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U-Chan Chung, Catherine Elissalde, Mario Maglione, Claude Estournès, M. Paté, et al.. Low-losses, highly tunable Ba_{0.6}Sr_{0.4}TiO₃/MgO composite. Applied Physics Letters, 2008, 92 (4), 042902 (3 p.). 10.1063/1.2837621 . hal-00258625

HAL Id: hal-00258625

<https://hal.science/hal-00258625>

Submitted on 28 Feb 2022

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To link to this article :

URL : <http://dx.doi.org/10.1063/1.2837621>

To cite this version : Chan Chung, U. and Elissalde, C. and Maglione, M. and Estournès, Claude and Paté, M. and Ganne, J.P. (2008) [*Low-losses, highly tunable Ba_{0.6}Sr_{0.4}TiO₃/MgO composite*](#). Applied Physics Letters, vol. 92 (n° 4). ISSN 0003-6951

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Low-losses, highly tunable $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3/\text{MgO}$ composite

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Spark plasma sintering (SPS) is an efficient tool to obtain highly densified ferroelectric-dielectric ceramic composites with clean interfaces and tunable properties. Dielectric MgO and ferroelectric $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BST) were combined in two-dimensional multilayer and three-dimensional random powders design. Their unmodified BST Curie temperature proves the suppression of interdiffusion while dielectric losses are below 0.5% and the tunability is 40% at room temperature. The composites and pure BST with similar densities ($>95\%$) were obtained, owing reliable comparison of their dielectric properties. Such SPS ceramics can be used as experimental input for simulation and are potential candidates for high frequency applications.

[DOI: [10.1063/1.2837621](https://doi.org/10.1063/1.2837621)]

Ferroelectric materials are widely considered for their potential use in the field of telecommunications (multilayer ceramic capacitors, tunable filters, wireless communication devices, etc.) However, the main drawback is their intrinsic losses which can be overcome by adding to them a low loss material. Composite materials such as $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BST) ($T_c=290$ K) combined with low permittivity and low losses nonferroelectric oxide, MgO, are well known candidates for microwave devices.¹⁻¹⁰ Relevant properties to such high frequency tunable devices are moderate dielectric permittivity (100–2000), high tunability (change of dielectric constant with applied electrical field $T(\%)=100\times(\epsilon(E)-\epsilon(0))/\epsilon(0)$), and low losses ($\tan\delta<0.5\%$). These parameters are correlated and sensitive to the MgO addition. The optimization can, thus, be achieved provided that both the dielectric content and the composite structure are well controlled. However, the full control of interfaces, which allows avoiding chemical reactions and/or interdiffusion effects, was not yet achieved using standard sintering routes. As a result of insertion of magnesium in the BST lattice, a decrease of the BST Curie temperature is observed for MgO addition as low as 5 wt.%.² This shift of T_c reduces the performances of the material at room temperature, in particular in terms of tunability that increases close to the Curie temperature. The modeling of ferroelectric/dielectric composites highlights the role of both the linear dielectric content and the architecture of the two phases on the final properties.¹¹⁻¹⁵ However, interdiffusion at interfaces in standard composites can obscure the physical description of such composites.

Both for the applications and for the physical understanding, we emphasize here the importance of the optimization of the ceramic microstructure and the identification of the parameters that control the dielectric properties. This highlights the role of sintering in the control of interfaces in BST/MgO bulk composites. A way to decrease the chemical reactivity between the ferroelectric and nonferroelectric phases is to dramatically increase the sintering kinetics using

advanced processes such as spark plasma sintering (SPS). The main outcome of SPS is to obtain high densification at lower temperatures and much shorter holding times compared to conventional sintering. Highly densified BST/MgO/BST (2 wt % MgO) multilayer composite ceramics with fully controlled interfaces were obtained by SPS.¹⁶ The suppression of interdiffusion between the two phases was achieved. Losses were significantly reduced compared to pure BST but such sandwich architecture is not suitable to get sufficient tunability. We then take advantage of the SPS process to obtain highly densified ceramics with different design.

