ELSEVIER

Ceramics International 30 (2004) 1241–1245

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Nano-ferroelectric based core–shell particles: towards tuning of dielectric properties

C. Huber [a], C. Elissalde [a,*], V. Hornebecq [b], S. Mornet [a], M. Treguer-Delapierre [a], F. Weill [a], M. Maglione [a]

[a] *ICMCB-CNRS, 87 Av. Dr. A. Schweitzer, 33608 Pessac, France*
[b] *Laboratoire MADIREL (UMR 6121) Université de Provence-CNRS Centre Saint Jérôme, F-13397 Marseille Cedex 20, France*

Received 1 December 2003; received in revised form 10 December 2003; accepted 22 December 2003

Available online 12 May 2004

Abstract

For microwave agile devices such as tunable resonators or phase shifters, low loss components exhibiting electric-field dependent dielectric properties are seeked. Ferroelectric/low loss dielectric composites are good candidates to improve dielectric properties of $Ba_xSr_{1-x}TiO_3$ (BST) for such applications. Nanosized ferroelectric powders have been successfully encapsulated in a thin surrounding shell made of a binary oxide. The conservation of the ferroelectric transition in the composite has been shown while preserving the size of the ferroelectric cores after sintering.

The dielectric properties of the composite can be tuned by changing the relative core/shell sizes, the intercore distance, the nature of the dielectric phase. Various synthesis routes have been used according to the required design of the final nanocomposite. Dielectric performances are presented and compared among the different nano-ferroelectric core–shell based particles obtained.

Keywords: A. Powders: chemical preparation; B. Nanocomposites; C. Dielectric properties; D. SiO_2

1. Introduction

The need for functional materials in numerous fields of applications, biology, nanotechnology, electronics, has stimulated the research in the design of tailored materials. Obtaining such specially designed materials in view to control and then to predict their properties requires complex synthesis, improvement of shaping and refinement of the final properties modelling. In the field of nanotechnology, important efforts have been made for the processing of core–shell colloidal materials with tailored structural and surface properties. Such coated particles are generally used to protect the initial cores and to change or improve their initial properties. In the field of ferroelectric materials, some attempts to elaborate tailored composite materials can be reported from the literature. Ceramic and sol–gel synthesis routes are mostly used. Earlier results concern a coating technique of $BaTiO_3$ particles with Ta_2O_5 [1]. Later, $Pb(Zn_{1/3}Nb_{2/3})O_3$ based composite materials were prepared by particle coating with a glassy thin fim layer of SiO_2-B_2O_3 [2]. Liu et al. have investigated the effect of a metal coating copper on the crystalline structure of barium titanate small particles [3]. In the field of multilayer ceramic capacitors (MLCC), numerous papers deal with core–shell structure resulting from a gradient of composition from the bulk to the boundaries of the grains. To achieve this, both a high dielectric susceptibility and a better temperature stability are required [4,5]. To be suitable for the integration in the design of electronic devices, it is important to reduce the thickness of the dielectric layer which is used to coat the ferroelectric cores. One of the approaches is to modify the surface of $BaTiO_3$ small particles by coating. Chen et al. reported the coating process of $MgTiO_3$ on $BaTiO_3$ via fused salt method [6]. A coating approach for synthesizing relaxors with high dielecric constant was also recently reported [7].

To process agile high frequency devices such as tunable resonators or phase shifters, the challenge is to decrease the dielectric losses of the material, keeping an sensitivity of the permittivity with the electric field. $(Ba_{1-x}Sr_x)TiO_3$ [BST(1−x)−x] based composites including a dielectric

* Corresponding author.
E-mail address: elissald@icmcb.u-bordeaux.fr (C. Elissalde).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.067

phase (MgO, $MgTiO_3$, ...) are promising candidates. Most of them have been obtained by solid state route [8,9]. In order to improve and to tailor the properties of BST-based composites, we proposed to apply the core–shell concept to these materials. Nanosized BST powders were embedded in an amorphous silica shell in order to obtain a core–shell BST@SiO_2 with controlled particle size [10]. The only work reported in earlier literature on $BaTiO_3$/silica core–shell concerns the stabilization of $BaTiO_3$ particles in acidic solutions [11].

An uniform SiO_2 layer, coating BST colloidal particles, is expected to create a loss barrier between grains. Tuning the thickness of the silica shell would allow to control the distance between grains in the network of ferroelectric particles. Dielectric performances of BST60-40 composites are compared increasing the amount of silica phase, from a thin nano shell to a silica gel matrix. The aim is to tune the properties (losses and adaptability) via a full control of the composite architecture of dense ceramics.

