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Design of New Tunable Ferroelectric Composites

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Non-linear dielectrics which display electric-field dependent dielectric properties can be used in microwave devices such as tunable resonators or phase shifters. The required performances are essentially moderate permittivity (100–1000), low dielectric losses ($\leq 1\%$) in the GHz frequency range, good thermal stability and high tunability of the dielectric susceptibility ($> 10\%$). The mixed perovskite $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ [BST] is an attractive candidate as its ferroelectric transition occurs close to room temperature and it displays high tunability but also strong temperature sensitivity and high frequency dielectric losses. To overcome these two deficiencies, ceramic/ceramic composites based on BST and a non-ferroelectric oxide such as MgO , MgTiO_3 , SnO_2 and SiO_2 were synthesized and compared to BST. For a better control of the losses a new concept based on a core-shell principle is presented. Through soft chemistry routes, a core made of BST grains is coated by a simple binary oxide shell. Modulation of the dielectric properties is expected by changing the core-shell structure. High frequency experiments are underway in order to check the GHz losses of these composites.

Keywords: Ferroelectric; BST; tunability; core shell; SiO_2

I. INTRODUCTION

Ferroelectric materials exhibiting high dielectric constant (around 1000) are the topic of a large number of research and development in the high frequency range (between 100 MHz and 10 GHz) due to the increasing interest of applications in telecommunication and radar fields. High permittivity (or dielectric constant) and low dielectric losses allow their integration as low dimension capacitors in electronic devices and even microwave devices thanks to their low frequency dispersion. Close to their transition temperature, ferroelectrics usually display non-linear properties under a DC electric field: the permittivity can be easily changed by applying a DC bias. Such property is used for tunable devices such as tunable capacitors, tunable resonators, phase shifter in radars. . . [1].

The required performances in the GHz frequency range for integration in telecommunication electronic devices are: (i) a moderate permittivity (100–1000), (ii) low insertion losses ($\leq 1\%$), (iii) a good thermal stability and (iv) a high tunability of the dielectric permittivity ($> 10\%$). Ferroelectric materials show high permittivity but strong temperature sensitivity at temperatures close to phase transition ($T_{\epsilon'_{\max}}$). Moreover, it has been shown that the maximal tunability is reached at $T_{\epsilon'_{\max}}$ and that losses increase in the GHz range. The challenge is to find a balance between all these incompatible specifications.

Among the family of BaTiO_3 -based ferroelectrics, the mixed perovskite $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ [BST] is an attractive candidate due to:—a value of $T_{\epsilon'_{\max}}$ close but below room temperature ($T_{\epsilon'_{\text{rmax}}} = 285 \text{ K}$) [2];—a high permittivity at $T_{\epsilon'_{\text{rmax}}}$ ($\epsilon' \approx 10000$) but at room temperature ϵ' is only of several thousands with a medium temperature dependance;—a high tunability and a low dielectric dispersion in the range 100 Hz–1 GHz;—dielectric losses close to 1%. To overcome the temperature dependance and lower dielectric losses, ceramic/ceramic composites were processed [3]. These composites are based on BST and a low loss dielectric oxide such as MgO , MgTiO_3 and more recently SnO_2 and SiO_2 .

The main scope of this work is to optimize the performances of tunable materials by considering new composites based on BST through a higher control in the composite design.

II. EXPERIMENTAL PREPARATION OF SAMPLES

BST ceramics have been synthesized through classic solid state route. Dried powders of carbonates BaCO_3 , SrCO_3 and oxide precursors TiO_2 were grinded in stoichiometric parts in ethanol, dried, and pressed in pellets. After calcination 2 h at 1200°C under O_2 , the obtained phase was checked by X-ray diffraction. The calcined pellets were grinded again. Pellets were uniaxially pressed before sintering at 1400°C during 4 h under O_2 . The compactness reaches 96%.

For processing ceramic/ceramic composites, the non ferroelectric phase was added between the calcination and sintering steps. MgO , MgTiO_3 and SiO_2 were added to sintered BST, grinded and sintered at 1400°C (1100°C for SiO_2). The weight percentages of non-ferroelectric phase was in the range 5% to 20%.

