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Low loss tunable dielectric $BaNd_2Ti_5O_{14}$ - $(Ba_{0.5}Sr_{0.5})TiO_3$ composite thick films☆

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ABSTRACT

An alternative low cost flexible processing is utilized to fabricate tunable dielectric thick-films with low loss. By using a combination of electrophoretic deposition with chemical solution deposition, 9 μm-thick $BaNd_2Ti_5O_{14}$-$Ba_{0.5}Sr_{0.5}TiO_3$ (BNT-BST) composite films are fabricated with a room-temperature relative permittivity of 287 and a loss tangent of 0.0013 at 1 MHz. Moreover, a dielectric tunability and a figure of merit of 12% and 96 at 33 kV/cm, respectively, are obtained by the incorporation of highly tunable ferroelectric BST in a non tunable BNT matrix, thus fitting the requirements of tunable dielectrics for such agile systems as band pass filters.

Within the high-Q dielectrics (Q is the inverse of dielectric loss), the BaO-Nd_2O_3-TiO_2 system represents an important commercial family of microwave ceramics due to the highest relative permittivity ε_r, low loss and high temperature stability [1, 2]. For example, availability of $BaNd_2Ti_5O_{14}$ (BNT) composition with Qf of 6199 and ε_r of 91.9 at 3.5 GHz, being commercially employed in passive microwave devices [3], has allowed BNT to be used in the 'front-end'[1] of communication systems and has had a significant impact on the miniaturization demand of portable systems of specific frequency microwave devices (1–5 GHz region), such as cellular devices and personal communication systems base-stations [4]. As a linear dielectric, BaO-Nd_2O_3-TiO_2 system does not exhibit electric-field tunability of the permittivity. Progress in microwave communications and continuing miniaturization of integrated circuitry, however, demands for tunable components, such as varactors, tunable oscillators, phase shifters and filters besides passive components [5, 6]. The main requirement for the materials to be used in such tunable devices is a combination of optimal ε_r value, high level of its tunability by electric field and low dielectric loss (tanδ). However, low loss in simultaneous conjunction with high tunability has been proved to be problematic [7, 8], and there is a trade-off between the tunability and loss in terms of physics-based models [9]. Independently of the technology, there appears to be an increase of the loss for higher tunability [6]. Planar microelectromechanical capacitive switches have the superior tuning potential with high Q, but size, cost and integration constitute limitations. For continuous moderate tuning ranges, highly doped GaAs varactor diodes may offer the best performance. Finally, ferroelectric capacitors are an alternative, if small size and low cost are mandatory [7, 8].

Among ferroelectrics, barium–strontium titanate ($Ba_{1-x}Sr_xTiO_3$) is the best known system for applications in tunable microwave devices [10–13], although intensive investigations are still aiming at the reduction of its loss [7, 14–18]. Efforts on improving the loss characteristics of $Ba_{1-x}Sr_xTiO_3$ include the mixing with high-Q modifiers such as MgO, Al_2O_3, among others [8, 19–26]. Within this context Nenasheva et al. [27] investigated ceramic composites of $Ba_{1-x}Sr_xTiO_3$ with $BaNd_2Ti_4O_{12}$ (Qf of 3500, ε_r of 80.8 at 3 GHz) [3]. Relative tunability n_r, being 31.7% at $E = 10$ kV/cm for the ceramics with 20 wt% of $BaNd_2Ti_4O_{12}$, was found to sharply decrease with $BaNd_2Ti_4O_{12}$ content down to 1.7% for 50 wt% of $BaNd_2Ti_4O_{12}$ [27].

For microwave tunable applications, however, films are generally more adequate than bulk, because films are easier to integrate with planar RF circuitry and more cost effective [6]. In the current work, moreover, a hybrid deposition technique for fabrication of composite thick films is shown to be successful to reach n_r of 12% at 33 kV/cm (while retaining low dielectric loss) on a composition with 95 wt% of $BaNd_2Ti_5O_{14}$ and only 5 wt% of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST). In this case $BaNd_2Ti_5O_{14}$ is chosen since it shows better dielectric properties than $BaNd_2Ti_4O_{12}$ [3]. The hybrid deposition technique consists of electrophoretic deposition (EPD) of BNT matrix combined with a post deposition sol-gel infiltration of BST. Because after EPD a porous deposit layer is obtained, it constitutes the ideal matrix to be infiltrated, thus guaranteeing a good dispersion of the filler. Indeed, hybrid sol-gel

