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To link to this article :

URL : <http://dx.doi.org/10.1007/s10832-007-9396-8>

To cite this version : Valdez-Nava, Zarel and Guillemet-Fritsch, Sophie and Tenailleau, Christophe and Lebey, Thierry and Durand, Bernard and Chane-Ching, Jean-Yves (2009) [*Colossal dielectric permittivity of BaTiO₃-based nanocrystalline ceramics sintered by spark plasma sintering.*](#) Journal of Electroceramics, vol. 22 (n° 1 - 3). pp. 238-244. ISSN 1385-3449

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Colossal dielectric permittivity of BaTiO₃-based nanocrystalline ceramics sintered by spark plasma sintering

Z. Valdez-Nava · S. Guillemet-Fritsch · Ch. Tenailleau · T. Lebey · B. Durand · J. Y. Chane-Ching

Abstract In pursuit of high permittivity materials for electronic application, there has been a considerable interest recently in the dielectric properties of various perovskite oxides like calcium copper titanate or lanthanum doped barium titanate. When processed in a particular way, this later material present at ambient temperature and at $f=1$ kHz unusual interesting dielectric properties, a so called “colossal” permittivity value up to several 10^6 with relatively low dielectric losses. Moreover and contrary to what is classically expected and evidenced for this type of materials, no temperature dependence is observed. This behavior is observed in nanopowders based ceramics. An assumption to explain the observed properties is proposed. These results have important technological applications, since these nanoceramics open a new route to the fabrication of very thin dielectric films.

Keywords Coprecipitation · Barium titanate · Nanoceramics · Spark plasma sintering · Dielectric properties

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1 Introduction

BaTiO₃ is a material presenting high ferroelectric properties that find applications in various fields and is often used to prepare multilayers capacitors. A way to increase the permittivity value and to reduce the Curie temperature is the substitution of a small amount of lanthanum in the perovskite lattice (0.05 per unit formula) [1–4]. Fine grained powders of various compositions of La doped barium titanate (Ba_{1-x}La_xTi_{1-x/4}O₃, 0 < x < 0.15) have been prepared recently by coprecipitation and the electrical properties of the corresponding conventional sintered ceramics have been determined [5].

Another way to increase the relative permittivity of such system is to retain small grains in the ceramic. Spark Plasma Sintering (SPS) is the adapted tool for producing well densified ceramics with small grain size, due to short time of experiment performed at relatively low temperature, compared to the conventional sintering process. Numbers of papers have been published on the SPS sintering of undoped barium titanate showing the interest of such technique (Table 1). Takeuchi et al. [6–9] obtained sintered pellets with an average grain size less than 1 μm, exhibiting a room temperature (RT) permittivity of 10,000 at 1 kHz. Buscaglia et al. [10] showed a broadening of the ferroelectric to paraelectric transition, in nanostructured BaTiO₃ ceramics sintered by SPS at 800 °C. Li et al. [11] reported the effect of the sintering temperature, the holding time, the heating rate and the synthesis method on the grain size and the density. The obtained dense BaTiO₃ ceramics showed a grain size of about 100 nm. Luan et al. [12] completed the study by HRTEM observations showing 180° ferroelectric domains and some twins. Up to date, no paper has reported the SPS sintering of La doped BaTiO₃ powders. The properties at room temperature of the as sintered barium

Table 1 Reported properties of BaTiO₃ ceramics sintered by SPS.

Reference	Densification (%)	Grain size	ϵ' (1 kHz, RT)	ϵ' max	T _c (°C)
Takeuchi et al. 1999 [6, 7]	95	<1 μm	10,000		
Takeuchi et al. 2002 [9]	>95	<0.5 μm	3,500	8,500	120
Buscaglia et al. 2004 [10]	96<<97	53 nm	<1,000		
Li et al. 2004 [11]	95	1 μm	5,000	10,000	120
Luan et al. 2004 [12]	99	200 nm	3,800	8,500	120

titanate ceramics were a little higher than the one of conventional sintered ones. In the present work, we report on the unusual extraordinary high values of permittivity measured for non doped and La doped barium titanates.

For that purpose, lanthanum doped barium titanate powders are prepared by a low temperature synthesis method and sintered by spark plasma sintering, and compared to the properties of undoped titanates prepared under the same conditions.