Core-shell composites were made of 40 nm BST grains embeded in SiO_2 shell grown by kinetically controlled polycondensation of active silicate

(NaOH, SiO₂) in aqueous phase. The pH of the solution was kept constant during the addition of the sodium silicate solution by adding simultaneously a sulfuric acid solution (0.085%). The resulting system was aged under stirring at 90°C to let silica shell grow.

The influence of various parameters on silica condensation such as the concentration of the silicate solution, the pH of the solution was studied. Some experiments were also carried out under ultra sounds and at various pH to increase the desaggregation of the BST cores before and while coating.

The obtained core shell composites were washed to eliminate Na⁺, SO₄²⁻ and possible other hydroxy counter ions and then sintered. Thermogravimetric and dilatometric experiments are under way to optimize the sintering parameters.

III. CHARACTERIZATION PROCEDURES

Transmission Electron Microscopy (TEM) Study

TEM observations were carried out with a Jeol 2000FX microscope. The samples were collected on a TEM grid dipped in the colloidal solution of core shell. Some aggregates might form while drying the solvent. Transmission electron micrographs were performed on BST pulver and on core-shell materials. BST grains of about 40 nm could be easily distinguished and high magnifications can be used to reveal the nanocoating of the grains.

Dielectric Measurements

For low frequency experiments (100 Hz to 15 MHz) a HP4194 analyzer was used. The gold electroded samples were connected by 2 silver wires of diameter 0.3 mm stucked by silver paste to the measuring cell. The cell enables measurements to be processed at various temperature thanks to an integrated oven and under controlled atmosphere. Two types of experiments were performed: (i) measurements of the capacitance Cp and the correlated dielectric losses Tan δ versus temperature T and frequency F and (ii) measurements of Cp, Tan δ versus temperature and the applied bias converted in an electric field E.

In experiments (ii), the HP4194 performed measurements of Cp and Tan δ at a given frequency (typically F = 100 kHz) and the applied bias was swept first from 0 to -40 V and then from -40 V to +40 V (by steps of 0.1 V) at each temperature stage. All these experiments were computer controlled. For such tunability measurements, disc samples were polished down to about

0.3 mm to enhance the applied electric field. Gold electrodes are deposited by Plasma Vapor Deposition on the two opposite faces of each disc. The tunability corresponds to the decrease of ϵ' with the applied field and is expressed in % of the permittivity at no applied bias $\epsilon'(T, E = 0)$. The non-linear coefficient behaviour $\epsilon'_{NL}(T)$ describing the dependance versus the applied field E is defined as follow: $\epsilon'(T, E) = \epsilon'_L(T) - \epsilon'_{NL}(T) * E^2$ ($\epsilon'_L = \epsilon'$ under no applied field).

Dielectric measurements were also performed on washed, dried and pressed core shell powder (non sintered). In this case the absolute value of the permittivity cannot be obtained since the air contained in the pore plays the role of a second phase of low permittivity ($\epsilon'_{air} = 1$). Nevertheless, as the variation of permittivity versus temperature is only due to the ferroelectric phase, the determination of the transition temperature is independent of the compactness.

Dielectric measurements at higher frequencies (1 MHz–1 GHz) were performed on a HP4191 impedance analyzer. The samples were connected mechanically to the analyzer port (PC7 connectors) and therefore had to be a well sintered ceramic. Moreover, a lack of precision on the measured capacity prevented from $\epsilon' = f(T, E)$ measurement at frequencies higher than 50 MHz.

IV. RESULTS

Through conventional solid state process a statistically dispersed composite is obtained. Such a designed composite is supposed to exhibit average properties between those of the ferroelectric phase and of the dielectric phase, according to the volume ratio. The dielectric losses of the composite should be then lower than those of BST if the non-ferroelectric phase shows lower values of $\tan \delta$ than those of BST. A broadening of the transition peak may be observed due to chemical fluctuations implying various slightly different transition temperatures in each local domain created (Fig. 1a and b). In comparison with BST, the dielectric characteristics and, as expected, the maximum of permittivity reached by BST/MgO 80/20 composites is decreased ($\epsilon'_{max} \approx 4000$) but the observed peak is broader and the temperature of transition is lower (Fig. 1b). Since BST is the only ferroelectric component, this lowering of $T_{\epsilon'_{max}}$ means that some interdiffusion between the dielectric and the ferroelectric phases occurred.

