Ceramics International 33 (2007) 35–40

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Re-investigation of synthesis of $BaTiO_3$ by conventional solid-state reaction and oxalate coprecipitation route for piezoelectric applications

L. Simon-Seveyrat *, A. Hajjaji, Y. Emziane, B. Guiffard, D. Guyomar

Laboratoire de Génie Electrique et Ferroélectricité – INSA Lyon, Bât.Gustave Ferrié,
8 rue de la Physique, 69621 Villeurbanne Cedex, France

Received 10 June 2005; received in revised form 28 June 2005; accepted 12 July 2005

Abstract

The formation of barium titanate powder by solid-state reaction and oxalate coprecipitation route is re-investigated by differential thermal analysis–thermo-gravimetry (DTA–TG) thermal analysis and high temperature X-ray diffraction (XRD). The temperature formation of the perovskite phase is lower for the chemical way than for the solid state one, and no intermediate product is detected. The obtained powder leads to ceramics with high dielectric and piezoelectric properties. For example the room temperature piezoelectric d_{33} coefficient is 260 pC/N (higher than the values usually published in the literature) and it shows a good stability under electrical solicitations. These properties make $BaTiO_3$ (BT) a lead-free high performance material for piezoelectric applications.

Keywords: B. X-ray methods; C. Thermal properties; C. Piezoelectric properties; D. $BaTiO_3$ and titanates

1. Introduction

$BaTiO_3$ (BT) is well known as fundamental ferroelectric perovskite oxide [1] and is often used in multilayer ceramic capacitors due to high dielectric constant and low loss characteristics [2]. A lot of studies have been led in order to decrease the grain size [3,4]. Basically, BT is prepared by solid-state reaction. In order to enhance the dielectric constant, alternative processing methods have been developed for the synthesis of fine-grained powders [5–7]. This could be achieved with chemical routes using non-oxide precursors which are more reactive than the conventional oxides or carbonates allowing the calcinations temperature to be lowered.

The aim of the paper is to re-investigate two ways of synthesis, not to obtain fine grains for capacitors but to get a suitable material for piezoelectric applications. Despite its relative low Curie temperature and piezoelectric properties inferior to those of $Pb(Zr,Ti)O_3$, lead-free $BaTiO_3$ remains attractive for environmental reasons [8]. The comparison is made between two ways of $BaTiO_3$ powder synthesis: solid-state reaction (ssr) and oxalate coprecipitation route (ocr) synthesis, from the formation of the perovskite phase to the dielectric and piezoelectric properties.

High temperature X-ray diffraction (XRD) and differential thermal analysis coupled with thermogravimetry (DTA–TG) were used in order to follow the formation of the barium titanate phase. Then ceramics were made with the powders from the two processes, sintered, poled and characterized. The sintering of chemically prepared BT powder yields dense ceramics with interesting dielectric and piezoelectric properties.

2. Experimental procedure

2.1. Powder synthesis

$BaTiO_3$ powder was prepared following the solid-state synthesis by firing at high temperature a mixture of $BaCO_3$ (Merck, 99%) and TiO_2 (Merck, 99%). The processing steps were: ball milling for 2 h, calcining at 1150 °C for 4 h then mixing the calcined product for 3 h.

The second way to make $BaTiO_3$ powder was a coprecipitation process [9,10]: $Ti(OC_4H_9)_4$ was dissolved in an aqueous solution of oxalic acid. Titanium hydroxide

---

* Corresponding author. Tel.: +33 4 72 43 89 92; fax: +33 4 72 43 88 74.
E-mail address: laurence.seveyrat@insa-lyon.fr (L. Simon-Seveyrat).

0272-8842/$30.00 © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.07.019

precipitated and reacted with oxalic acid to form soluble $TiOC_2O_4$. When the solubilisation of titanium was complete, barium acetate was added slowly and a double oxalate $BaTiO(C_2O_4)_2{\cdot}4H_2O$ was obtained.