2 Experimental

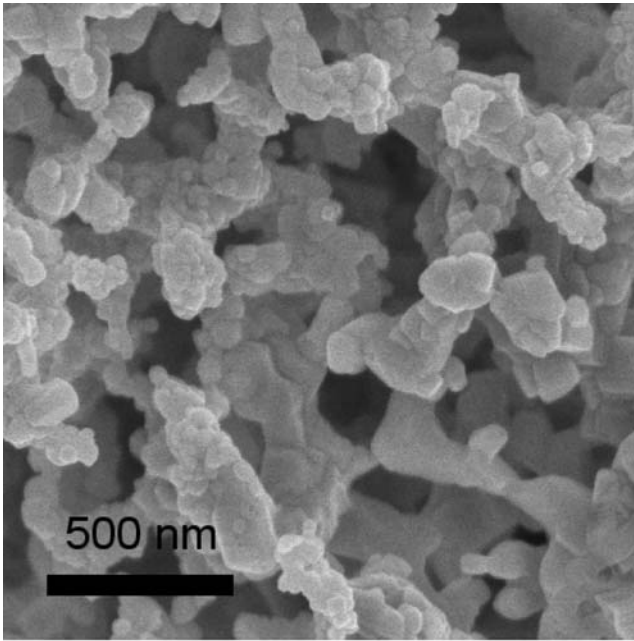
The samples of composition BaTiO₃ and Ba_{0.95}La_{0.05}TiO₃ were prepared as follows. The starting materials, BaCl₂·2H₂O (Prolabo), TiCl₃ (Prolabo, $d=1.20$, % min=15) and LaCl₃·7H₂O (Prolabo, 99%) were weighted in appropriate proportions. They were dissolved in water and the coprecipitation was performed by addition of a solution of oxalic acid dissolved in ethanol. TiCl₃ was chosen because it is easier to handle than TiCl₄. The full oxidation of Ti³⁺ in Ti⁴⁺ in the solution was ensured by air bubbling during the reaction and was evidenced by the visual observation of the color change from brown to yellowish. The volume of water was taken much lower than the one of ethanol, in order to decrease the dielectric constant of the precipitation media. Since the nucleation of the particles is favored compared to the growth, smaller particles, homogeneous in size and composition, are likely to be obtained. The precipitated oxalate was separated from the liquid phase by centrifugation, then washed several times with ethanol and dried overnight at 100 °C. The precipitated oxalate was transformed into oxide by a calcination at 850 °C for 4 h in static air.

Sintering was performed by means of a Dr. Sinter 2080 device from Sumimoto Coal Mining. The doped BaTiO₃ powder (0.9 g) was placed inside a graphite die of 8 mm diameter and an electrical current up to 350 A was applied under a pressure of 50 MPa. No sintering aid was added. The samples are heated at a temperature comprised between 1050 and 1210 °C (heating rate=50 °C/min). After 3 min dwell, the electric current was turned off and the pressure was released. It took approximately 1 min for the sample to cool down from the temperature dwell to 600 °C. The

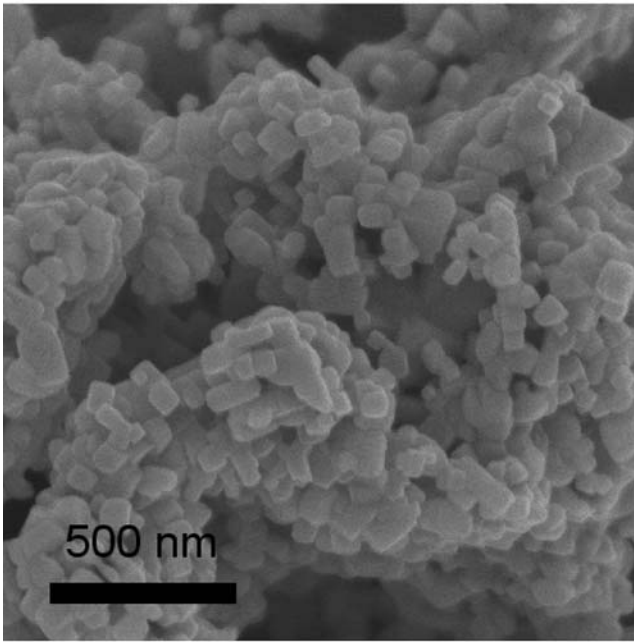
presence of a thin carbon layer was observed at the surface of the as-sintered pellets, due to graphite contamination from graphite foils inserted between the die, punches and the ceramic powder. This layer was easily removed by polishing the surface. The ceramics appeared dark blue colored in the volume. In fact, the atmosphere during the sintering led to the reduction of some Ti⁴⁺ into Ti³⁺, a well known phenomena in SPS sintering.