The composites BST/MgTiO₃ and BST/SiO₂ and BST/SnO₂ exhibit the same trends (Fig. 2a–c).

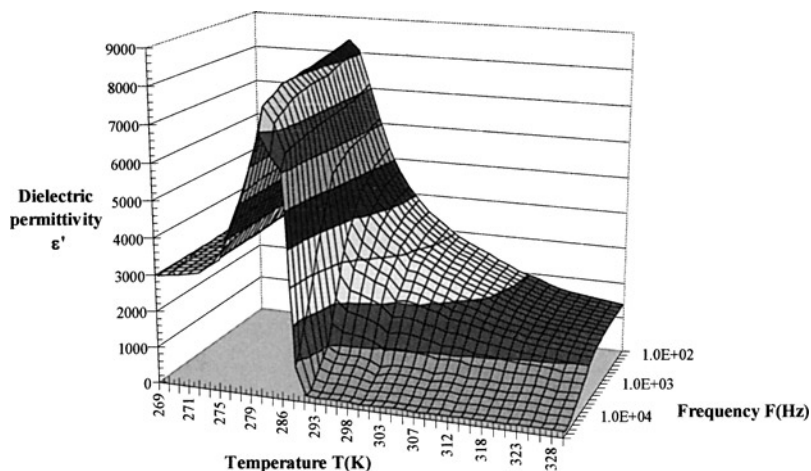


Figure 1a. Dielectric permittivity ϵ' of BST versus temperature and frequency.

The dielectric phase SiO_2 added to BST decreases drastically the temperature sensitivity of the composite, but the permittivity also sinks. The new composite BST/SnO_2 is promising, as it reaches characteristics of known composites such as BST/MgO and $\text{BST}/\text{MgTiO}_3$. However, the sintering process has to be optimized.

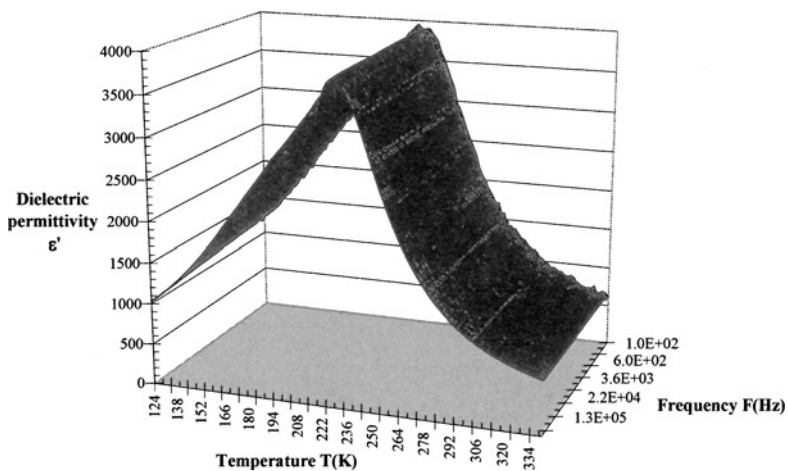


Figure 1b. Dielectric permittivity ϵ' of the composite BST/MgO —80/20 versus temperature and frequency.

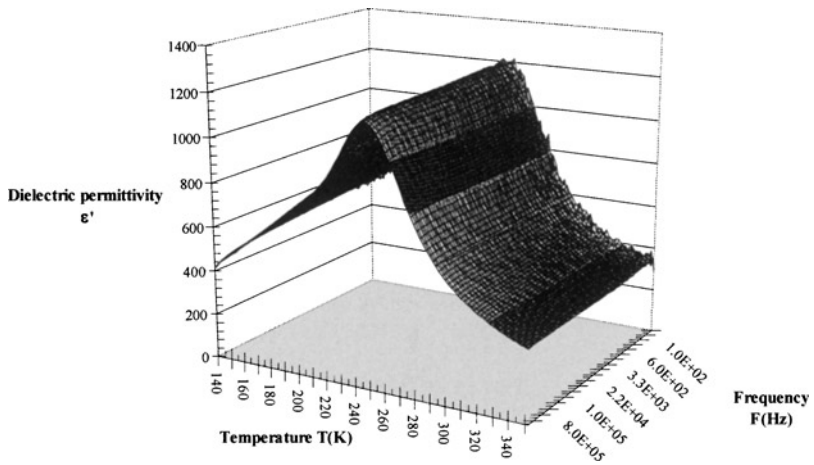


Figure 2a. Dielectric permittivity ϵ' of BST/MgTiO₃—80/20 versus temperature and frequency.

