity corresponding to (hkl), such as (001) and (311) becomes weaker. These observations indicate a ($hk0$) preferred growth orientation of SNTN thick films, which is dependent on the sintering temperature.

Figure 5 portrays the XRD Pole Figures corresponding to (410) ($2\theta = 29.95^\circ$) diffraction reflection of SNTN thick films sintered at different temperatures. Lines in the pole figure represent the points with the same intensity when the sample is tilted (-90° to 90°) and rotated 360° for a certain reflection (2θ). A maximum in the center, corresponding to a tilt angle of 0° , means that most of the crystallites in the sample have the planes corresponding to this 2θ parallel to the surface. Therefore, one can say there is a preferential orientation. According to Figure 5, pole figures for films sintered at 1250 and 1300°C are quite similar and lines distributed diffusely around the center, pointing to a non preponderant crystallographic orientation in these films. However for films sintered at 1350 and 1400°C , the projected

piercings gradually grouped in a central circle, being more obvious for the films sintered at 1450 °C, indicating a preferred orientation along (410).

The variation of the permittivity and loss tangent, measured at room temperature in the direction normal to the substrate plane, of SNTN thick films sintered at different temperatures as a function of the frequency is presented in Figure 6. As the sintering temperature increases from 1250 to 1300 °C, the permittivity of SNTN films increases obviously from ~250 to ~375 ($\pm 0.1\%$), which can be attributed to the densification of the film. However, with further increasing of the sintering temperature the dielectric permittivity dropped markedly to ~175 and ~150, as for the films sintered at 1350 °C and 1400 °C, respectively, independently of a high density of these films, as well. The loss tangent for SNTN films sintered at 1250 °C decreases from 0.22 to 0.01 with increasing frequency from 1 kHz to 1 MHz. The loss tangent for films sintered at 1350 and 1400 °C lies in the range below 0.1. Low loss tangent with values < 0.01 are obtained for SNTN films sintered at 1300 °C.

Temperature dependences of permittivity and loss tangent of SNTN films sintered at different temperatures were collected from around room temperature up to around 350 °C and are shown in Figure 7. The corresponding dielectric properties of SNTN bulk ceramics sintered at 1300 °C (with a relative density above 98% and grain size $\sim 3 \mu\text{m}$ [8]) are also presented for comparison. For SNTN bulk ceramics, the temperature dependence of dielectric permittivity has one diffuse peak around 250 °C (corresponding to the diffuse paraelectric - ferroelectric transition) and a dielectric relaxation (originating from the polarization in the *ab* plane) around -50 °C, while a temperature stable dielectric region with $\epsilon \sim 300$ exists between these two dielectric anomalies. [8] As shown in Figure 7(a), a high temperature diffuse peak of the dielectric permittivity appears for all the

samples, corresponding to the diffuse paraelectric - ferroelectric transition, while the transition temperature decreases a little bit with increasing film's sintering temperature. The permittivity value of the films increases obviously when the sintering temperature increases from 1250 to 1300 °C. This could be attributed to the increased film density. Then the permittivity value decreases for films sintered at higher temperatures (1350 and 1400 °C). This decrease might originate from the elongated grain growth that occurred in films sintered at higher temperature. Since the main contribution to the permittivity in TTBs comes from the polarization along *c* axis, and the in plane elongated grain grows along *c* axis while the dielectric measurement is perpendicular to the film surface, then the main dielectric signal comes from the *ab* plane of the tungsten bronze structure, therefore the measured permittivity is lower, as the sintering temperature increases and the microstructure becomes more and more elongated along *c* axis. The loss tangent for films sintered at 1250 and 1300 °C is similar to that for bulk ceramics, with low loss < 0.01 and increases quickly at higher temperature, due to the thermal activation of carriers. For films sintered at 1350 and 1400 °C, there is a loss peak around 100 °C, corresponding to the permittivity relaxation.

In order to get a full image of the dielectric properties, low temperature dielectric permittivity and loss tangent were collected from room temperature down to -260 °C (~10K) for bulk ceramics and thick films sintered at 1300 °C and 1400 °C, as shown in Figure 8. Dielectric relaxation around -50 °C ~ -100 °C which was observed in SNTN bulk ceramics before, also exists in the thick films, together with a loss peak. For these low temperature relaxations, the temperature of both the dielectric constant and loss tangent maximum increases gradually with frequency for both bulk ceramic and film samples.

This relaxation keeps the permittivity at a quite high level, and forms a relatively temperature stable region between the two dielectric anomalies (diffuse peak and the relaxation). The highest permittivity value of ~375 are obtained for films sintered at 1300 °C in the temperature range from about -50 to 200 °C, with quite low loss tangent value < 0.01 in the frequency range from 1 kHz to 1 MHz.

Figure 9 shows the capacitance change (C_p) as a function of temperature for 1300 °C sintered SNTN thick films and bulk ceramics. C_p is calculated from the permittivity values using the formula of $C_p = \epsilon S / 4\pi k d$ (ϵ is the permittivity, S is the area of the electrode, k is the static electricity constant, d is the distance between top and bottom electrode). The capacitance shows a deviation < $\pm 7.5\%$ between -95 and 280 °C for thick films and -70 and 295 °C for bulk ceramics, which fits the requirements of X7R capacitor. Both films and ceramics have low losses (< 0.01) from room temperature up to 100 °C, and high permittivity ~ 375 and ~ 280, respectively. Repeating ceramics and films procedure on several separate batches resulted in similar dielectric data and temperature stability to that shown in Figures 7 - 9.