The accurate chemical composition of the oxide powder was determined by using induced coupled plasma spectroscopy (ICP AES Thermo-Optec ARL 3580). The oxide powder morphology was observed with a Field Electron Gun Scanning Electron Microscope (JEOL 6700F). The structure was determined by X-ray diffraction analysis. The data were collected on a Bruker D4 Endeavor X-ray diffractometer (CuK _{α} =0.154056 nm and CuK _{β} =0.154044 nm) from 20° to 100° (2-theta) in 4 h. Pellet density was determined using Archimede method. The densification is given in percent with an error of $\pm 0.3\%$. Raman spectra were acquired in the 100 to 1,000 cm⁻¹ range at 300 K in a LabRAM HR800 high resolution Raman spectra microscope (Jobin-Yvon), with a He-Ne laser of 632.82 nm. X-ray photoemission spectra were collected with a VG Escalab 220i XL apparatus, in collaboration with CeCaMA at ICMCB Bordeaux laboratory. Carbon contamination due to SPS processing technique was determined through the spectrometric quantification of CO₂. Sample was placed in a tubular furnace and a mixture of 20% O₂ and 80% N₂ was passed through the furnace. The system is connected to a Fourier transform infrared analyzer (FTIR) Nicolet 510P that collects spectroscopic data at regular intervals. The sample was heated from 300 to 1273 K at constant gas flow rate. The total CO₂ that was produced from the sample was calculated from the integration of the curve over time. By comparing to a known calibration gas mixture, the total amount of carbon in the sample can be determined. Electron Energy Loss Spectroscopy (EELS) experiments were made in a transmission electron microscope Philips CM20 with a Gatan EELS measurement device. Transmitted electrons were collected in the EELS apparatus with an entrance diaphragm of 1 mm and an energy dispersion of 0.2 eV.

Prior to electrical measurements, the ceramic disks were coated with silver paste electrodes and fired at 850 °C.



(a)



(b)

Fig. 1 FEG-SEM micrographs of undoped BaTiO_{3-x} (a) and La 5% doped $\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$ (b) powders

Electrical measurements were performed in the frequency range 0.1 to 100 kHz and at temperatures ranging from -100 to 200 °C thanks to a TA instrument DEA 2970.

3 Results

FEG SEM pictures of the calcined powder [Fig. 1(b)] confirm that La-doped BaTiO_3 powder is constituted of small particles. In this case, the average grain size (50 nm) is lower than the one of undoped BaTiO_3 prepared under the same conditions [Fig. 1(a)]. The particles are mostly agglomerated, due to partial sintering during the calcination procedure. As expected, the BaTiO_3 powder crystallizes in the tetragonal perovskite structure while if doped with lanthanum, it has the cubic perovskite structure. Buscaglia et al. [13] showed that the substitution of Ba by La reduces the tetragonal distortion and that the structure becomes cubic for a lanthanum constant $x \geq 0.05$.

The dense dielectrics ceramics were prepared from nanoscale chemically homogeneous powders by Spark Plasma Sintering (SPS) method at two different temperatures (1050 and 1210 °C). The sintered materials displayed a blue color due to the reducing sintering atmosphere. Both doped and non doped BaTiO_{3-x} nano materials, sintered at 1050 and/or 1210 °C display a density value higher than 96% d_{th} (Table 2).

Because our dense ceramics sintered by SPS are brittle, microstructure observation and identification of grain boundaries by microscopy investigation are difficult. Although there is some uncertainty, an average grain size ~ 250 nm was determined for the BaTiO_{3-x} ceramic and 50 nm for $\text{La}_{0.05}\text{Ba}_{0.95}\text{TiO}_{3-x}$ material sintered at the same temperature i.e. 1050 °C (Fig. 2).

