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Electrical characteristics of $BaTiO_3$ ceramics from hydrothermal prepared powders

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Abstract

$BaTiO_3$ nanopowders were synthesized by hydrothermal method: treatment at 150 °C or 250 °C for 7 h of a mixture of $TiCl_3$ and $BaCl_2$ or TiO_2 and $BaCl_2$. After sintering treatment at 1250 °C in air for 10 h or 20 h, the corresponding ceramics were obtained and characterized. The ceramics present a heterogeneous microstructure, depending of the nature of the precursor. The grain size and the grain size distribution in the ceramic bulk are directly related to the powder characteristics, and they govern the electrical properties. For small grain size with low grain size distribution, the permittivity at room temperature is large and the Curie temperature is 100 °C. For large grain sizes in very small grains matrix, the permittivity at room temperature is slightly lower and the phase transition occurs at higher temperature (120 °C).

Keywords: Hydrothermal; Sintering; Dielectric properties; $BaTiO_3$; Capacitors

1. Introduction

$BaTiO_3$ is an electronic ceramic, widely used in the manufacture of thermistors, multilayer capacitors (MLCs), and electro-optic devices.[1] Traditionally $BaTiO_3$ is prepared by solid state reaction via the calcination of $BaCO_3$ and TiO_2 at high temperature (1100 °C).[2] The hydrothermal synthesis of ceramic powders is of great interest because of the possibility of producing highly crystallized, well dispersed and sintering-active powders. One of the advantages of hydrothermal process is that conventional Teflon-lined bombs can be used. This last point is very important for highly caustic solutions that are usually present in the synthesis of $BaTiO_3$. In this paper, $BaTiO_3$ powders have been synthesized using the hydrothermal method. Different titanium sources have been used, $TiCl_3$ and TiO_2. The barium source is $BaCl_2{\cdot}2H_2O$. The synthesis was performed at two temperatures, namely 150 °C and 250 °C. We report here the physical and chemical characteristics of the obtained powders, in relation with the dielectric properties of the corresponding ceramics.

2. Experimental

The starting materials were barium chloride ($BaCl_2{\cdot}2H_2O$, Prolabo), $TiCl_3$ (Prolabo) and TiO_2 anatase (Rhodia). An aqueous solution of barium and titanium was obtained by mixing 0.015 mol $TiCl_3$ or TiO_2 and 0.024 mol $BaCl_2{\cdot}2H_2O$ in deionised water. The solution pH was raised to 13.5 by adding a solution of KOH under stirring, than transferred to a cylindrical autoclave and treated for 7 h at 150 °C or 250 °C under autogenous pressure. After cooling down to room temperature, the pH of the reaction medium was decreased to 6 by addition of a 0.2 M HCl so as to dissolve the very little proportion of $BaCO_3$ formed beside $BaTiO_3$. The reaction product formed was then filtered, washed several times with distilled water and oven dried at 110 °C for 24 h. The powders prepared were uniaxially pressed at 250 MPa in the form of discs. The disk shaped were 6 mm in diameter and 1.5 mm in thickness. The pressed pellets were sintered at 1250 °C at a 80 °C/h

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ramp in ambient atmosphere, for 10 h and 20 h as a dwell time. Finally the upper electrode (silver) is screen printed and heated at 700 °C for 1/2 h. The phase was identified using X-ray diffractometry at room temperature (Siemens D 501 diffractometer for powders, $\lambda_{\mathrm{Cu\,K\alpha}} = 1.5418$ Å). Microstructural studies were performed using electron microscopy (Jeol JSM 6400 for SEM and Jeol 2010 FX for TEM). Electrical characterizations are realized using a Hewlett-Packard HP 4284A precision LCR meter from 100 Hz to 100 kHz and from room temperature to 200 °C, with a 10° step.

3. Results and discussion

3.1. Powders

The XRD patterns of $BaTiO_3$ powders synthesized using $TiCl_3$ as titanium source at 150 °C and 250 °C for 7 h fit well with the peak positions of standard cubic-phase of barium titanate. No split of the $\{2\,0\,0\}$ peak around $2\theta = 44.95°$ can be seen, indicative that no tetragonal phase is present. The powder prepared from a Ti^{4+} salt (TiO_2 anatase) and $BaCl_2{\cdot}2H_2O$ also crystallizes in the cubic phase of $BaTiO_3$. No additional TiO_2 is observed.