2. Processing the composites

Core–shell composites were made of BST60-40 nanograins embedded in SiO_2 shell grown by kinetically controlled polycondensation of active silicate (NaOH, SiO_2) in aqueous phase. They are noted BST@SiO_2. After dispersion by ultrasound in water, the pH of desaggregated BST suspension was kept constant during the addition of the sodium silicate solution by adding simultaneously a sulfuric acid solution (0.085%). BST cores of 50 and 150 nm were used. The resulting system was aged under stirring at 90 or 60 °C to let the silica shell grow. Not only the addition temperature but also the solution concentration, the addition rate and the ageing time were modified to study the influence of these parameters on silica condensation. Thanks to an experiment plan based on variance analysis (Taguchi's method), one could quantify the effect of each coating parameter on the shell's thickness. Transmission electron microscopy (TEM) was carried out with a JEOL 2000FX microscope operating at 200 kV. A drop of the suspension was deposited on a copper grid with lacey carbon. The TEM micrographs show 150 nm BST particles with very thin coating of about 5 nm (Fig. 1). The thin SiO_2 shell continuously covers the BST cores even at edges and corners. Fig. 2 illustrates an optimized composite with a thickness of the shell of approximately 40 nm. The obtained core–shell composites were washed to eliminate Na^+, SO_4^{2-} and possible other hydroxide counter ions before sintering. Thermogravimetric and dilatometric experiments were carried out to optimize the sintering parameters. As a result, two preliminary steps at 250 and 600 °C are necessary to eliminate organic species resulting from the soft chemistry route used and the sintering temperature of these composites appears to be much lower than the one of pure BST (only 1100 °C instead of 1400 °C) which is of prime interest for microelectronic applications.

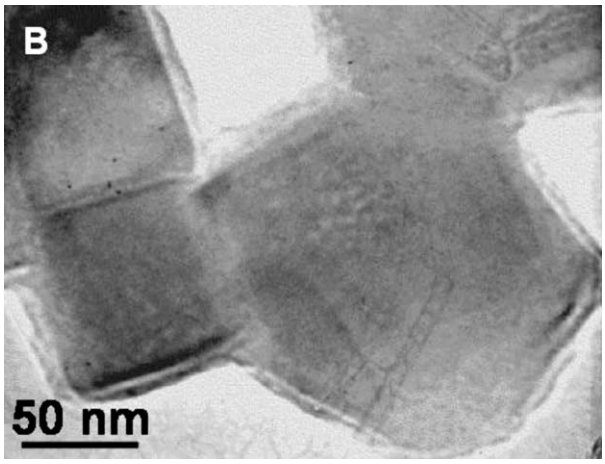

Fig. 1. Transmission Electron micrographs of 150 nm BST particles coated with 5 nm silica layer.

For relatively thick SiO_2 shells, BST@SiO_2 composites are equivalent to BST nanograins dispersed into a silicate matrix (noted BST/SiO_2). That is why we also processed this latter composite. The first step of the incorporation of BST particles (50 nm) in a silica gel is the peptization of the surfaces particles using a HNO_3 1 M solution in order to minimize the agglomeration by electrostatic repulsions and then to improve the dispersion of the nanpowder in the starting aqueous solution at pH 2 (solution 1). Tetraethyl orthosilane (TEOS; Si $(OC_2H_5)_4$) is used for the synthesis of the SiO_2 network which occurs in two stages: hydrolysis and polycondensation. The preparation of a prehydrolyzed ortho esters of silicic acid solution (solution 2) is done by mixing TEOS and HCL solution at pH = 2. The BST/SiO_2 gel is obtained after mixing of solutions 1 and 2 and after polycondensation step. The volumic fraction of BST nanopowders is varied from 30 to 75%. The incorporation of nanoparticles was checked by TEM (Fig. 3). Electron microprobe confirmed the good dispersion of particles in the matrix. The gels were sintered at 1000 °C during 2 h under oxygen atmosphere.

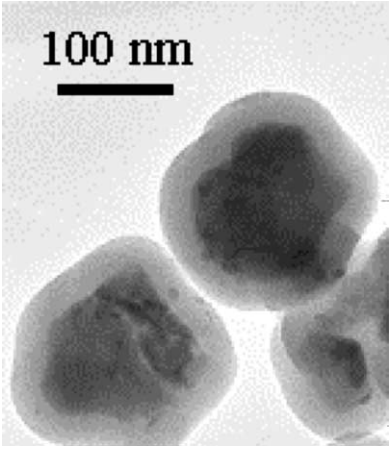

Fig. 2. Transmission Electron micrographs of optimized 150 nm BST particles coated with 40 nm silica layer.