The processing steps of the coprecipitation process may be described by these equations:

$$(C_4H_9O)_4Ti + 2H_2C_2O_4 + 4H_2O \rightarrow 4C_4H_9OH + 2H_2C_2O_4 + TI(OH)_4(s)$$

$$Ti(OH)_4(s) + 2H_2C_2O_4 \rightarrow TiOC_2O_4 + 3H_2O$$

$$TiOC_2O_4 + H_2C_2O_4 + Ba(CH_3COO)_2 + 4H_2O \rightarrow BaTiO(C_2O_4)_2{\cdot}4H_2O(s) + 2CH_3COOH$$

The calcination of the precursor powder is made at 650 °C for 10 h and an additional treatment is made at 800 °C for 4 h in order to control the grain growth.

2.2. X-ray diffraction, thermal analysis and grain size distribution

X-ray diffraction data were obtained with a X'Pert Pro MPD Panalytical diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) with an incident-beam monochromator. The diffractometer was equipped with an Anton Paar HTK16 high-temperature chamber. The diffraction patterns were recorded over the angular range 20–80° (2θ) with a step length of 0.016° (2θ) and a counting time of 60 s step^{-1} (160 s step^{-1} for cell parameter determination). The extraction of peak positions for indexing and the determination of cell parameters were carried out respectively with X'Pert High Score and X'Pert Plus programs supplied by Panalytical. For high temperature measurements, powder is pasted on a fine alumina plate which is put directly on the metal striper in the furnace. The measurements were operated under ambient atmosphere (air). The temperature was raised from room temperature to 1150 °C for solid-state reaction and 1050 °C for chemical way synthesis at 5 °C/min. The scans were measured with a holding time of 15 min at the given temperature. As the HTK16 was operated using metal strip heater, the furnace has been calibrated before measurements. The calibration was performed using the transformation temperature of two NBS-ICTA standards [11] and a pure tetragonal lead zirconate titanate ceramic $Pb(Zr_{0.40}Ti_{0.60})O_3$ with the same experimental procedure just described. The results are presented in Table 1. Then the measured temperatures were corrected with the following linear relation:

$$\text{Corrected temperature } (^\circ\text{C}) = \frac{(\text{measured temperature } (^\circ\text{C}) - 2.4761)}{1.0568}$$

The thermal behaviour was studied by DTA–TG under flowing air (TG96, Setaram). Approximately 50 mg of the precursor mixture was accurately weighed in an alumina crucible. The temperature was raised from room temperature to 1200 °C at 10 °C/min under air flow.

Grains size distribution was controlled by a laser Coulter LS130 granulometer and a specific area analyser Monosorb Quantachrom (based on BET theory).

2.3. Dielectric and piezoelectric properties

The powder was pressed into pellets of the size Ø 16 mm × 2 mm after addition of 10% mass polyvinyl alcohol. The samples were heated at 600 °C for 4 h in order to eliminate the organic products then sintered at temperatures between 1330 and 1370 °C for 2 or 4 h with a 2 °C/min heating rate. Silver electrodes were deposited onto both main sides of the compacts to conduct dielectric measurements. Poling was made in a silicon oil batch at 110 °C for a few minutes under 2 kV/mm, then by applying the electric field during cooling.

Densities (ρ) of the sintered ceramics were estimated from the mass and volume measurements in air. The dielectric losses ($t_g\delta$) and the permittivity (ε_r) were measured under low level (1 V/mm, 1 KHz) with an impedancemeter (HP 4284A). The piezoelectric coefficient d_{33} was measured at a 100 Hz frequency with a Berlincourtmeter (Channel Products Inc). Measurement of ε_r were performed versus electric field with the 4284A apparatus and a Shering bridge. Measurements of the converse piezoelectric coefficient d_{33} were performed versus electric field with the help of a capacitive sensor device.

3. Results and discussion

3.1. Formation of barium titanate phase from solid-state reaction and oxalic chemical way

In the classical preparation method, i.e. solid-state reaction, the raw materials are witherite $BaCO_3$ and anatase TiO_2. For $BaCO_3$ and TiO_2 powders, the volume mean grain size

Table 1
Calibration of the HTK16 furnace for high temperature X-ray diffraction measurements

Reference material	Phase transformation	Transformation onset temperature (°C)	Measured onset temperature (°C)	ΔT (°C)
$BaCO_3$[a]	Orthorhombic → rhombohedral	808	845	37
$SrCO_3$[a]	Orthorhombic → rhombohedral	928	985	62
$Pb(Zr_{0.40}Ti_{0.60})O_3$[b]	Tetragonal → cubic	412	445	33

[a] NBS–ICTA certified transformation onset temperature.