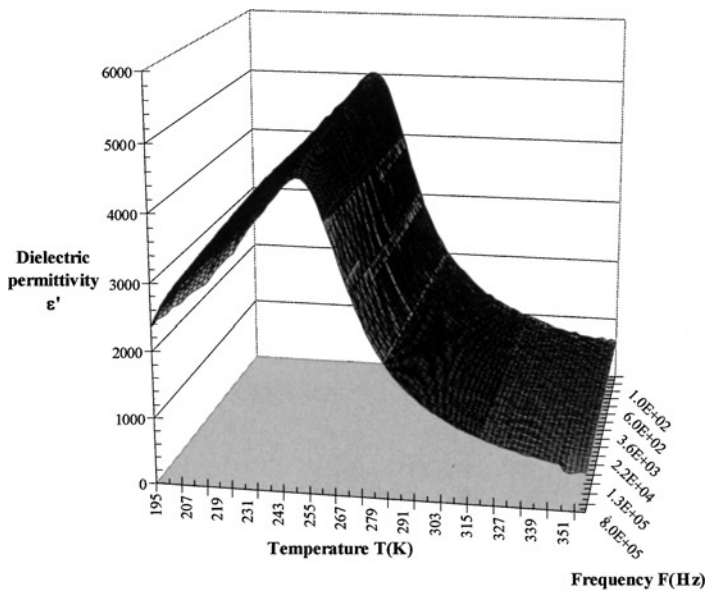


Figure 2b. Dielectric permittivity ϵ' of BST/SnO₂—95/5 versus temperature and frequency.

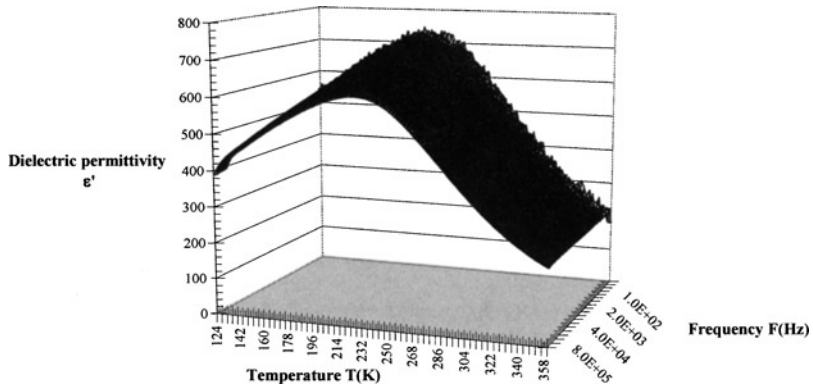


Figure 2c. Dielectric permittivity ϵ' of BST/SiO₂—95/5 versus temperature and frequency.

Tunability of BST was measured at various temperatures, close to room temperature (Fig. 3). The variation of about 20% of the permittivity with a moderated applied field ($E = 1.3$ kV/m) is compatible with the applications mentioned previously. Unfortunately the strong dependence versus temperature implies a very good thermal stabilization for the use in devices. Therefore composites were considered to increase the thermal stability, but due to the shift of the transition temperature to lower temperatures, the tunability at room temperature drastically sinks. The improvement of the tunability of the promising composites is under investigation.

The integration in microelectronic requires dielectric losses lower than 1%, which is achieved for BST at temperatures above about 280 K and frequencies higher than 10 kHz. The dielectric phase added to the composite was supposed to decrease the dielectric losses and enhance the temperature—frequency domain for integration.

Actually, for BST 95% + 5% SnO₂ composite (Fig. 4a and b), it is true only for the temperature domain $T > 248$ K ($\tan \delta < 1\%$). The dielectric losses are lowered for low frequencies but increase with increasing frequencies, exceeding 1% at 100 kHz already. An optimization of the ceramic quality of BST/SnO₂ composite may improve further the losses.