IV. SUMMARY

Thick $\text{Sr}_4\text{Nd}_2\text{Ti}_4\text{Nb}_6\text{O}_{30}$ (SNTN) films were fabricated by electrophoretic deposition (EPD) on Pt foils under different processing conditions. The anisotropic microstructure development in SNTN thick films prepared by EPD on Pt foils and its impact on the dielectric properties was studied in this work. Contrary to the microstructure of bulk ceramics, anisotropy of the grain growth was observed in SNTN films with increasing sintering temperature, and concomitantly an elongated grain growth and preferential crystallographic orientation along $(hk0)$ observed for the highest sintering temperatures. The increasing grain elongation with increasing sintering temperature arises from

the anisotropic crystal structure of SNTN materials and the constrained sintering of thick films, where the in-plane stress is the main effect factor to the development of elongated grain growth. The increase of the sintering temperature affects markedly the microstructure development of the thick films and, consequently affects the dielectric behaviour. It was proven that grain growth elongation resulted in a significantly lower permittivity value, confirming the main contribution of the *c* axis vibration to the dielectric constant in tungsten bronze materials. The best temperature-stable dielectric properties stable to $\pm 7.5\%$ of the room temperature value were obtained in 1300 °C sintered thick films, with $\epsilon > 375$, which was considerably higher than the value for bulk ceramics (~ 280), and loss < 0.01 from -95 to 280 °C in the frequency range of 1 kHz $\sim$ 1 MHz which fit the requirements of X7R capacitor. These findings are of technological relevance since they demonstrate that control of substrate constraint and sintering conditions can be used to control grain anisotropy and thus dielectric properties of TTBs thick films.

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Table 1 Average grain size and aspect ratio of SNTN films versus the sintering conditions.

Sintering Conditions	1250°C/1h	1300°C/1h	1350°C/1h	1400°C/1h
Average Grain Size(μm)	2.47	2.28	3.17	4.07
Aspect Ratio	1.18	2.22	2.67	3.49

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure Captions

Figure 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 .

Figure 2 Top view SEM micrographs of the surface of SNTN thick films sintered at: (a) 1250 $^{\circ}\text{C}$, (b) 1300 $^{\circ}\text{C}$, (c) 1350 $^{\circ}\text{C}$, and (d) 1400 $^{\circ}\text{C}$ for 1 h, respectively. For the films sintered at temperature above 1300 $^{\circ}\text{C}$, grains show obvious elongated shape and enhancement of this elongation occurs with increasing sintering temperature.

Figure 3 SEM micrographs of fractured cross sections of SNTN films sintered at various temperatures for 1 h: (a) 1250 $^{\circ}\text{C}$, (b) 1300 $^{\circ}\text{C}$, (c) 1350 $^{\circ}\text{C}$, and (d) 1400 $^{\circ}\text{C}$. Films show uniform thickness around 30 μm and good adhesion to the substrate and no particular defects. (The platinum substrate is visible in the bottom of the pictures).

Figure 4 XRD patterns of SNTN powders (calcined at 1250 $^{\circ}\text{C}$ for 3h) and thick films sintered at different temperatures. With increasing sintering temperature the intensity of (*hk*0) peaks increases, while the intensity of (*hkl*) peaks decreases.

Figure 5 X-ray Pole Figures corresponding to (410) ($2\theta = 29.95^{\circ}$) diffraction reflection of SNTN thick films sintered at (a) 1250 $^{\circ}\text{C}$, (b) 1300 $^{\circ}\text{C}$, (c) 1350 $^{\circ}\text{C}$, and (d) 1400 $^{\circ}\text{C}$, respectively. With increasing sintering temperature, the projected piercings moved inside the second circle, becoming more concentrated in the centre, indicating a (*hk*0) crystallographic preferred orientation.

Figure 6 a) Permittivity and b) loss tangent of SNTN thick films sintered at various temperatures as a function of frequency. 1300 $^{\circ}\text{C}$ sintered films show high permittivity and low loss with very good frequency stability.

Figure 7 a) Permittivity and b) loss tangent of SNTN bulk ceramics (sintered at 1300 $^{\circ}\text{C}$ - black lines) and thick films sintered at various temperatures (1250 $^{\circ}\text{C}$ - blue lines, 1300 $^{\circ}\text{C}$ - green lines, 1350 $^{\circ}\text{C}$ - yellow lines, 1400 $^{\circ}\text{C}$ - red lines)

collected from RT up to $\sim 400\text{ }^{\circ}\text{C}$ in the frequency range of $1\text{ kHz} \sim 1\text{ MHz}$ (arrows indicate increasing frequency). All samples show a diffuse dielectric peak corresponding to the diffuse ferroelectric transition, characteristic of SNTN. $1300\text{ }^{\circ}\text{C}$ sintered films show high permittivity and low loss with good temperature stability.

Figure 8 a) Permittivity and b) loss tangent of SNTN bulk ceramic and thick films sintered at different temperatures collected from RT down to $\sim -260\text{ }^{\circ}\text{C}$ in the frequency range of $1\text{ kHz} \sim 1\text{ MHz}$ (arrows indicate increasing frequency). All samples show low temperature dielectric relaxation. $1300\text{ }^{\circ}\text{C}$ sintered films show higher permittivity and lower loss.

Figure 9 Capacitance change (C_p) from value at $25\text{ }^{\circ}\text{C}$ as a function of temperature for $1300\text{ }^{\circ}\text{C}$ sintered SNTN thick films (circle) and bulk ceramic (square) at 1 MHz . The capacitance shows a deviation $< \pm 7.5\%$ between $-95\text{ }^{\circ}\text{C}$ and $280\text{ }^{\circ}\text{C}$ for thick films and $-70\text{ }^{\circ}\text{C}$ and $295\text{ }^{\circ}\text{C}$ for bulk ceramics, which fit the requirements of X7R capacitors.