In the present study, microstructural and dielectric characterizations are presented in three-dimensional (3D) random composites with low MgO content (4 wt %), i.e., increasing ferroelectric/dielectric interfaces compared to the multilayer composite. The mixed BST and MgO powders were loaded into the cylindrical pressure die. The applied uniaxial pressure was 50 MPa. The sample was heated at a rate of 100 °C/min to 1200 °C and quenched after 3 min, obtaining a density close to 97%. Using standard sintering, temperatures higher than 1300 °C and holding times of around 10 h are required. Scanning Electron Microscope (SEM) micrographs of the fracture surface of the as obtained ceramics were recorded using a JSM 6330A, JEOL (Fig. 1). The dark islands were revealed to be MgO by energy dispersive analysis. Chemical contrast micrographs show these inclusions to be composed of several agglomerated MgO grains [Fig. 1(b)]. The initial agglomerates are flattened due to the uniaxial pressure applied during the sintering leading to thin disk like islands (ellipsoid on the fracture) in the final dense ceramic. The BST matrix is mostly heterogeneous with a skeleton made of large grains ($>$ few microns) and smaller grains closer to the MgO inclusions (200 nm to 1 μm). This duplex microstructure can be the consequence of differential sintering due to MgO inclusions in the BST matrix. As a result, retardation in densification of the BST regions in the

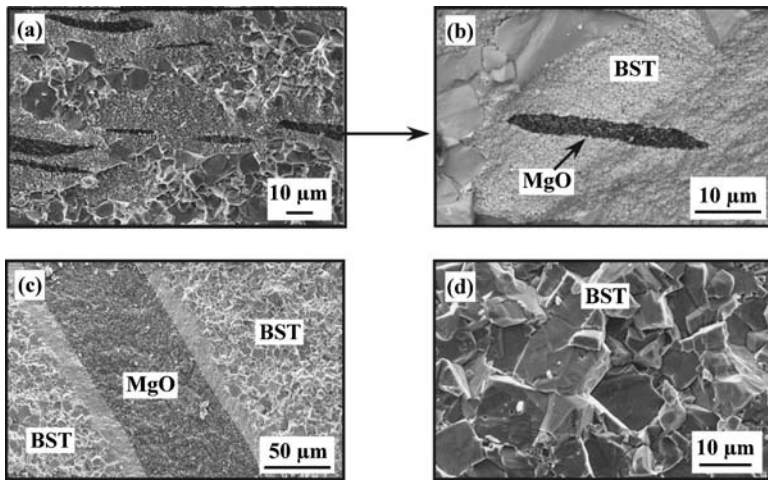


FIG. 1. SEM micrographs of (a) 3D random BST/MgO composite with (b) a zoom of the corresponding chemical contrast image (magnesia is not homogeneously dispersed in the BST matrix, the dark area corresponds to several MgO grains), and (c) sandwich BST/MgO/BST composite and (d) BST sintered by SPS.

vicinity of the inclusions is observed while grain growth, as in pure BST, is preferred between the inclusions.^{17–19} The pressure applied during SPS sintering helps to promote densification and highly densified composites are, however, obtained. On the contrary, the magnesia grain size is quite monodisperse (around 300 nm). Using SPS processing, clean and chemically sharp interfaces were obtained between the two phases. Multilayer BST/MgO/BST composite and pure BST sintered in exactly the same SPS conditions are also shown in Fig. 1. The three ceramics have similar densities (97%).

Dielectric investigations were carried out on electrode disk samples using a Wayne Kerr component analyzer 6425 (100 Hz–100 kHz) and an impedance analyzer HP4194 (1 MHz). As evidenced in Fig. 2, the Curie temperature of BST is not altered by the increasing number of dielectric/ferroelectric interfaces confirming, as in the sandwich composite, the absence of interdiffusion. We recall that using conventional sintering a shift of T_c of about 30 °C is observed at MgO content of only 1 wt %.² At room temperature, the permittivity is close to 2500 and dielectric losses are lower than 0.5% at 10 kHz. The dielectric MgO phase significantly reduces the dielectric losses down to values that, at low frequency, fit the applications requirements ($\tan \delta < 0.5\%$). Such low values are still observed at 1 MHz.