The crystallite size of $BaTiO_3$ obtained from X-ray data using Scherer's equation is a little lower than the one calculated from specific surface area values. Powders prepared from $TiCl_3$ and from TiO_2 probably form polycrystalline elementary grains and agglomerates which consequently leads to a lower apparent specific surface area and thus to higher calculated particle size. The particle morphology of the crystallized powders obtained from $TiCl_3$ at 150 °C and 250 °C (Fig. 1) is spherical. The powders obtained at 150 °C seem to be more agglomerated than the one prepared at higher temperature. Spherical agglomerates for the 150 °C powders with diameters of about 70 nm were visible. The presence of excess $BaCl_2{\cdot}2H_2O$ can explain the formation of hard agglomerates since $BaCO_3$ is detected in the synthesized powders. Because the starting $BaCl_2{\cdot}2H_2O$ solution did not contain $BaCO_3$ impurities, $BaCl_2{\cdot}2H_2O$ can absorb CO_2 and form $BaCO_3$ during the synthesis, and probably contribute to form agglomerates. The size of the crystallites can be estimated at 20 nm for 150 °C synthesis temperature and 70 nm for 250 °C synthesis temperature. The morphology of the $BaTiO_3$ powders synthesized from TiO_2 is also spherical. The crystallite size is 60 nm for the two temperatures of preparation (Figs. 1 and 2). There is no significant difference in grain size for the powders prepared from the two titanium sources. It is plausible that the solid TiO_2 dissolves and re-precipitates during the hydrothermal treatment, which is a mechanism often described in the literature.

3.2. Ceramics

The sintering treatment has been performed at 1250 °C in air for 10 h and 20 h. The densities of the pellets are reported in Table 1. In most cases, the densification increases slightly if the sintering dwell is longer. Only the tetragonal $BaTiO_3$, which is the common phase observed,[3] was detected by X-ray diffraction analysis. The tetragonal $BaTiO_3$ phase

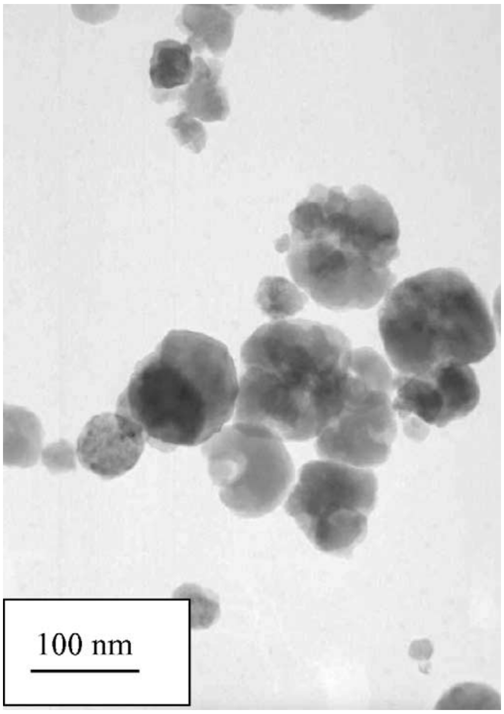


Fig. 1. TEM pictures of $BaTiO_3$ powders synthesized using TiO_2 as titanium source at 150 °C.