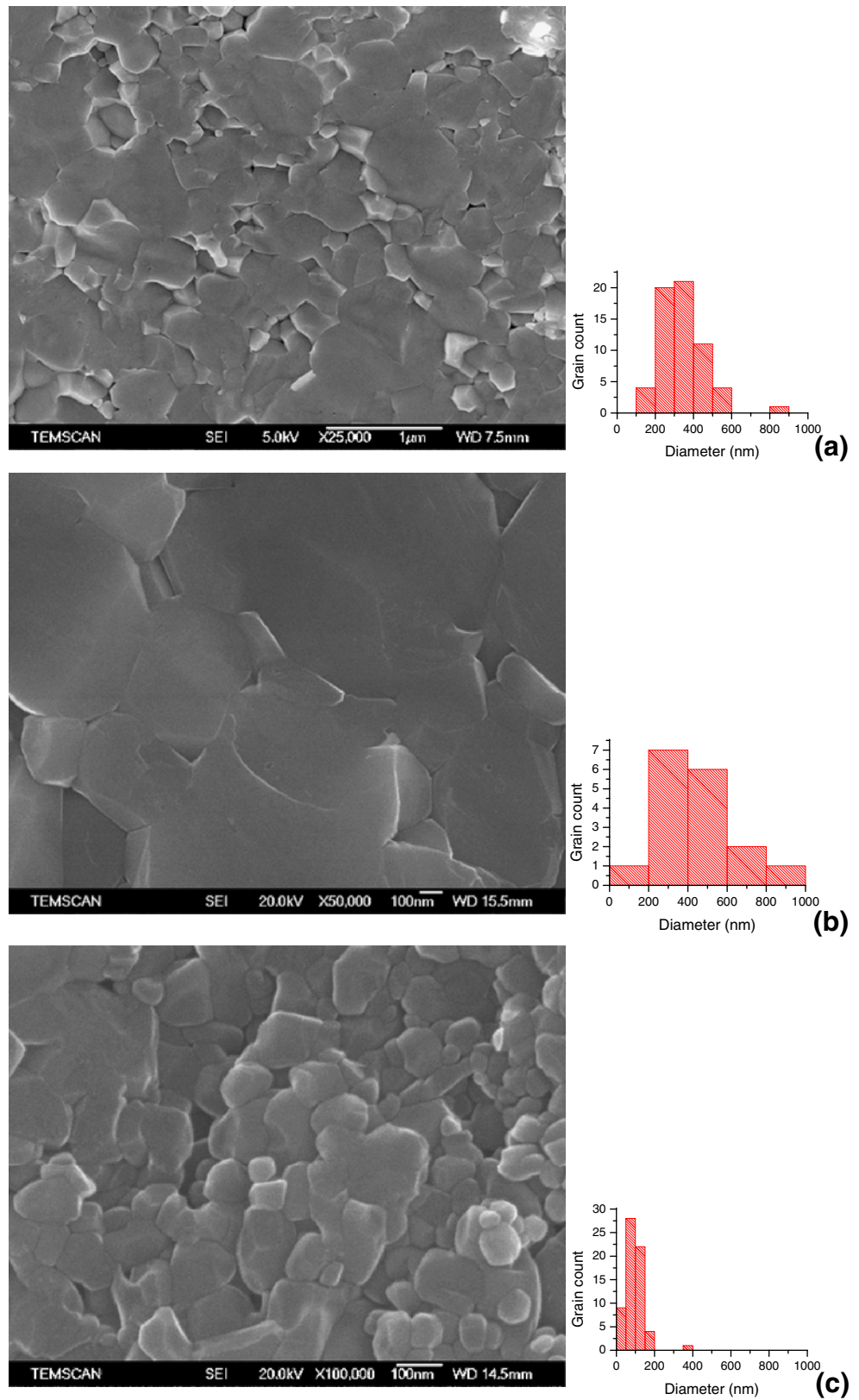
The diffraction patterns show that the materials consist of a mixture of cubic (or pseudo cubic) and tetragonal phases (Fig. 3). The inserts show the (111) pattern as well as (002) and (200) reflections for the tetragonal phase. Since the tetragonal phase was reported as unstable for grain size lower than $0.7 \mu\text{m}$, our nano material consists of an unexpected mixture of $\sim 66\%$ of tetragonal and $\sim 33\%$ of cubic phase determined using a Rietveld method. This is consistent with previous results showing coexistence of both phases using the SPS technique with submicrometer-sized grains. The Raman spectra of the BaTiO_{3-x} and

Table 2 Chemical composition, sintering temperature, densification, structure, oxygen deficiency and $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio in studied ceramics.