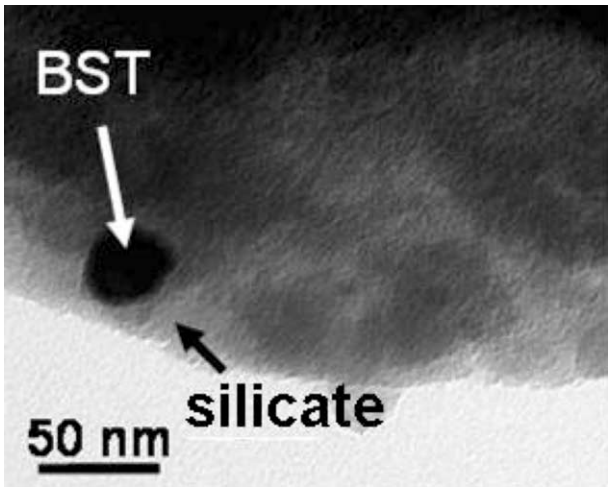

Fig. 3. TEM picture of silica gel containing BST nanoparticles.

3. Properties of composites

Dielectric measurements were performed on dense cylinders provided with sputtered gold electrodes on opposite faces. The permittivity ε' and the dielectric loss $\tan d$ were measured with an HP4194 analyser under frequency ranging from 100 Hz to 10 MHz, at various temperatures between 120 and 500 K. The tunability, defined by: $[\varepsilon'(E)\text{-}\varepsilon'(E = 0)]/\varepsilon'(E = 0)$, where E is the applied electric field, was deduced from the variation of the permittivity under a dc bias (−40 to 40 V on a 1 mm thick pellet) at 100 kHz and at various temperatures. The experiments reported here were performed on 150 nm BST core–shell in light of size effects on the Curie temperature evidenced in a previous work [12]. In fact, It appears that for a grain size below 150 nm the Curie temperature of pure BST60-40 decreases and does not meet the applications requirements, i.e. 275 K.

The thermal evolution of the permittivity showed that the temperature of transition of the ferroelectric nanograins is conserved in the core–shell, the Curie temperature of the 150 nm BST@SiO_2 is effectively found close to 275 K (Fig. 4). On the contrary when increasing the silica amount up to the gel, no dielectric anomaly as a function of temperature is observed whatever the volume fraction of BST (Fig. 5). The permittivity ε' decreases, as expected, with increasing the amount of SiO_2, i.e. the shell thickness from 10 to 20 nm. Tunability is retained in the core–shell composites. At room temperature and at a frequency of 50 kHz a value of 2% corresponding to 1 kV/cm applied field was measured on an optimized thin core–shell (Fig. 6). The value of ε' becomes very low in the gel which is not in favor of a possible tunability. However, the dielectric losses, in both core–shell and gel materials, are significantly decreased and more stable as a function of temperature as compared to that of pure BST (Figs. 4 and 5). As an example for the core–shell BST (150 nm)@SiO_2 (20 nm) the value of $\tan\delta$ is close to 0.01% on the whole temperature range (150–400 K) (Fig. 4).