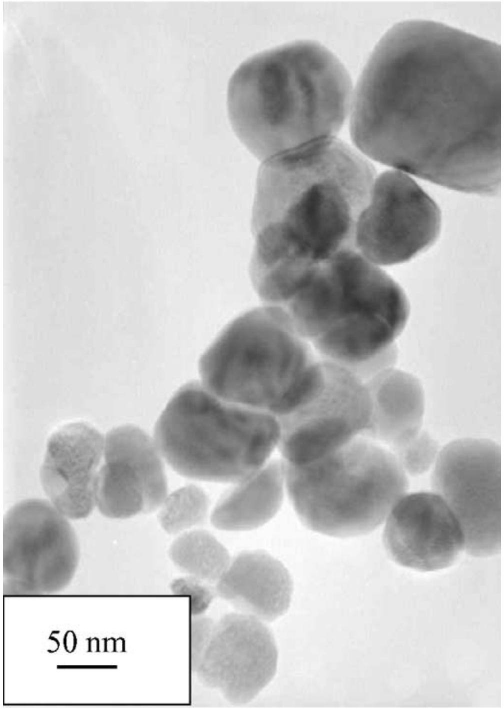
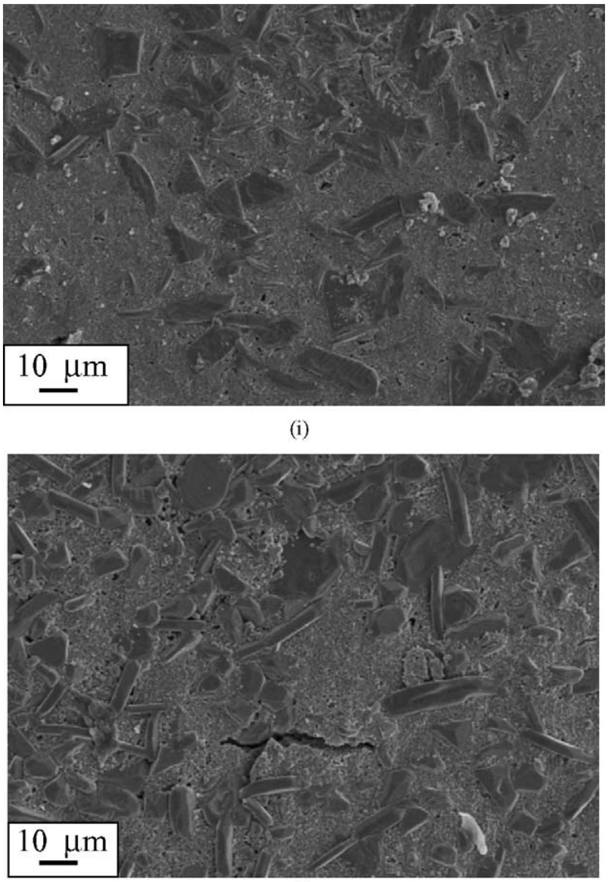


Fig. 2. TEM pictures of $BaTiO_3$ powders synthesized using TiO_2 as titanium source at 250 °C.

Table 1
Density of the ceramics after sintering at 1250 °C for 10 h and 20 h

Ti precursor	Synthesis temperature (°C)	Dwell time (h)	% d_{th}
$TiCl_3$	150	10	98.8
		20	97.3
	250	10	94.5
		20	95.6
TiO_2	150	10	94.2
		20	99.8
	250	10	92.2
		20	94.3