Composition	Sintering temperature (°C)	Densification (%)	Structure	x (EMPA)	x (EELS)	$\text{Ti}^{3+}/\text{Ti}^{4+}$
BaTiO_{3-x}	1050	96	T+C	0.36		0.015
$\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$	1210	99	T+C	0.39	0.36	0.036
	1050	96	T+C	0.36		0.029

T+C: tetragonal+cubic perovskite

Fig. 2 FEG-SEM micrographs and grain size distribution of undoped BaTiO_{3-x} (1050 °C) (a) and La 5% doped $\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$ ceramics at 1210 (b) and 1050 °C (c)

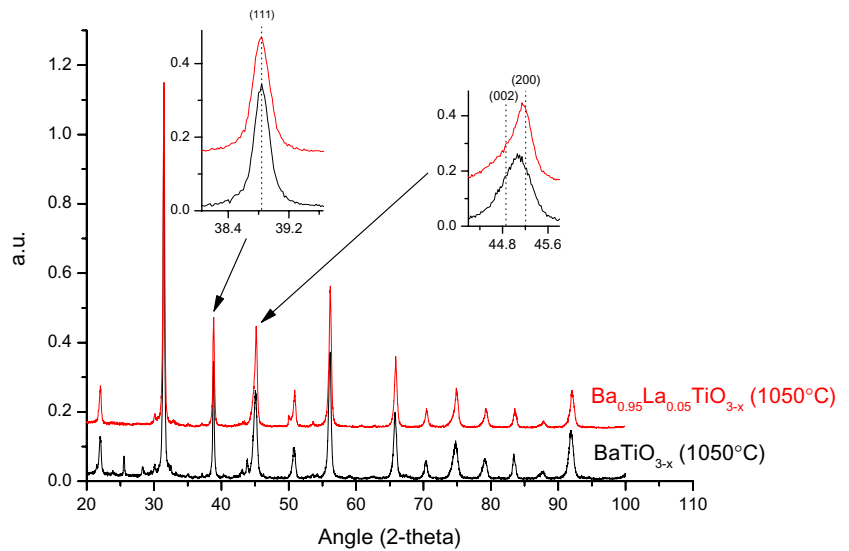


$\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$ (Fig. 4) ceramics are in agreement with X-ray diffraction data. They show for all samples the characteristic peaks related to both cubic and tetragonal phases. Less defined peaks were observed in the case of La-

doped samples. Note the presence of a broad peak at 513 cm^{-1} suggesting polydispersity of vibrating modes.

The spectrometric quantification of CO_2 allows to determine the total amount of carbon (1.4×10^{-5} mole) present in

Fig. 3 X-ray diffraction pattern of undoped BaTiO_{3-x} (1050 °C) and La 5% doped $\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$ (1050 °C) ceramics



the sample of 1.8 g. If we assume that all the carbon reacted with the gas mixture, a total carbon concentration in the sample of 93 ppm can be estimated. The experiment was limited to 1550 K, due to apparatus limits. However the carbon content not taken into account at higher temperature is estimated to be very low.

All the studied ceramics are O_2 deficient (Table 2). Electron probe microanalysis showed a surprisingly large oxygen substoichiometry (noticed x) in the BaTiO_{3-x} and in the $\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$ samples. EELS measurements made on one sample ($\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$ sintered at 1210 °C) confirmed the oxygen content of the ceramic. The distribution of O, Ti, and Ba are very homogeneous along the grain and the grain boundary. The calculations were made without multiple scattering contribution correction, that indicate a semi-quantitative information only. However the data are in good agreement with the EPMA results (Table 2).