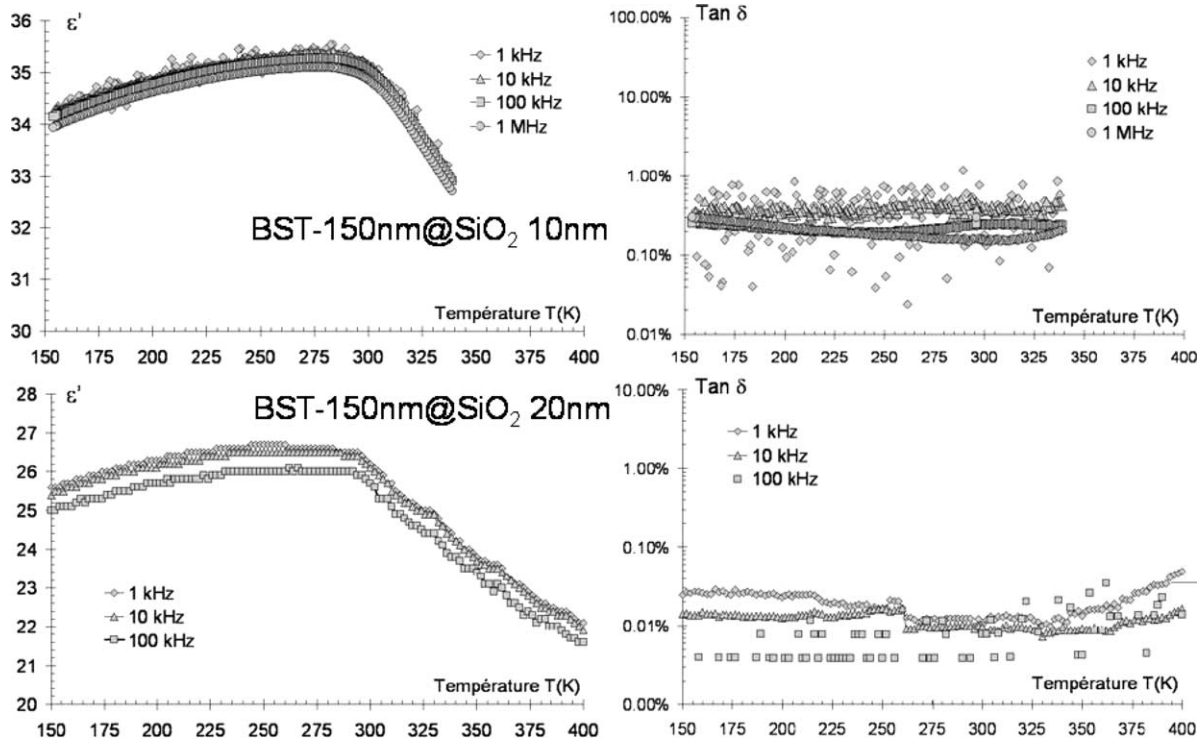

Fig. 4. Temperature dependences of ε'_r and $\tan\delta$ at different frequencies for sintered 150 nm core–shells with different silica shell thickness.

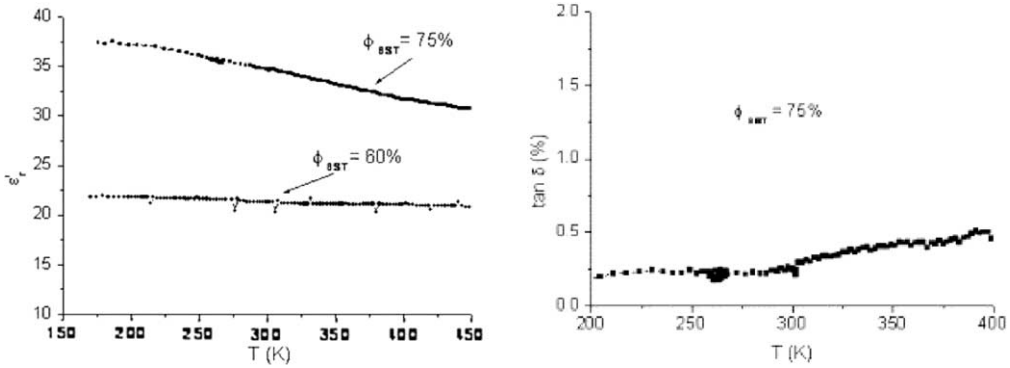

Fig. 5. Temperature dependences of ε'_r and $\tan\delta$ for various charges of BST (ϕ_{BST}) in a silica gel.

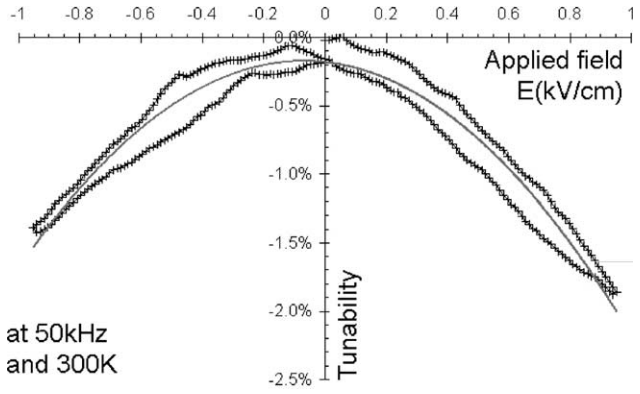

Fig. 6. Room temperature tunability of sintered optimized BST (150 nm)@SiO_2 core–shell.