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☆ To the memory of Dr. Aiying Wu.
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[1] The antennae side is known as the front-end, and the signal processing and user interface is the 'backend.' Loss is more difficult to tolerate at the front-end

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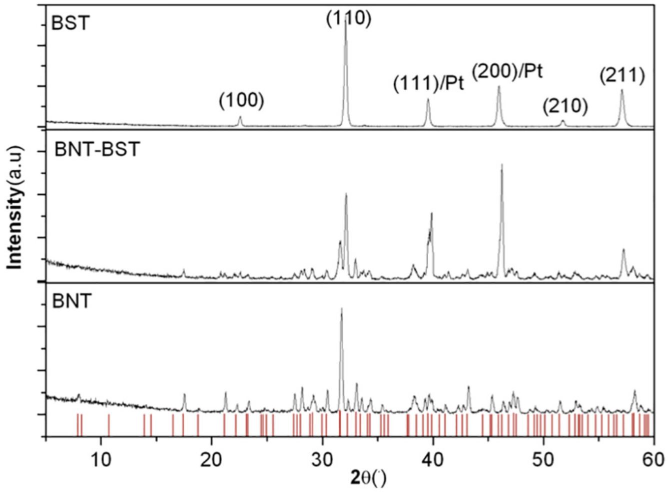

Fig. 1. XRD patterns of BNT, BNT-BST composite and BST thick-films deposited on Pt foils and sintered at 1300 °C/1 h. The diffractions lines of JCPDS card 33-0166 are indicated at the bottom in red.

techniques have been reported for the fabrication of functional oxides like thick piezoelectric films and composites [28], while EPD has recently emerged as an alternative to such established thick film deposition methods as screen-printing and tape-casting [29–31]. Moreover, EPD is a quite inexpensive and versatile technique, characterized by the unique ability to coat complex geometries [29].

In our previous works we have used EPD for processing of BNT thick layers on platinum foils [32–34] and even for multi-layering high-permittivity composites (BNT and $BaLa_4Ti_4O_{15}$) for high frequency applications [35]. Thus, in this work BNT powders and suspension were prepared and their EPD performed in acetone with I_2 dissolved in 2-propanol according to the optimal procedure reported by us elsewhere [34].

Separately BST solution was prepared by sol-gel. $Ba(CH_3COO)_2$ (Merck, 99%), $Sr(CH_3COO)_2 \cdot 1/2H_2O$ (ABCR, 98%), and $Ti(OC_4H_9)_4$ (Merck, >98%) were used as starting materials. Glacial acetic acid (CH_3COOH, Merck, >99.8%) and ethylene glycol ($HOCH_2CH_2OH$, Merck, >99.5%) were used as the solvent, and acetylacetone ($C_5H_8O_2$, Merck, >99.5%) as the stabilizer for Ti alkoxide. $Ba(CH_3COO)_2$ and Sr (CH_3– $COO)_2 \cdot 1/2H_2O$ powders with a molar ratio of 5:5 were dissolved in acetic acid and heated to 80 °C under constant stirring. $Ti(OC_4H_9)_4$ was stabilized with a mixture of ethylene glycol and acetylacetone. The stabilized $Ti(OC_4H_9)_4$ solution was mixed with $Ba(CH_3COO)_2$/Sr $(CH_3COO)_2$ solution with a molar ratio of 1:1 under constant stirring. After stirring for 2 h, the solution concentration was adjusted to 0.25 mol/l and stirred for 1 h more. Using this sol, BST thin layers were deposited onto BNT-coated Pt substrates by spin coating. Then the resultant composite green films were pyrolyzed at 300 °C for 5 min and the process repeated for 10 times so as to acquire around 500 nm thickness for the upper BST films that, taking into account similar density for BNT and BST, roughly corresponds to 5 wt% of BST content. The as prepared BNT-BST composite films were then sintered in air at 1300 °C for 1 h. Fortunately, both BST and BNT sinter at similar temperature around 1300 °C [7, 32] that minimizes the risk of the formation of intermediate reactions.

For comparison, BST thick films were also prepared on Pt foils by EPD. BST powders were obtained from the same sol used for the infiltration step. The dried sol was calcined at 1200 °C for 1 h. The calcined BST powders were ball milled for EPD experiments and BST thick films were prepared under identical protocol as the one used for the fabrication of BNT thick films.