[b] Transformation onset temperature determined with thermo-mechanical analysis (TMA96 Setaram).

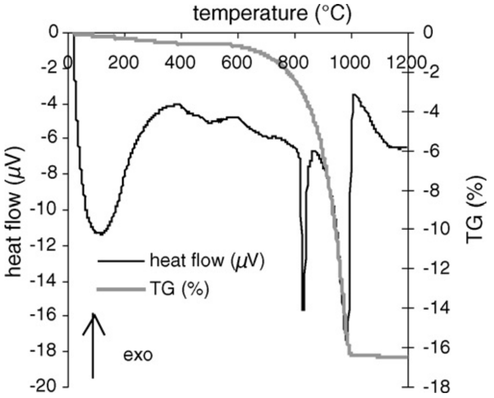

Fig. 1. Thermal analysis of the formation of $BaTiO_3$ by solid-state reaction.

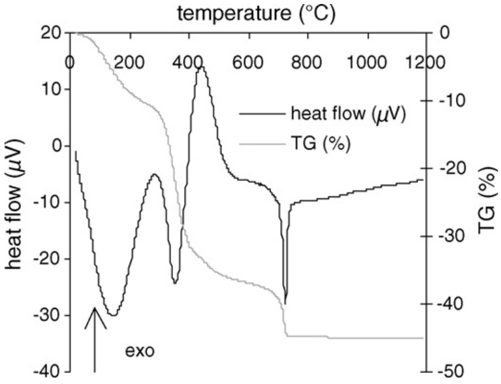

Fig. 3. Thermal analysis of the formation of $BaTiO_3$ by oxalate coprecipitation route.

determined by laser granulometry is 2.2 and 0.7 µm, respectively. Fig. 1 shows the DTA–TG curves of the mixture after the ball milling step. The first endothermic phenomenon in the range 20–250 °C is not associated with a mass loss so it corresponds to a physical transformation. Then two great endothermic peaks are observed at high temperatures: the first peak (onset point: 820 °C, top peak: 830 °C) is attributed to the transition from witherite orthorhombic $BaCO_3$ to the rhombohedral phase. The second peak (onset point: 927 °C, top peak: 985 °C) is due to the formation of $BaTiO_3$. The mass loss, starting between 700 and 800 °C, is of 16% which corresponds to the loss of one CO_2 mol according to the reaction: $BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2$.

The precursor solid-state powder was also studied by XRD in order to point out the intermediate phases as shown in Fig. 2.

Before 750 °C, it is observed a slight shift toward the low angles of the 28°, 34 and 47° (2θ) barium carbonate peaks. The $BaTiO_3$ perovskite phase started to appear at temperatures comprised between 780 and 880 °C. At 950 °C both orthorhombic (witherite) and rhombohedral $BaCO_3$ phases are observed (the transition phase begins around 850 °C). At 1050 °C, there is no witherite $BaCO_3$ anymore but only a little amount of rhombohedral $BaCO_3$ and $BaTiO_3$ is well formed.

Using conventional synthesis many authors [12,13] observed that $BaTiO_3$ always proceeds via the formation of predominantly Ba_2TiO_4 and even $BaTi_4O_9$. The intermediate Ba_2TiO_4 phase is detected as very little amounts in our mixture, as it was shown by the peak at 28 °C–2θ between 880 and 1050 °C. No trace of $BaTi_4O_9$ was detected.

The second way of $BaTiO_3$ processing is the chemical way previously described. The DTA–TG curve of the precursor powder is presented Fig. 3.

From ambient temperature to 1000 °C, the total mass loss was 46% of the mass of the sample. This corresponds to the decomposition of the $BaTiO(C_2O_4)_2{\cdot}4H_2O$ product obtained after the coprecipitation process. The first endothermic peak near 200 °C was related to the loss of four H_2O molecules. The peaks between 300 and 600 °C correspond to the formation of CO and CO_2 for the endothermic one and to the $CO + O_2 \rightarrow CO_2$ reaction for the exothermic one: $BaTiO(C_2O_4)_2$ decomposes into $BaTiOC_2O_4$. Then the formation of $BaTiO_3$ is the last endothermic peak (onset point: 711 °C; top peak: 725 °C).