4. Conclusion

New silica based ferroelectric composites were successfully synthesized by soft chemistry route. Core–shell BST with different size of cores have been coated with silica. As opposed to conventional solid state process, it is possible to control the BST@SiO_2 composites architecture as the distance between ferroelectric grains in the sintered composite depends directly on the kinetic parameters of the coating. Adequate tuning of the synthesis parameters allowed us to adjust the thickness of the silica shell from about 5 to 40 nm. Increasing at the extreme the amount of silica goes back to the embedding of BST nanoparticles in a gel. Dielectric measurements have shown a significant improvement of the dielectric losses in all the silica composites. Values as low as 0.01% in a large temperature range were observed in a BST@SiO_2 core–shell (20 nm shell thickness). The permittivity decreases strongly with the amount of silica phase. If the ferroelectric-paraelectric transition temperature remains the same temperature both in pure BST and core–shell materials, it does not appear anymore in the gel. Experiments performed on a BST@SiO_2 with a 150 nm core and a 20 nm thickness shell has shown satisfactory tunability. From potential applications point of view, these architecture controlled innovative composites are promising as their permittivity can be tuned as a function of SiO_2 content and the dielectric loss coefficient can vary from 1% down to 0.01% according to the shell size or to the BST charge for BST/SiO_2 gel composites. The sintering stage of the core–shell has to be optimized. The kinetic of the sintering is considered to be governed by the silica phase [13]. According to the kinetics of the matter transport at the selected sintering temperature, the silica thickness between grains in the final sintered core–shell will differ from the one of the initial powder. A better understanding of sintering mechanisms is necessary to optimize the sintering conditions in order to control the silica shell thickness in the dense composite. This core–shell concept applied to ferroelectric material also opens the route for innovative composites by varying not only the dimension of the core and the shell but also their chemical composition.

References

[1] T.M. Harkulich, J. Magder, M.S. Vukasovich, R.J. Lockhart, Ferroelectrics of ultrafine particle size. II. Grain growth inhibition studies, J. Am. Ceram. Soc. 49 (6) (1966) 295.
[2] Z. Yue, X. Wang, L. Zhang, X. Yao, Temperature stable $Pb(Zn_{1/3}Nb_{2/3})O_3$—stable composite ceramics prepared by particle-coating method, J. Mater. Chem. 16 (6) (1997) 1354.
[3] X. Liu, W.Y. Shih, W.-H. Shih, Effects of copper coating on the crystalline structure of fine barium titanate particles, J. Am. Ceram. Soc. 80 (11) (1997) 2781.
[4] S.H. Yoon, J.H. Lee, D.Y. Kim, Core–shell structure of acceptor-rich, coarse barium titanate grains, J. Am. Ceram. Soc. 85 (12) (2002) 3113.
[5] S. Gablenz, C. Damm, F.W. Müller, G. Israel, M. Rössel, A. Röder, H.-P. Abicht, Preparation and characterization of core–shell structured TiO_2–$BaCO_3$ particles, Solid State Sci. 3 (2001) 291.
[6] R. Chen, A. Cui, X. Wang, L. Li, Barium titanate coated with magnesium titanate via fused salt method and its dielectric property, Mater. Sci. Eng. B99 (2003) 302.
[7] H. Gu, W.Y. Shih, W.-H. Shih, Single-calcination synthesis of pyrochlore-free $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics using a coating method, J. Am. Ceram. Soc. 86 (2) (2003) 217.
[8] L.C. Sengupta, E. Ngo, M.E. O'Day, S. Stowell, Fabrication and characterization of barium strontium titanate and a non ferroelectric oxide composites for use in phased array antennas and other electronic devices, in: Proceedings of the IEEE 9th International Symposium on Applications of Ferroelectrics, Institute of Electrical and Electronics Engineers, New York, vol. 5, 1994, p. 622.

[9] S. Nenez, A. Morell, M. Pate, M. Maglione, J.C. Niepce, J.P. Gane, Dielectric properties of barium strontium titanate/non ferroelectric oxide ceramic composites, Key Eng. Mater. (2002) 206.
[10] C. Huber, M. Treguer-Delapierre, C. Elissalde, F. Weill, M. Maglione, New application of the core–shell concept to ferroelectric nanopowder, J. Mater. Chem. 13 (2003) 650.
[11] W.-H. Shih, D. Kisailus, Y. Wei, Silica coating on barium titanate particles, Mater. Lett. 24 (1995) 13.
[12] V. Vornebecq, C. Huber, M. Maglione, M. Antonietti, C. Elissalde, Adv. Mater., in press.
[13] A. Jagota, Simulation of the viscous sintering of coated particles, J. Am. Ceram. Soc. 77 (8) (1994) 2237.