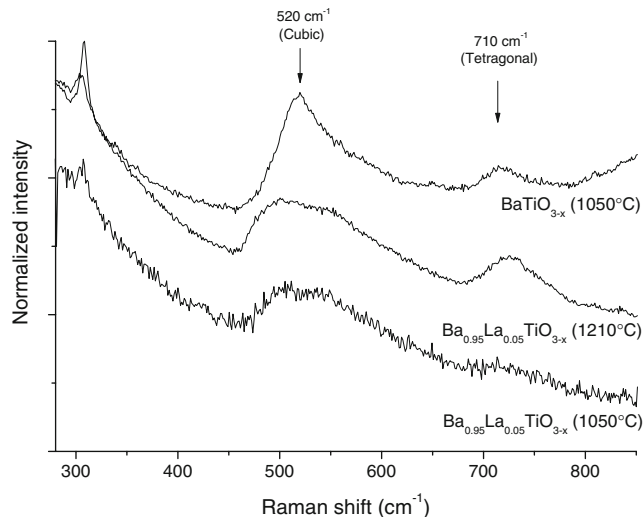


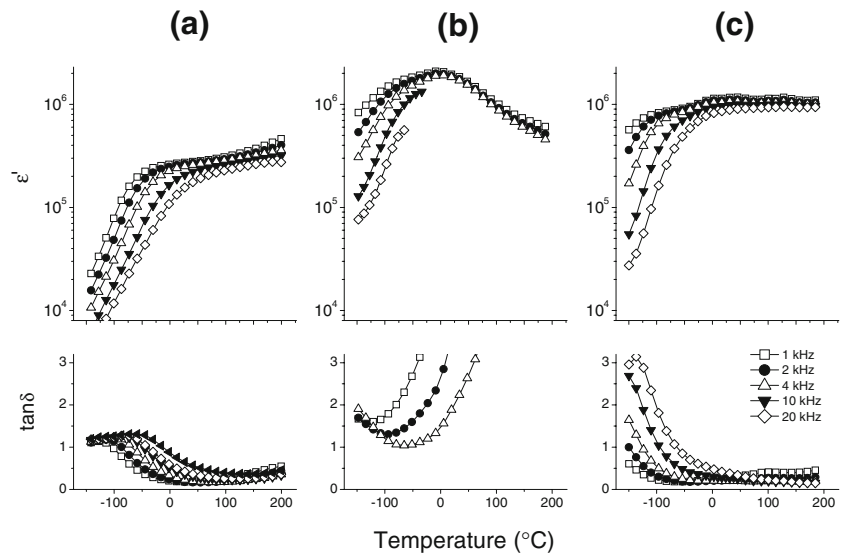
Fig. 4 Raman spectra of undoped BaTiO_{3-x} (1050 °C) and La 5% doped $\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$ (1050 and 1210 °C)

The oxygen loss during the sintering process varies with the temperature, the lanthanum content, the heating and cooling rate, the microstructure and the pellet density. We do not know if it occurs preferentially at grain boundaries or in the bulk. The large oxygen deficiency creates a disequilibrium of the charge in the ceramics. It can be compensated via two mechanisms, the formation of a large amount of Ti^{3+} in the material and/or the presence of Ti vacancies for electro-neutrality. Both lanthanum doping and sintering temperature can influence the amount of oxygen in the structure. Hence, balanced compensation mechanism occurs via the electronic “La donor doping” effect where $\text{Ba}^{2+}=\text{La}^{3+}+\text{e}^-$ and the subsequent formation of Ti^{3+} and to the reducing sintering atmosphere. Although there is evidence of Ti^{3+} in our materials, a precise quantitative determination can be altered when using a microscopic characterisation technique such as XPS. Measurements have been performed on freshly fractured ceramics. Besides the confirmation of Ti^{3+} in all ceramics, XPS measurements tend to show that Ti^{3+} concentration increases with La-doping. Indeed, $\text{Ti}^{3+}/\text{Ti}^{4+} \sim 1.5$ and 3.6 for BaTiO_{3-x} samples sintered at 1050 °C and $\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$ samples sintered at 1210 °C, respectively (Table 2).

The variations of relative permittivity and of $\tan\delta$ with temperature are shown in Fig. 5 for various frequencies. These ceramics show tremendous permittivity values, up to 10^6 (at ambient temperature and at $f=1$ kHz). First of all, it is important to notice that such huge values of permittivity have never been reported before for barium titanate based materials. These permittivity values are even higher than the ones of the so-called giant dielectric permittivity $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCT) materials [14, 15].

Moreover, in most cases, the dielectric losses remain in an acceptable range whatever the materials and the frequency and temperature ranges. No Curie like transition

Fig. 5 Variation of relative permittivity (ϵ') and loss ($\tan \delta$) as a function of temperature for various frequencies for undoped BaTiO_{3-x} sintered at 1050 °C (a) and La 5% doped $\text{Ba}_{0.95}\text{La}_{0.05}\text{TiO}_{3-x}$ ceramics sintered at 1210 (b) and 1050 °C (c)



corresponding to structural changes is observed. This behaviour is very unusual and contrary to the results that have been previously reported [16].

