

Electrical characteristics of BaTiO₃ ceramics and thick films from hydrothermal prepared powders

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Abstract

It is known that the dielectric properties of BaTiO₃ ceramics strongly depend on the sintering ability of the starting powders and therefore of their morphological characteristics (size distribution, crystallite size, agglomeration state). Finally divided BaTiO₃ powders were synthesized by hydrothermal method : treatment at 150 °C and 250 °C for 7 hours of a mixture of TiCl₃ and BaCl₂ or TiO₂ and BaCl₂. Then the powders were spread in thick film using the doctor blade method or compacted in pellets by uniaxial pressing and finally sintered by heating in air. The sintering parameters were adjusted to optimise the density of the final materials. The microstructure, densities and dielectric constants of the ceramics and films have been determined and correlated to the powder quality.

Keywords : Hydrothermal- A. Sintering- C. Dielectric properties- D. BaTiO₃- E. Capacitors

Introduction

BaTiO₃ is an electronic ceramic, widely used in the manufacture of thermistors, multilayer capacitors (MLCs), and electro-optic devices¹. Traditionally BaTiO₃ is prepared by solid state reaction via the calcinations of BaCO₃ and TiO₂ 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 which is very important for highly caustic solutions which are usually present in the synthesis of BaTiO₃. In this paper, BaTiO₃ powders have been synthesized using the hydrothermal method. Different titanium sources have been used, TiCl₃ and TiO₂. The barium source is BaCl₂.2H₂O. 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 and thick films.

Experimental

The starting materials were barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, Prolabo), TiCl_3 (Prolabo), 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 $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in deionised water. The solution pH was raised to 13.5 by adding a solution of KOH under stirring, then transferred to a cylindrical autoclave and treated for 7 hours at 150 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 hours. The BaTiO_3 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 ramp in ambient atmosphere, for 10 and 20h as a dwell time. The thick film paste is prepared by mixing the fine barium titanate powder and a suspension of organic materials (solvent, dispersant, plasticizing and additives to improve the rheological behavior of the paste) with a mass ratio of 1/3-2/3. After 3 days of mixing, the viscosity of the paste is adjusted to approximately 2000 cp (by adding solvent) using a RVDV-E Brookfield viscometer. The bottom electrode made of platinum is screen printed on an alumina substrate and fired at 900 °C for ½ hour. The paste containing the BaTiO_3 powder is then deposited by the “doctor blade” method and slowly heated at 400 °C for 40h in order to evacuate the organic part. The structure is sintered at 1200 °C in air to obtain the dense film. Finally the upper electrode (silver) is screen printed and heated at 700 °C for ½ hour.

The phase was identified using X-Ray diffractometry at room temperature (Siemens D 501 diffractometer for powders, $\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$). Microstructural studies were performed using electron microscopy (Jeol JSM 6400 for SEM and Jeol JSM 6700F SEM FEG). Electrical characterizations are realized on the different type of ceramic materials (massive and thick film), using a Hewlett Packard HP 4284A precision LCR meter.

Results and discussion

Powders

XRD patterns of BaTiO_3 powders synthesized using TiCl_3 as titanium source at 150°C and 250°C for 7h fit well with the peak positions of standard cubic-phase of barium titanate. No split of the $\{2\ 0\ 0\}$ peak around $2\theta = 44.95^\circ$ can be seen, indicative that no tetragonal phase is present. The powder prepared from a Ti^{4+} salt (TiO_2 anatase) and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ also crystallizes in the cubic phase of BaTiO_3 . No additional TiO_2 is observed.

The crystallite size of BaTiO₃ 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 TiCl₃ and from TiO₂ 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 TiCl₃ at 150°C and 250°C (Figure 1) is spherical. Interestingly 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. One of the reasons for the formation of hard agglomerates could be the presence of excess BaCl₂·2H₂O in the synthesized powders. Namely, BaCO₃ detected in the synthesized powders are formed during the process. The starting BaCl₂·2H₂O solution used did not contain BaCO₃ impurities. So during the hydrothermal synthesis retained BaCl₂·2H₂O can absorb CO₂ and form BaCO₃, which might contribute to the formation of agglomerates. The size of the crystallites can be estimated to 20 nm for 150°C synthesis temperature and 70 nm for 250°C synthesis temperature. The morphology of the BaTiO₃ powders synthesized from TiO₂ does not change much, compared to the one of the TiCl₃ powder. The crystallite size is 60 nm for the two temperatures of preparation (Figure 2).

