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Layered composite thick films for dielectric applications

Paula M. Vilarinho [a,*], Amit Mahajan [a,c], Iasmi Sterianou [b,d], Ian M. Reaney [b]

[a] Department of Materials and Ceramic Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
[b] Department of Engineering Materials, University of Sheffield, Sheffield S1 3JD, UK

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Abstract

Electrophoretic deposition has been successfully used for the preparation of multilayer composite thick films of the temperature stable microwave dielectric ceramics $BaLa_4Ti_4O_{15}$ (BLT) ($\varepsilon_r = 44$, $Qf_0 = 44{,}000$ GHz) and $Ba_4Nd_{9.33}Ti_{18}O_{54}$ (BNT) ($\varepsilon_r = 82$, $Qf_0 = 10{,}000$ GHz). The composites exhibit permittivity intermediate between the end members that may be tuned by modifying the ratio between and/or thickness of each layer, thereby tailoring the films for specific applications. In demonstrating an alternative way to tailor functional properties, these results have broad implications for a large number of thick film-based devices.

Keywords: Films; Composites; Dielectric properties; Perovskites; Functional applications; BNT/BLT

1. Introduction

In the last decade, the market for wireless telecommunication has expanded rapidly and there are a large number of applications that require antennas and filters such as portable phones, bluetooth short range connections, office voice, video and data transmission through wireless local area networks (WLAN) and global positioning systems (GPS).[1] To satisfy this every increasing demand for filters and antennas, high frequency, high volume efficient and lightweight integrated components are required which must be fabricated at relatively low cost.[2]

As filters and antennas become miniaturized, thick film deposition technology is under consideration to replace some dielectric components presently fabricated from bulk ceramics. Thick films for applications at RF frequencies have been utilised for several decades. Most notably the multilayer ceramic capacitors (MLCC), which are used as filters in, printed circuit boards.[3] Thick films operating at MW frequencies are mainly employed in the fabrication of low temperature co-fired ceramic (LTCC) modules in which passive components and circuits are embedded in low loss ceramic substrates.[4] All thick films are deposited from powder slurry. The distinction between thick-film methodologies lies in the techniques used to deliver the powder to the substrate, which include tape casting, screen-printing, jet printing and electrophoretic deposition (EPD).[5]

In EPD, charged powder particles, dispersed or suspended in a liquid medium migrate under the influence of an electric field (electrophoresis) and are attracted and deposited (deposition) onto a conductive substrate of opposite charge. Two groups of parameters determine the process characteristics: (i) those related to the suspension, and (ii) physical parameters such as the type of electrode, the voltage/intensity relationship, and deposition time. The appropriate choice of the processing parameters will determine the quality of the film.[6]

The importance of EPD comes from its unique features of high flexibility and simplicity for applications in which various materials or combinations of materials may be deposited on a wide range of shapes, the ability to create porous structures, its cost-effectiveness, and its ability to be scaled-up for large volume fabrication. In addition, EPD enables the fabrication of highly uniform layers with an easy control of the layer thickness, once the conditions of deposition are determined.[6] EPD can be applied to any class of materials available in the form of fine powders, including ceramics, metals, polymers, and glass. It has gained commercial usage for coatings on complex monolithic shapes, laminated and graded freestanding objects, and for infiltration of porous materials and woven fibre performs

* Corresponding author. Tel.: +351 234 370 354/259; fax: +351 234 370 204.
E-mail addresses: paula.vilarinho@ua.pt (P.M. Vilarinho), mahajan@ua.pt (A. Mahajan), i.sterianou@sheffield.ac.uk (I. Sterianou), i.m.reaney@sheffield.ac.uk (I.M. Reaney).
[c] Tel.: +351 234 370 354; fax: +351 234 370 204.
[d] Department of Engineering Materials, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK. Tel.: +44 0114 222 5998/5941/5467l; fax: +44 0 114 222 5943.

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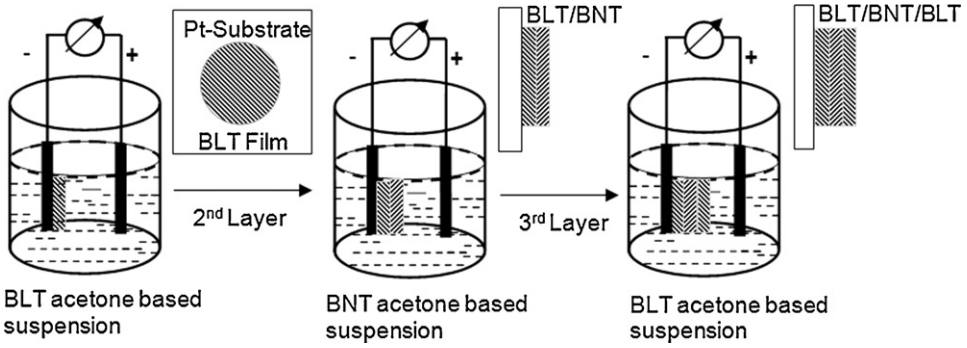