In comparison with BST properties, the dielectric data performed on all the sintered ceramic/ceramic composites show a slight decrease of the dielectric losses and a broadening of the transition peak, leading to a lower temperature sensitivity of the permittivity. However, the systematic decrease of the transition temperature $T_{\epsilon'_{\max}}$, due to the interdiffusion of the two phases leads to a decrease of the tunability at room temperature. Another

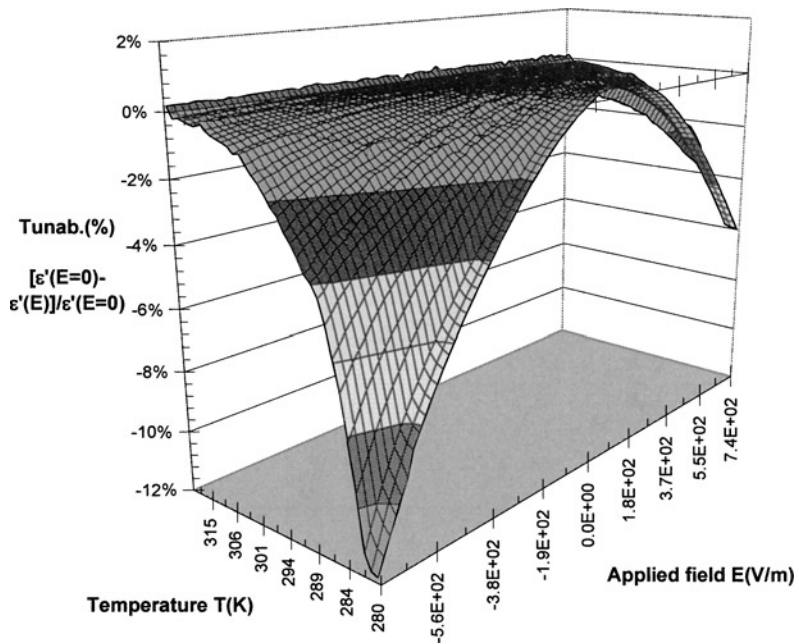


Figure 3. Variations of dielectric permittivity ϵ' of BST versus applied field and temperature at 100 kHz.

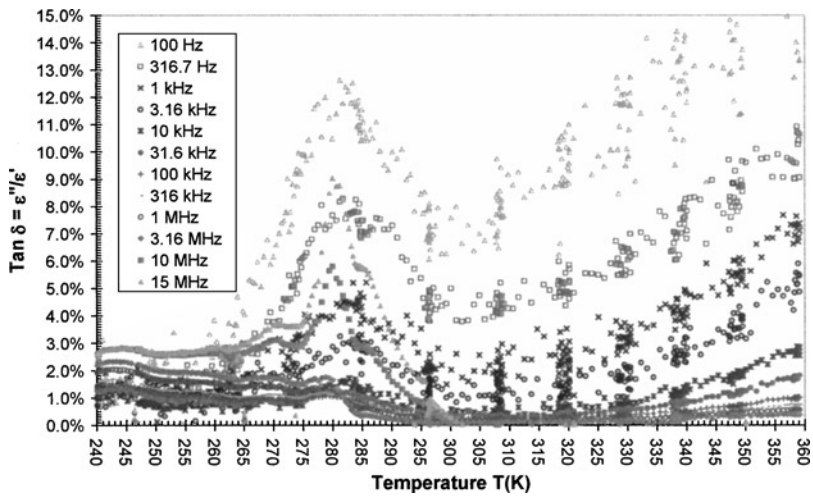


Figure 4a. Dielectric losses of BST ceramic.