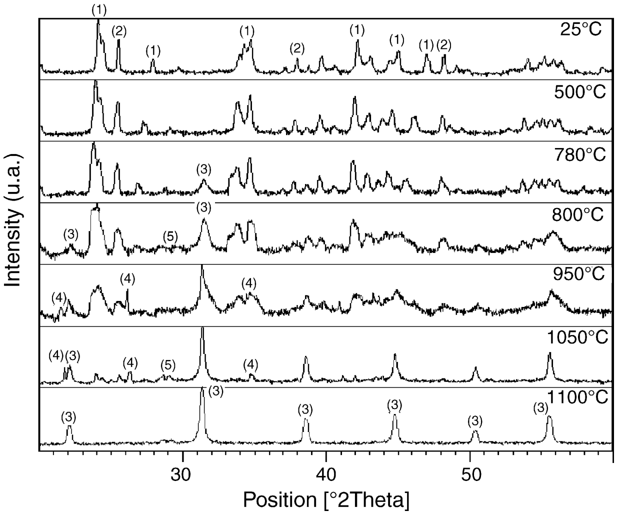

Fig. 2. XRD data in temperature of the precursor solid-state reaction (ssr) powder: (1) witherite $BaCO_3$; (2) TiO_2; (3) $BaTiO_3$; (4) rhombohedral $BaCO_3$; and (5) Ba_2TiO_4.

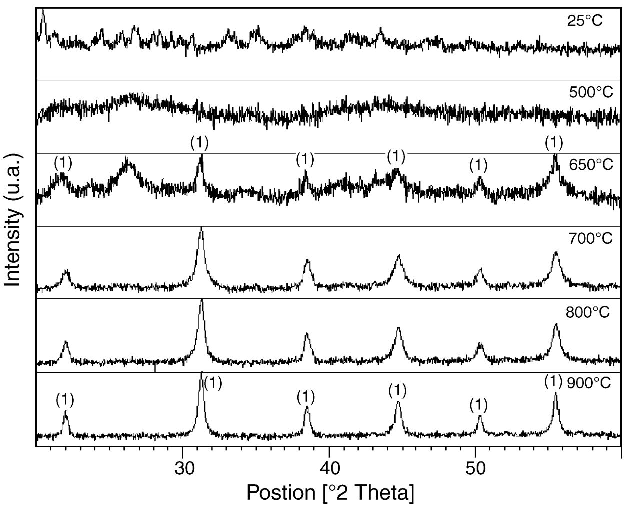

Fig. 4. XRD data in temperature of the precursor oxalate coprecipitation route (ocr) powder: (1) $BaTiO_3$.

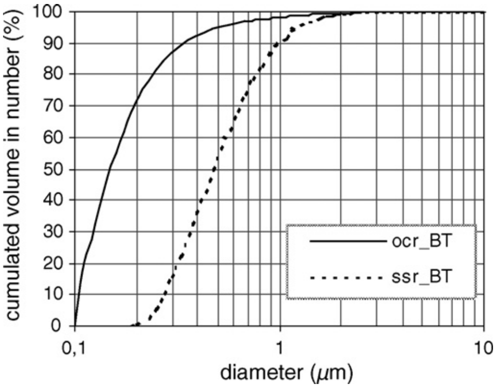

Fig. 5. Grain size distribution determined by laser granulometry for the two BT powders.

The mass loss for each decomposition and/or formation is compatible with the interpretations.

The XRD data (Fig. 4) are in acceptance with these results since they confirm the formation of perovskite phase between 650 and 700 °C. No intermediate phases like $BaCO_3$ or Ba_2TiO_4 are detected.

3.2. Comparison of the two $BaTiO_3$ powders

The last section has shown that the $BaTiO_3$ perovskite phase prepared via the co-precipitation process was formed at a temperature largely lower than the solid state process one (200 °C lower for the chemical synthesis). This leads to powder with finer grains as it is shown in Fig. 5. The median particle size (in number) of chemically obtained BT powder is approximately four times finer than BT powder from oxides precursors (d_{50} (ocr) = 0.15 μm – d_{50} (ssr) = 0.46 μm). The specific surface area is three times higher for the chemical way powder: S_{sp} (ocr) = 12.0 m^2/g – S_{sp} (ssr) = 3.9 m^2/g.