The real part of the complex permittivity remains high (up to and larger than 10^6) and quasi constant once the polarisation phenomenon corresponding to the maximum of the relaxation process has been achieved. This relaxation may be directly observed by the location of the maximum losses (as may be seen in Fig. 5(a)) or by a decreasing slope and a sudden variation of it [Fig. 5(b) and (c)] in the lowest part of the temperature range under study. It is well known that the dielectric properties of the barium titanate ceramics depend on their grain size. Recently, dense non doped BaTiO_3 nanoceramics with an average grain size as low as 50 nm have been prepared by SPS [10]. In that case, the dielectric data show a broad phase transition with a maximum permittivity of 1100 at 390 K and 1 kHz. Obviously, since our ceramics have similar grain size and show quite different behaviour, the oxygen content of the samples has to be taken into account. The electrical properties of barium titanate ceramics are very sensitive to oxygen content [3]. The pellets sintered in pure O_2 atmosphere are reported as insulating while those reheated in air for 30 min after sintering present a semi conducting bulk and resistive grain boundaries. West et al. [3] suggested that the semiconductivity of the samples heated in air or argon is associated entirely with the creation of oxygen vacancies. Barium titanate can be doped with La^{3+} ions via partial substitution for Ba^{2+} ions. The charge balance is maintained by the creation of Ti^{4+} vacancies. The samples processed in an atmosphere of 1 bar of O_2 and at 1350 °C are insulating and free from electronic defects associated with O_2 loss and/or the reduction of Ti^{4+} to Ti^{3+} . In this case, for $x=0.05$, ϵ' reaches a maximum of 19,000 at

ambient temperature, compared to 10,000 at 130 °C for undoped ceramics [4]. So in the present work, the high value is linked to the combination of a site doping and the formation of Ti vacancies.

The precise physical phenomenon able to explain the behaviour of our ceramics is still under discussion. However, the most likelihood among different possible mechanisms could be an interfacial polarisation taking place at the grain boundaries. The very small size of the grains (100 nm) may explain why a Maxwell–Wagner like (MW) polarisation is observed in a relatively high frequency and low temperature range. This mechanism is associated to a charge accumulation at the interfaces among the different “constituting” materials due to the difference in both their permittivities and conductivities. It could be the result of macroscopic motions of charge carriers (electrons, holes and ions) within the bulk towards interfaces. Due to the size of the grains and for the ac applied electric field, positive charge carriers (respectively negative) would have sufficiently time or energy to drift to the vicinity of the negative polarized interface (respectively positive) in order to build-up a space-charge supposing quasi blocking interface even for these temperature and frequency ranges.

Once this polarisation phenomenon has occurred, the properties remain constant, demonstrating that no other polarisation mechanism occurs. The localisation of the temperature and the frequency ranges for the relaxation depend on the nature of the material and is influenced by the lanthanum content and the grain size.

The material in Fig. 5(b) on the other hand exhibits temperature dependence. Such a decrease has to be associated to the huge losses values of the material in the same temperature and frequency range leading to questions regarding its capacitive nature.

4 Conclusion

Nanometric powders of barium titanate and lanthanum doped barium titanate have been prepared by coprecipitation synthesis. Using the spark plasma sintering technique, with a sintering dwell of 3 min in the temperature range $990 < T < 1210$ °C, ceramics of densification higher than 96% were obtained. The grain size of these ceramics is comprised between 50 and 250 nm and confirm that little grain growth occurs during the sintering by SPS. The electrical characteristics of these ceramics are significantly different from those of conventionally sintered ones and from those previously reported in the literature for SPS sintered barium titanates. In the temperature range -100 and $+150$ °C, no Curie transition was observed anymore and the value of the relative permittivity is colossal. It reaches 1.10^6 (at ambient temperature and at 1 kHz) in the most favourable case. The proposed mechanism to explain these unusual properties is based on an interfacial polarisation involving polarons due to the presence of Ti^{3+} cations.

Acknowledgements The authors thank Ch. Calmet for the FEG SEM observations, G. Raimbeaux and C. Estournes for the help in the SPS experiments and Ch. Labrugere for the XPS measurements.

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