In addition, electric field tunability of the permittivity was tested. The permittivity measured at 100 kHz can be significantly changed applying an electric field of 2 kV/mm (Fig. 3). Tunability as high as 40% was obtained at 300 K which is compatible with the tunability of pure BST. The 3D BST/MgO composites sintered using SPS have, thus, reached the two main requirements for applications: losses lower than 1% and tunability close to 50%.

Moreover, an accurate comparison of the dielectric performances between BST and two BST/MgO composites with different design is proposed. Note that, avoiding two drawbacks (inherent to conventional sintering) such as cross chemical substitution and porosity effects, the identification of the parameters that control the dielectric properties is more relevant. The dielectric properties can be tuned not only varying the MgO content but also changing the composite architecture. For similar low dielectric concentrations (<5 wt %), the permittivity is strongly affected by the connectivity of the two phases when comparing two-dimensional (2D) and 3D composites (Fig. 2). The transition peak is much more depressed and more diffuse in the sand-

wich composite. The sandwich can be described as a connection in series of capacitors. As a result, the effective permittivity of the stack is accurately evaluated using a series model and referring to the pure BST values.¹⁶ A significant decrease of the Curie Weiss temperature (T_0) is observed while the Curie constant remains close to that of pure BST (Fig. 4). Sherman *et al.* have demonstrated theoretically that in a layered model, the addition of the dielectric has an impact identical to a downward shift of the Curie Weiss temperature.¹³ This change comes from the mixing law in such 2D architectures and was also shown in the thin films literature.²⁰ On the other hand, when the dielectric constituent is randomly distributed in the BST matrix, the determination of the effective permittivity using usual mixing laws

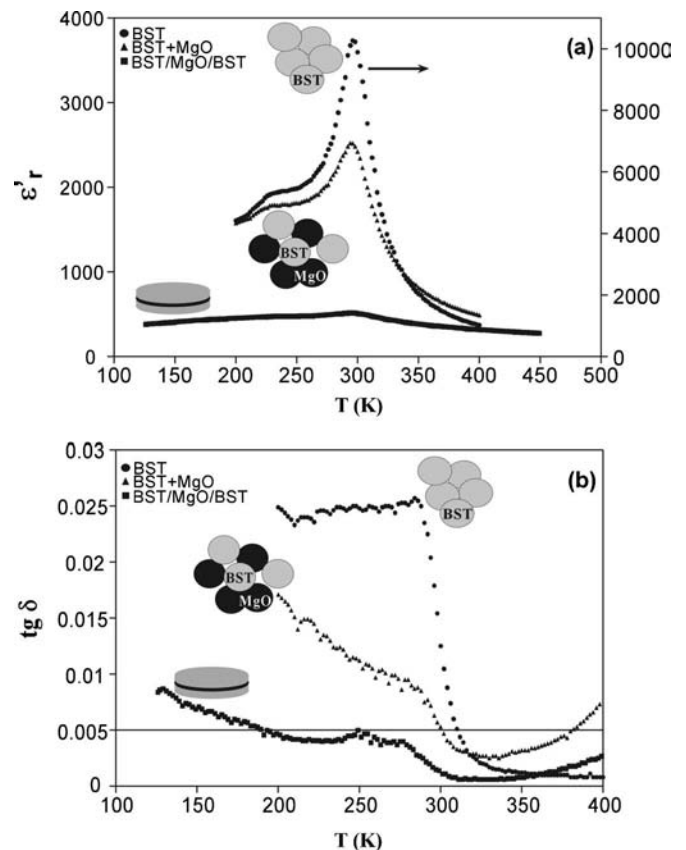


FIG. 2. Thermal variations of (a) dielectric permittivity and (b) losses at 10 kHz of spark plasma sintered BST, two-dimensional multilayer, and three-dimensional BST/MgO.