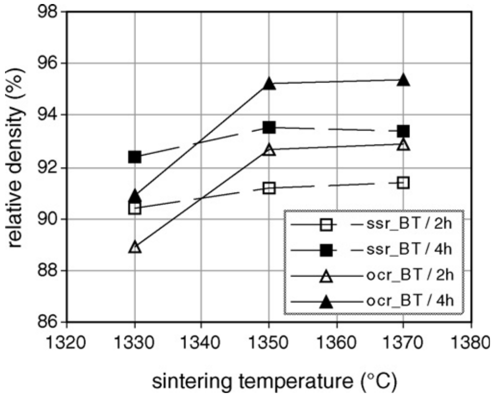

Fig. 6. Optimisation of the sintering conditions for ssr and ocr BT ceramics.

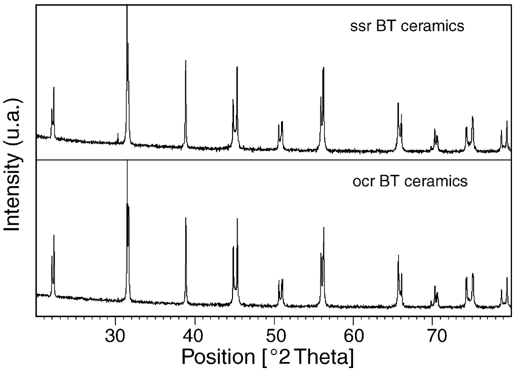

Fig. 7. XRD diagram of the ceramics prepared via the two processes and sintered at 1350 °C.

Table 2
Cell parameters of the ceramics prepared via the two processes and sintered at 1350 °C

	ssr_BT	ocr_BT
a (Å)	3.9945 (2)	3.9933 (1)
b (Å)	3.9945 (2)	3.9933 (1)
c (Å)	4.0368 (3)	4.0359 (2)
$\alpha = \beta = \gamma$ (°)	90	90

Table 3
Room temperature dielectric and piezoelectric properties of the ceramics prepared via the two processes (sintering temperature: 1350 °C)

	ssr_BT	ocr_BT
Dielectric constant ε_r	2050	2200
tan δ (%)	1.8	1.4
d_{33} (pc/N)	185	260
Density (g/cm^3)	5.65	5.75
Curie point (°C)	140	139

3.3. Sintering and characterization of barium titanate ceramics

Fig. 6 shows the evolution of the relative density as a function of the sintering temperature and the sintering step. The optimal sintering temperature is 1350 °C for 4 h and with a 2 °C/min heating rate. Except for 1330 °C, the values of densities are superior for ceramics prepared by oxalate coprecipitation route.

Fig. 7 and Table 2 respectively show the X-ray diffraction diagrams and the cell parameters of the sintered pellets prepared via the two processes. The ceramics have been crushed into powder before measurements.

In both cases, the tetragonal phase is observed and only a very slight difference is observed in the cell parameters.

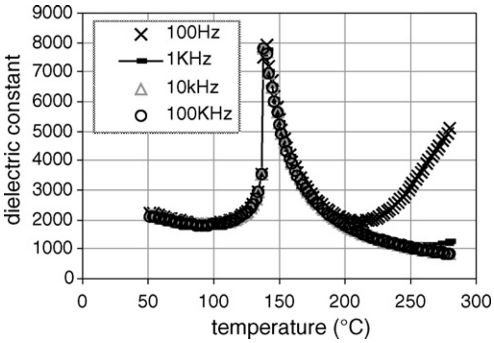

Fig. 8. Temperature dependence of the dielectric constant at four frequencies for a ceramic prepared from oxalate coprecipitation route.

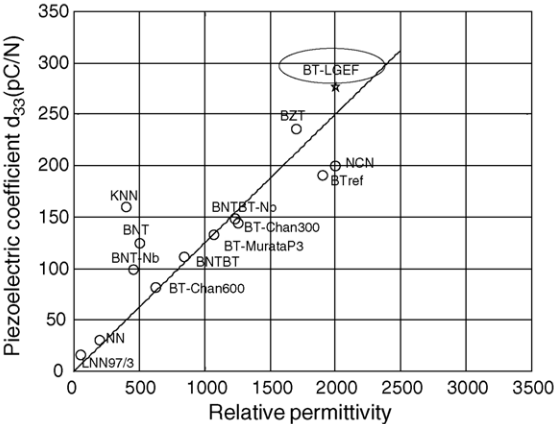

Fig. 9. Piezoelectric coefficient d_{33} vs. relative permittivity for some perovskite-type lead free ceramics (line: $g_{33} = 14 \times 10^{-3}$ V m/N) [8].