Fig. 1. Schematic diagram of the BLT/BNT/BLT composite thick film fabrication.

in composites. EPD has also been exploited at the laboratory scale for the fabrication of high performance functional thick films of ferroelectrics such as $BaO–Re_2O_3–TiO_2$ (Re = Nd)[7,8] and $Pb(Zr,Ti)O_3$.[9]

In 2005, Zheng et al.[10] reported the fabrication of temperature stable composites based on mixtures of $BaLa_4Ti_4O_{15}$ (BLT) ($\varepsilon_r = 44$, $Qf_0 = 44{,}000$ GHz) and $Ba_4Nd_{9.33}Ti_{18}O_{54}$ (BNT) ($\varepsilon_r = 82$, $Qf_0 = 10{,}000$ GHz). The premise of this work was to establish a range of materials suitable for MW applications in which ε_r may be modified by altering the concentration of the end members according to standard mixing rules. This approach gave a range of MW ceramics whose properties were suited for filters and antennas but it was noted that some phases arising from the reaction of BNT and BLT were present which increased dielectric loss and made ε_r difficult to predict accurately. One determining factor that influenced the extent of reaction between BLT and BNT was the high surface area of contact in a classic 3–3 composite. One approach to minimise the reaction is therefore, to fabricate layered composites using a thick film deposition technique in which the interface between the end members is largely planar. Such geometry may be achieved in a number of possible ways. For example, the end members may be tape casted and laminated in the required ratio but such a technique would only be limited in its exploitation to planar devices. A more flexible approach, explored in this contribution, is to deposit multilayers of BNT and BLT using EPD. In this manner filters and antennas with complex geometries may be fabricated. This contribution identifies such a process through which scaling to small device sizes for radio and high frequency operation may be combined with tailoring of functional properties.

2. Experimental

BNT and BLT powders were prepared by conventional oxide solid state reaction with the reagent graded powders of $BaCO_3$, Nd_2O_3, La_2O_3 and TiO_2, all having purity above 99%. Powders were mixed according to their stoichiometry in teflon jars containing zirconia balls and ethanol. The ball milling was performed for 24 h followed by drying for 12 h. The calcinations were performed at 1200 °C/3 h for BNT and 1300 °C/3 h for BLT. Calcined powders were ball milled to obtain fine particle size, which is essential for the suspension stability. The suspension stability was investigated by means of particle size distribution, suspension UV light transmittance and zeta potential. The particle size and zeta potential was measured by electrophoretic light-scattering spectrophotometer (Coulter Delsa 440SX Zetasizer), the median particle size of BNT and BLT was ~0.6 μm. The degree of dispersion of BNT powders in the different suspensions was evaluated by transmittance of UV light measurements using an UV spectrophotometer (UV-2101/3101PC, Shimadzu scientific instruments, Inc., USA).

Suspensions were prepared in 100 ml of acetone in basic media (with addition of triethanolamine) for both powders. The suspensions were ultrasonically and magnetically stirred for 2–4 min before every deposition. Depositions were carried out onto 25 μm thick platinum foils, that were used as substrates and working electrodes (cathode) and were separated by 2 cm in a glass beaker. The deposition was carried out with a DC power supply (dc voltage source, Glassman high voltage, Inc.). During the application of the external field the charged particles of BNT and BLT move towards the counter electrode and deposit on the substrate forming a continuous layer.

BNT/BLT (BNT lower layer, BLT upper layer), BLT/BNT (BLT lower layer, BNT upper layer) and BLT/BNT/BLT (BLT lower and upper layer, BNT middle layer) composites films were deposited layer by layer. After each deposition and prior to the sintering, films were dried in desiccators so that the residual organics evaporate slowly and minimise the formation of pores and cracks. In case of BLT/BNT/BLT films, after the deposition of the first two layers the sample was heat treated for 1 h at 1000 °C to avoid film detaching from the substrate and intermixing between the layers during the deposition step. The thickness of each layer was varied by altering the deposition parameters (time and voltage). After drying the films were sintered in air at 1500 °C for different dwell times. A schematic diagram of the composite preparation is presented in Fig. 1.

The geometrical density (δ) of the green films was calculated assuming $\delta = m/V$ g/m^3, where m stands for the mass of the film and V for the volume. The phase assemblage, microstructure, morphology and thickness of BNT and BLT thick film composites were characterized using X-Ray Diffraction (XRD) (Rigaku, Geigerflex D/Max-C, Cu Kα series and Phillips Xpert, Cu Kα, MRD diffractometer) and Scanning Electron Microscope (SEM) (Hitachi, S-4100). Cross sections of the composite films were prepared, polished with silicon carbide papers followed by a fine