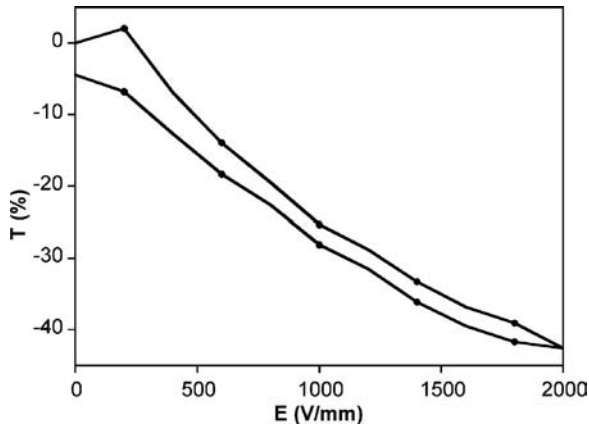


FIG. 3. Electric field tunability of the permittivity at 100 kHz in three-dimensional BST/MgO ceramic composite. Tunability is defined as $T(\%) = 100 \times [\varepsilon(E) - \varepsilon(0)] / \varepsilon(0)$, where $\varepsilon(E)$ and $\varepsilon(0)$ are the permittivities under and without an applied electric field, respectively.

is more difficult. As shown on Fig. 4, T_0 is only very slightly decreased comparing with pure BST whereas the Curie constant is significantly modified. In bulk 3D composites, the Curie Weiss temperature should not be affected whereas the change in microstructure compared to pure BST and induced by the presence of dielectric inclusions could lead to the modification of the Curie constant. Such correlation was mentioned in studies based on grain size effect on the dielectric properties and also referred in the case of the model built for polycrystalline thin films.^{20,21}

The performance of the ceramics in terms of dielectric losses can also be discussed according to the connectivity of the ferroelectric and dielectric phases. Below T_C , the most efficient loss barrier is the MgO layer in the sandwich composite. Such a strong decrease in losses is not attributed to a doping effect as regards to the unmodified Curie temperature.¹⁵ The higher loss values of the composites above 350 K (paraelectric state) comparing with pure BST

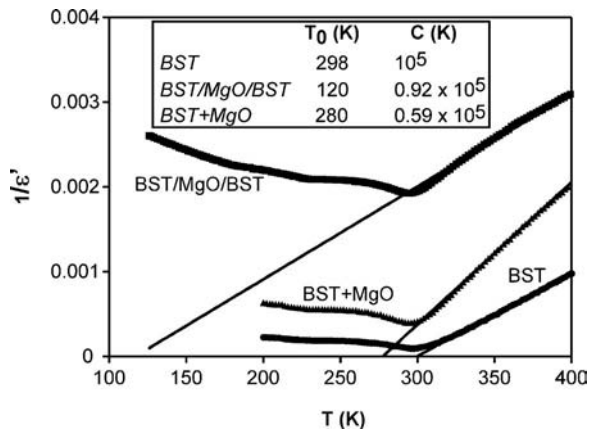


FIG. 4. Inverse permittivity as a function of temperature at 10 kHz for BST, BST/MgO/BST, and BST+MgO SPS ceramics. Inset: values of the Curie Weiss temperature (T_0) and the Curie constant (C) obtained from the fit.

are probably due to charged defects at the interfaces corresponding to extrinsic losses which appear only at low frequencies. The higher magnitude of this effect in the case of the 3D composite is in good agreement with the higher number of interfaces.

Using spark plasma sintering, cross-diffusion effect was avoided in BST/MgO composites whatever the connectivity of the ferroelectric and dielectric phases. It was, thus, demonstrated in this work that improved permittivity and loss values are obtained in three-dimensional random composite while keeping a tunability compatible to that of pure BST. Microstructure optimization resulting from the use of advanced sintering process such as SPS allows reliable comparison of the dielectric properties with pure BST. In our diffusionless composites, we were able to tune separately the Curie Weiss temperature and the Curie constant using 2D and 3D architectures. In progress measurements at microwave frequency will provide more information on the intrinsic nature of the dielectric losses in these composites.

This work was supported by the French National Agency for Research under contract ANR ACOR2.

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