The dielectric and piezoelectric properties of the sintered pellets are presented in Table 3.

The properties of the ceramics from the coprecipation process are very good and superior to those usually published [14], especially for the d_{33} piezoelectric coefficient. Fig. 8 presents the evolution of the permittivity as a function of the temperature at four frequencies (100 Hz, 1 kHz, 10 kHz and 100 kHz) for a ceramic prepared from chemical way. Maximum permittivity value is around 8000 and is independant of the frequency.

Fig. 9 presents some piezoelectric properties of lead-free ceramics like alkaline niobates (NN: $NaNbO_3$, LNN: $LiNbO_3$-$NaNbO_3$, KNN: $KNbO_3$–$NaNbO_3$), bismuth sodium titanates (BNT) and other barium titanate based compositions.

The quasi-linear relation found between d_{33} and ε_r corresponds to a g_{33} value of 14×10^{-3} V m/N. BT ceramics prepared from chemical process shows dielectric and piezoelectric coefficients superior to those of other lead free materials.

The evolution of the properties versus electric field for the ceramics prepared from the coprecipitation process is given in Fig. 10.

The results have been used to calculate the Rayleigh coefficients [15,16] defined as

$$\alpha_{\mathrm{AC}}^{\mathrm{T}} = \frac{1}{\varepsilon_{33_o}^{\mathrm{T}}}\frac{\delta\varepsilon_{33}^{\mathrm{T}}}{\delta E_{\mathrm{p}}} \quad \text{and} \quad \gamma_{\mathrm{AC}} = \frac{1}{d_{33_o}}\frac{\delta d_{33}}{\delta E_{\mathrm{p}}}$$

where E_p is the peak value.

The piezoelectric d_{33} coefficient shows a very good stability up to 3×10^5 V/m.

The values of the α_{AC}^{T} and γ_{AC} are of the same order of those obtained for commercial PZT ceramics as shown in Table 4.

Table 4
Values of Rayleigh coefficients for ocr BT, PZT5A (soft commercial PZT) and PZT4D (hard commercial PZT)

	α_{AC}^{T} (m/V)	γ_{AC} (m/V)
ocr_BT	15×10^{-7}	4×10^{-7}
PZT5A	13×10^{-7}	9.8×10^{-7}
PZT4D	1.6×10^{-7}	2.9×10^{-7}

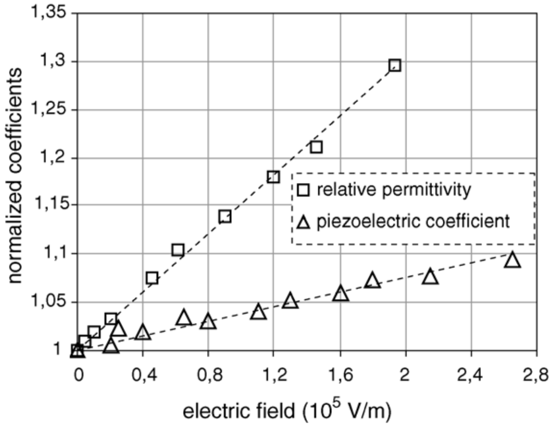

Fig. 10. AC electric field dependence of both ε_r and d_{33} for ocr samples at 1 kHz.

The α_{AC}^{T} coefficient for ocr BT is similar to the soft PZT one and the γ_{AC} coefficient is similar to the hard PZT one.