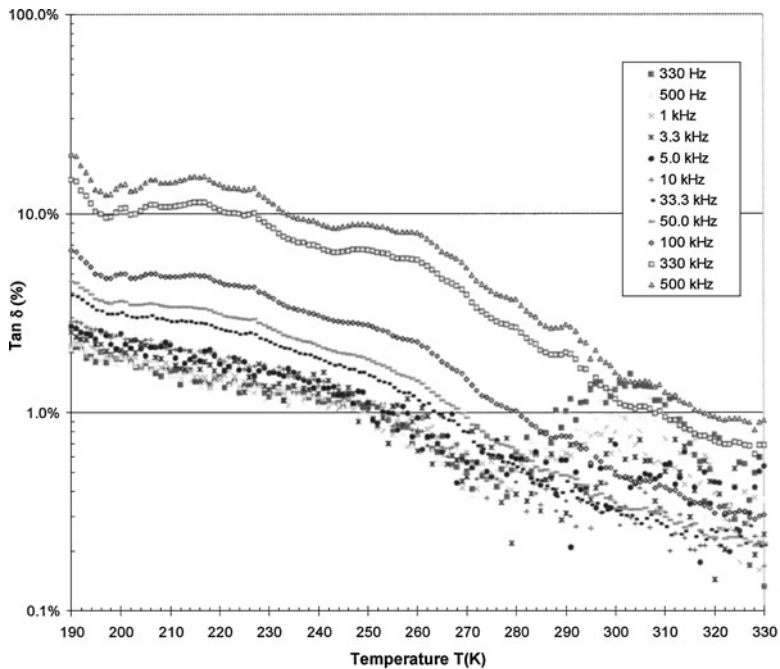


Figure 4b. Dielectric losses of BST/SnO₂—95/5 composite.

drawback of such ceramic/ceramic composites is the possible occurrence of charged defects resulting from the interdiffusion, which could improve the dielectric losses.

Statistical dispersion of BST grains in a low loss material may not separate all grains one from another unless a very low percentage of BST is used. This will induce a drastic decrease in ϵ_r , but a too long distance between BST grains is also likely to decrease the ferroelectric behaviour of the composite. Therefore a new design of composites is proposed. The aim is to isolate the ferroelectric grains one from another. Through soft chemistry route cores made of ferroelectric grains (BST) have been covered by a shell of dielectric material (SiO₂) to act as a loss barrier. After sintering, a well dispersed network of BST grains embedded in a SiO₂ matrix can be obtained. Despite this core-shell design has already been developed to tune magnetic properties [4], it is completely original in the field of ferroelectrics [5, 6, 7]. Moreover such a design enables to lower the sintering temperature as only the non-dielectric phase has to be sintered. Decreasing the sintering temperature

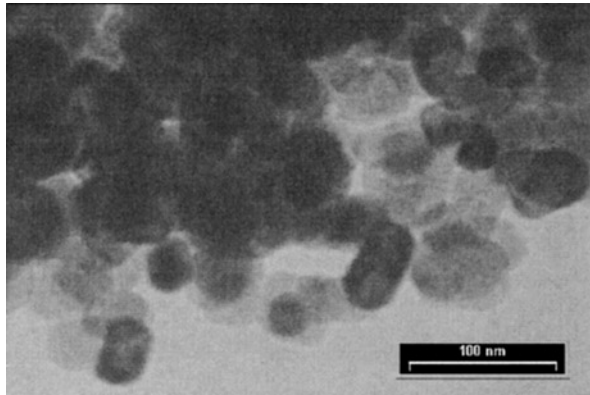


Figure 5a. BST crystallized grains used as cores.

is a way to avoid interdiffusion between the ferro and non-ferro phases. Transmission electron micrographs performed on core-shell materials show crystallized particles embedded in an amorphous shell (Fig. 5a and b).

The non optimized sintering conditions prevent an absolute measure of the dielectric permittivity of the core shell composites but it was possible to confirm that the intrinsic properties of the BST are kept. The measurement of the capacitance of pressed, non-sintered core shell powder: BST @ SiO₂ (with

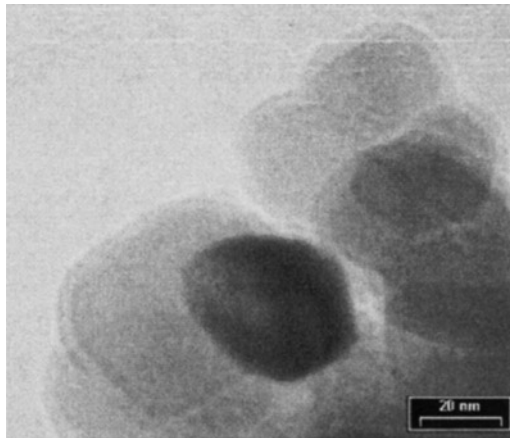


Figure 5b. BST cores of about 40 nm nanocoated with a SiO₂ shell of about 5 nm thickness.