The phase evolution, microstructure, and thickness of BNT, BST and BNT–BST thick films were characterized using X-ray diffraction (XRD, Rigaku, Geigerflex D/Max-C series, and Philips XPert MRD) and scanning electron microscopy (SEM, Hitachi, S-4100). The dielectric tunability measurements were performed at a frequency of 1 MHz in the parallel plate capacitor geometry with Pt foil as a bottom electrode and Au top electrodes, sputtered using a shadow mask of 0.6 mm diameter and post-annealed at 200 °C for 30 min to improve the interface between the metal and the film, using a precision LCR-meter HP 4284A.

Fig. 1 depicts XRD patterns of $BaNd_2Ti_5O_{14}$ - $(Ba_{0.5}Sr_{0.5})TiO_3$ (BNT-BST) composite thick films on Pt foils sintered at 1300 °C for 1 h. For comparison the XRD patterns of BST and BNT thick films are also included. Two main crystalline phases, the cubic $Ba_{0.5}Sr_{0.5}TiO_3$ perovskite structure (JCPDS card 39–1395) and the orthorhombic $BaNd_2Ti_5O_{14}$ one (JCPDS card 33-0166) are observed. Within the ternary system, BaO-Nd_2O_3-TiO_2, different phases have been reported, that include, $BaNd_2Ti_3O_{10}$ (BNT 113) and $BaNd_2Ti_5O_{14}$ (BNT 115) firstly reported by Kolar et al. [1] and the intermediate compound with the compositional ratio of 114 ($BaNd_2Ti_4O_{12}$) described by Razgon et al. [36] and Mudrolyubova et al. [37]. The composition and stoichiometry of BNT 115 have been the subject of discussion. $BaTi_4O_9$, $Nd_2Ti_2O_7$ and TiO_2 were reported as secondary phases of BNT 115 powders [38, 39]. Indeed, it is currently accepted that BNT 114 is the stoichiometric nominal formula. However, commercially employed in microwave devices BNT 115 possesses better dielectric properties than BNT 114 [3], being therefore used in composite material studied in this work.

Typical microstructures of BNT, BST and BNT-BST thick films are depicted in Fig. 2. As seen from Fig. 2(a, left) BNT consists of needle-like grains in agreement with our previous studies [32–34], while BST

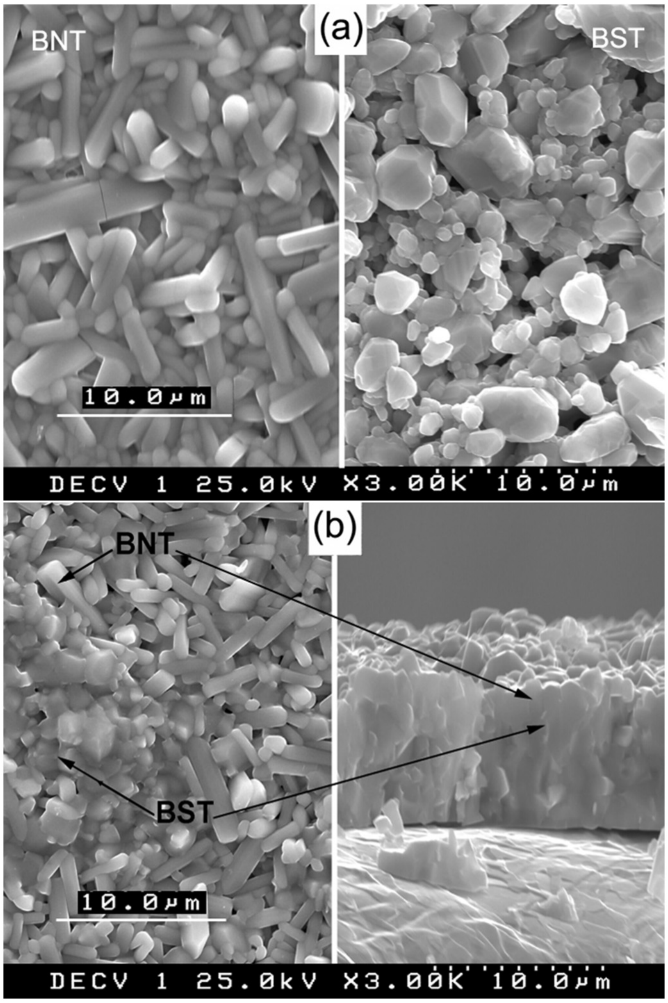

Fig. 2. SEM surface micrographs of (a, left) BNT, (a, right) BST, (b, left) BNT-BST composite films and (b, right) cross section of BNT-BST films.