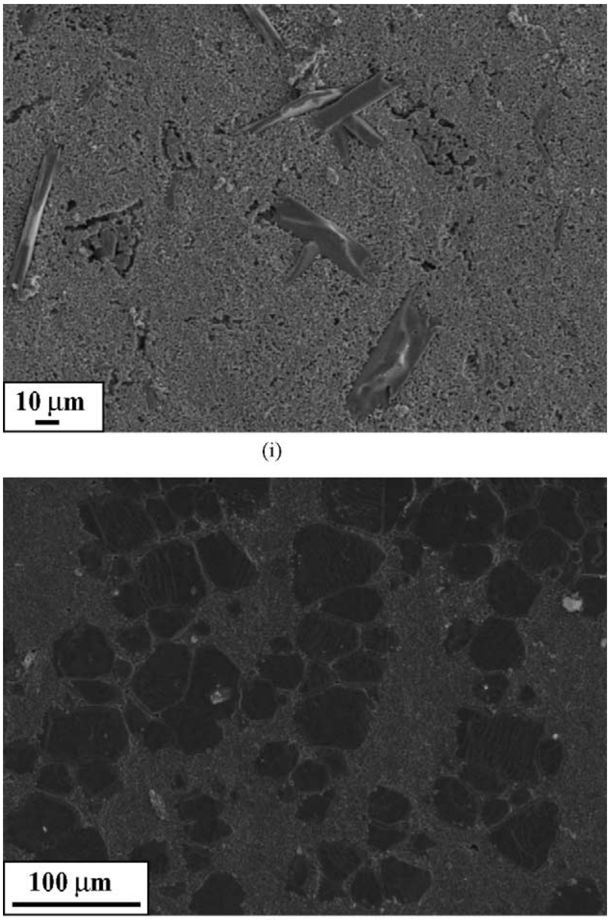
appears as the grains grow, typically above a critical size. The microstructure of $BaTiO_3$ ceramics sintered at 1250 °C for 10 h and 20 h is shown in Figs. 3 and 4. Abnormal grain growth[4] is noticed for the sample prepared with TiO_2 (synthesis temperature 150 °C or 250 °C). The microstructure of these ceramics is bimodal, constituted of large (up to 60 μm) angular grains growing in a fine-grained (1 μm) matrix. The samples issued from the powders prepared using $TiCl_3$ as precursor showed less large grains in the fine grained matrix.



(i)

(ii)

Fig. 3. SEM micrographs of $BaTiO_3$ ceramics synthesized using $TiCl_3$ as titanium source at 250 °C, sintered 10 h at 1250 °C (i) and 20 h at 1250 °C (ii).



(i)

(ii)

Fig. 4. SEM micrographs of $BaTiO_3$ ceramics synthesized using TiO_2 as titanium source at 250 °C, sintered 10 h at 1250 °C (i) and 20 h at 1250 °C (ii).

3.3. Dielectric properties

Our discussion is limited to the ceramics obtained from the powders prepared at 250 °C. The changes in the permittivity values at 1 kHz versus the temperature are given in Fig. 5. The Curie temperature (T_c) is in between 105 °C and 110 °C for $TiCl_3$ starting powders based ceramics whereas it is near 120 °C for TiO_2 powders based ceramics. At this temperature, the permittivity value reaches a maximum of 7000 for the former and 11,000 for the later. Whatever the ceramics, the permittivity depends on the dwell time but this dependence differs according to the starting powders. Hence for TiO_2 based ceramics, the value at room temperature (RT) is roughly the same whatever the dwell time whereas at T_c a larger permittivity value is obtained for the shortest sintering dwell time. For the $TiCl_3$ starting powders based ceramics, the temperature dependence is less marked. A shift in the permittivity changes versus temperature is observed: the permittivity decreases on the whole temperature range when the dwell time increases from 10 h to 20 h.

In order to find a valid explanation of these behaviours, we have to consider the different parameters which may influence