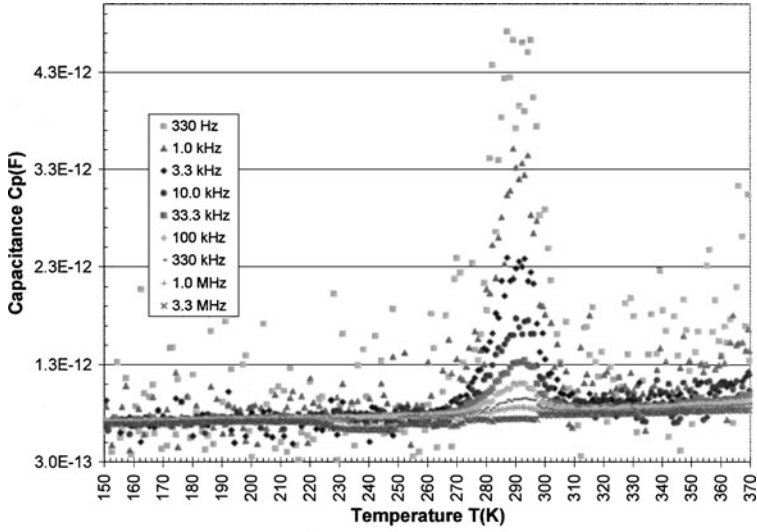


Figure 6. Dielectric measurements of non-sintered core shell BST @ SiO₂ pressed powder.

about 20% wt SiO₂) versus temperature and frequency showed a dielectric anomaly at T = 285 K (Fig. 6). The transition temperature observed remains the same compared to the BST one. Such a result is of utmost importance because the transition temperature is usually lowered in ceramic/ceramic composites (especially ceramic/ceramic composite BST/SiO₂ 80/20, see Table I).

TABLE I Comparison of composites

Composite (ceramic/ceramic)	T (max ϵ'_r) (K)	ϵ'_r max
Ref. BST	285	9000
80%BST-20%MgO	242	3800
80%BST-20%MgTiO ₃	248	1200
80%BST-20%SiO ₂	no peak	20
95%BST-5%SiO ₂	224	750
80%BST-20%SnO ₂	206	750
95%BST-5%SnO ₂	250	5000

V. CONCLUSION

The original idea of proposing a core shell structure for ferroelectric composites proved to be efficient and gives even better composites than classical mixing/co-sintering methods, as the transition temperature of the ferroelectric phase is maintained in core shell. This means that the ferroelectric phase is not disturbed by avoiding interdiffusion of dielectric and ferroelectric phases. The shell is also very likely to create a loss barrier between BST grains. Nevertheless, the compactness of the obtained material has to be improved before carrying on further dielectric characterizations. The sintering parameters will also be optimized for the promising BST/SnO₂ composite as an alternative to BST/MgO and BST/MgTiO₃ classical composites.

The next step will be the modulation of the core-shell properties by tuning either the grain size of the ferroelectric phase BST or the silica shell thickness. This last point opens important perspectives because ferroelectric/dielectric composites could be formed with a very easy and accurate control over the intercore distance in order to build an organized network. The distance between the ferroelectric grains and correlated loss barrier thickness could be adjusted to find the best compromise between the high permittivity of the core and the low losses of the shell. The non-linear dielectric properties as a function of the dielectric field will also be investigated.

REFERENCES

- [1] L. C. Sengupta and S. Sengupta, *Mat. Res. Innovat.* **2** (1998).
- [2] T. Mitsui and Landolt-Börnstein, vol. 3, Berlin: Springer-Verlag, 1969.
- [3] S. Nenez, University of Bourgogne, Thesis (2001).
- [4] CNRS, B. Chevalier et al., French Patent FR2791580, 2000-10-06, International Patent WO0059622, 2000-10-12.
- [5] T. Lee and I. A. Aksay, *Crystal Growth and Design* **1**(5) (2001).
- [6] F. Caruso, *Adv. Mater.* **13**(1) (2001).
- [7] P. Mulvaney, L. M. Liz-Marzán, M. Giersig, and T. Ung, *T. Mater. Chem.* **10** (2000).