4. Conclusion

The $BaTiO_3$ perovskite phase obtained by the oxalate coprecipitation chemical way is formed at approximately 700 °C instead of 900 °C for the solid-state reaction. From high temperature X-ray diffraction data and thermal analysis, the barium titanate formation has been studied and it is shown that no intermediate phase like Ba_2TiO_4 or $BaCO_3$ was formed during the calcination of the precursors powder. The powder from this chemical process is made of finer grains and leads to ceramics with very good properties. The piezoelectric d_{33} constant is more than 260 pC/N at around 25 °C. This value is largely higher than usually published ones for barium titanate ceramics: classically room temperature ε_r (1kHz) and d_{33} values are respectively around 1700 and 190 pC/N [17]. The electrical and piezoelectric properties are also largely superior to the other perovskite lead-free materials. The evolution of these properties versus electric field shows a similar behavior to the PZT one.

References

[1] W.S. Clabaugh, R. Swiggard, R. Gilchrist, Preparation of barium titanyl oxalate tetrahydrate for conversion to barium titanate of high purity, J. Res. Nat. Bur. Stds. 56 (1956) 289–291.

[2] Y. Sakabe, K. Minai, K. Wakino, High-dielectric constant ceramics for base metal monolithic capacitors, Jpn. J. Appl. Phys. Suppl. 20-4 (1981) 147–150.

[3] J. Del Cerro, M. Mundi, C. Gallardo, J.M. Criado, F.J. Gotor, A. Bhalla, Sintering temperature influence on phase stability in barium titanate ceramics with very small grain size, Ferroelectrics 127 (1–4) (1992) 59–64.

[4] P. Nanni, A. Testino, V. Buscaglia, M. Viviani, Synthesis of barium titanate: influence of Ba/Ti ratio on the ceramic properties, Ceram. Eng. Sci. Proc. 22 (4) (2001) 43–50.

[5] C. Miot, C. Proust, E. Husson, Dense ceramics of $BaTiO_3$ produced from powders prepared by a chemical process, J. Eur. Ceram. Soc. 15 (1995) 1163–1170.

[6] A.V. Prasadarao, M. Suresh, S. Komarneni, pH dependent coprecipitated oxalate precursors – a thermal study of barium titanate, Mater. Lett. 39 (1999) 359–363.

[7] M. Stockenhuber, H. Mayer, J.A. Lercher, Preparation of barium titanates from oxalates, J. Am. Ceram. Soc. 76 (1993) 1185–1190.

[8] P. Gonnard, L. Simon-Seveyrat, Environmentally Conscious Electroceramics, Processing of Electroceramics, Bled, Slovenija, Conference Notes, August 31th–September 3rd, 2003, pp. 331–345.

[9] S. Rimlinger, L. Eyraud, P. Eyraud, Elaboration of perovskite by decomposition of coprecipitated oxalates for electronic ceramics, Ferroelectrics 94 (1989) 221–228.

[10] B. Guiffard, M. Troccaz, Low temperature synthesis of stoichiometric and homogeneous lead zirconate titanate powder by oxalate and hydroxide coprecipitation, Mater. Res. Bull. 33 (12) (1998) 1759–1768.

[11] S.T. Misture, Large-volume atmosphere-controlled high-temperature X-ray diffraction furnace, Meas. Sci. Tech. 14 (2003) 1091–1098.

[12] T. Yamaguchi, S.H. Cho, M. Hakomori, H. Kuno, Effects of raw materials and mixing methods on the solid-state reactions involved in fabrication of electronic ceramics, Ceramurgia Int. 2 (1976) 76–80.

[13] K.H. Felgner, T. Muller, H.T. Langhammer, H.P. Abicht, On the formation of $BaTiO_3$ from $BaCO_3$ and TiO_2 by the microwave and conventional heating, Mater. Lett. 58 (2004) 1943–1947.

[14] M.C. Cheung, H.L.W. Chan, C.L. Choy, Study on barium titanate ceramics prepared by various methods, J. Mater. Sci. 36 (2001) 381–387.

[15] V. Perrin, M. Troccaz, P. Gonnard, Non linear behavior of the permittivity and of the piezoelectric strain constant under high electric field drive, J. Electroceram. 4 (1) (2000) 189–194.

[16] D. Damjanovic, M. Demartin, Contribution of the irreversible displacement of domain walls to the piezoelectric effect in barium titanate and lead zirconate titanate ceramics, J. Phys. Condens. Matt. 9 (1997) 4943–4953.

[17] N. Setter, in: N. Setter (Ed.), ABC Piezoelectricity and Piezoelectric Materials, Piezoelectric Materials in Devices, Lausanne, Switzerland, 2002, pp. 1–28.