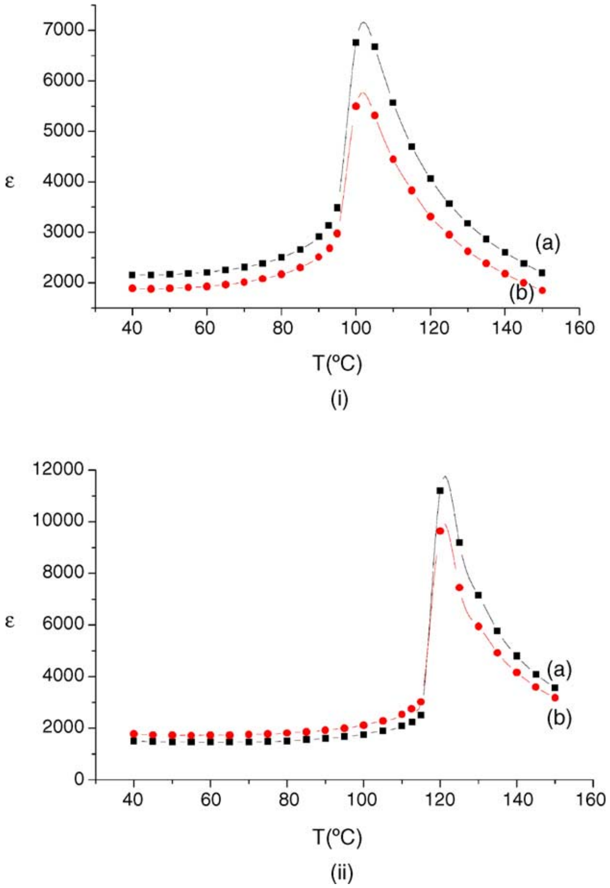


Fig. 5. Permittivity vs. temperature of $BaTiO_3$ ceramics synthesized sintered 10 h and 20 h at 1250 °C, using $TiCl_3$ as titanium source at 250 °C (i) and using TiO_2 as titanium source at 250 °C (ii).

the permittivity value, that are the density, the grain size, and the grain size distribution. In the present study, the slight increase of the density with the dwell time (Table 1) cannot explain the decrease of permittivity observed at T_c nor the value at room temperature for both types of ceramics. The density is not the most predominant parameter.

Many studies have already been published on the size effect in ferroelectric ceramics and their conclusion is that the dielectric constant increases as the grain size is reduced from 10 μm to 1 μm. The maximum being obtained for 1 μm. Kinoshita,[5] Wang et al.[6] claimed that the finer the grain size was, the higher the dielectric constant at room temperature. The value of 1 μm being an approximation of the 0.9 μm proposed by Wang, of the 0.8 μm proposed by Niepce et al.,[7] of the 1 μm suggested by Duran[8] or of the 1.4 μm proposed by Hirata.[9] This behaviour is attributed to both an increase in domain wall density and to an increase in the residual internal stresses. The formation of 90° domains below T_c is the mean of minimizing this internal stress energy. Nevertheless, if too small grains are present (the width of the 90° domains being fixed near 1 μm) no 90° domain may exist and the permittivity value is decreased.

Since the grain size distribution in the ceramics under study are bimodal, the discussion is not straightforward. The value of the dielectric constant at room temperature depends both on the amount of small sized grains and of the size distribution. Hence, for $TiCl_3$ based ceramics, the permittivity value is the largest for the smallest dwell time (10 h) leading to the coexistence of approximately the same amount of small grains (near 400 nm) and of grains of size 10–20 μm. The increase in the dwell time increases the amount of the 10–20 μm grains up to near 75% leading to a diminution of ε. In the case of TiO_2 based ceramics two different situations are encountered: the presence of big grains (size 50 μm) in a finely divided matrix containing either very small grains (near 500 nm, case of $TiCl_3$, dwell time of 10 h) either small grains of 1 μm (case of $TiCl_3$, dwell time of 20 h). Since the ratio in the permittivity value for grains of 500 nm and of 1 μm is roughly 2, it is not surprising that the highest permittivity corresponds to the later case ($TiCl_3$, dwell time of 20 h).

At the Curie temperature (T_c), the contrary is observed since the maximum permittivity is obtained in the decreasing order for TiO_2, dwell time 10 h, TiO_2 dwell time 20 h, $TiCl_3$, dwell time 10 h, $TiCl_3$ dwell time 20 h. Such an observation tends to prove that at T_c, the parameters which drive the properties are not the same. However, it has to be noticed that whatever the material under study, the increase in the amount of the big grains leads to a decrease in the permittivity value.

Last, as already reported by Miot[10] and Kinoshita[5] who showed that T_c increased with the grain size, we observe that the ceramics presenting the smallest grain sizes present the lowest T_c.

4. Conclusion

The hydrothermal method has been used to synthesize barium titanate powders. Two different sources of titanium have been used, namely $TiCl_3$ and TiO_2. After sintering, the ceramics behaviors are related to the density, the grain size and the grain size distribution that tightly depend on the type of Ti salt that has been used for the powders synthesis. The permittivity at room temperature and at the transition temperature is driven by two antagonist phenomena related to the presence of large grains in a matrix constituted of fine grains. The Curie temperature is also affected by this parameter. The main physical mechanism behind the grain size is the existence of domains in ferroelectric materials and their impact on the electrical properties.

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