Ceramics

The sintering treatment has been performed at 1250°C for 10h and 20h. The densities of the pellets are reported in Table 1. An extension of the dwell time of sintering from 10h to 20h allows to increase the densification, that reaches 99.8% in some cases. X-ray diffraction analysis only evidenced tetragonal BaTiO₃, which is the common phase observed in such cases³. The tetragonal BaTiO₃ phase appears as the grains grow, typically above a critical size. The microstructure of BaTiO₃ ceramics sintered at 1250°C for 10h and 20h is shown in Figures 3 and 4. Abnormal grain growth is noticed for the sample prepared with TiCl₃ (synthesis temperature 150°C or 250°C). The microstructure of these ceramics is bimodal, constitute with large (up to 60 μm) angular grains growing in a fine-grained (1μm) matrix. Samples of powders prepared using TiO₂ as precursor showed less large grains in the fine grained matrix. The increase of the dwell time has a weak effect on the final density but modifies the grain size and the grain size distribution, especially for powders prepared from TiO₂ (Table 1 and Figure 4).

Thick films

The films are characterized after the sintering treatment. A cross section observation is seen on Figure 5. The different layers are homogeneous in thickness. The interface between the layers is coherent. The different thickness are :Al₂O₃ : 630 μm, Pt electrode: 16 μm, BaTiO₃ : 60 μm, Ag electrode: 47 μm.

Dielectric properties

We have limited our investigation to the ceramics obtained from the powders prepared at 250 °C. The evolution of permittivity at 1 kHz as a function of temperature is reported on Figure 6. Different behaviors are observed, depending on the type of titanium source. For TiCl₃ starting powders based ceramics, the Curie temperature (T_c) is approximately 105-110°C whereas for TiO₂ powders based ceramics, it is near 130 °C. Regarding the permittivity value, it reaches a maximum of around 4000 for the former and 8000 for the later at T_c. Moreover, for TiO₂ powders based ceramics and for the same sintering temperatures, the permittivity at room temperature is larger for the longest dwell time than for the shortest one. But it is just the contrary which is observed at the Curie temperature: the largest permittivity value is obtained for the shortest dwell time! On the other hand, for TiCl₃ starting powders based ceramics, a shift without any crossover of any kind in permittivity changes vs temperature is observed. In this last case the permittivity decreases on the whole temperature range when the dwell time increases. [The permittivity value is a function of the sintering](#) temperature and of the conditioning pH⁴. In our case the pH is constant (13.5) so it will not influence our results. In the case of stoichiometric barium titanate, the permittivity should vary inversely with the grain size and proportionally to the ceramic density. This last parameter is globally the same in our study. Regarding the grain size, many authors have already emphasized its role on the permittivity value. Kinoshita⁵ was the first one to claim that the finer the grain size was, the higher the dielectric constant. He also noticed that the cubic to tetragonal transition temperature was slightly modified as the grain size was reduced. These observations have been confirmed more recently by Wang et al⁶ who observed that the dielectric constant at ambient temperature depended on the grain size and reached a pronounced maximum value at an average grain size of 0.9 μm value which is not so different of the 0.8 μm proposed by Niepce et al⁷ or of the 1 μm suggested by Duran⁸. Hirata⁹ proposed a grain size of 1.4 μm. Regarding the difference in T_c, the grain size has also a strong effect on it. The temperature dependence has already been attributed to this micro-structural factor. Miot¹⁰ showed that T_c was increased with the grain size and that, at this temperature, for the two grain sizes he studied, the larger one (1.6 μm), presented the largest permittivity value compared to the smallest ones (< 1 μm). This is in good agreement with our observations in both cases and particularly for ceramics pellets using powders having TiCl₃ for titanium source.

Finally, for the smallest grain size, the simplest explanation is based on the ratio of cubic phase present in the ceramic which are not concerned by the ferroelectric transition. All these aspects may be related to the existence of domains in ferroelectric materials which are size dependent. Hence, these materials have movable domain

walls leading to the different hysteresis behaviors observed. The increase in the dielectric constant at room temperature when decreasing the grain size 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. Therefore, for too small grain sizes since the width of the 90° domains has been fixed near 1 μm , no 90° domain may exist, reducing at the same time the dielectric constant and the Curie temperature¹¹. Therefore, it is not surprising that the bimodal material obtained using TiCl_3 for titanium source and sintered during the smallest dwell time (10h), presenting large (up to 60 μm) angular grains growing in a fine-grained (1 μm) matrix present a larger permittivity value at room temperature than any other material studied here and that the phase transition occurs at the lowest temperature value. This bimodal aspect of the material associated to a strong inhomogeneity in the grain size leads also to heterogeneously distributed internal stresses.

Thick films

Last and despite all our attention during their manufacture, we have still not been able to realize thick layers with hydrothermally prepared powders since in most of case an electrical short circuit was obtained between the two metallic plates. However, we succeed in making thick films starting with coprecipitated powders.

Conclusion

The different dielectric behavior presented may be related to, and are explained by, the grain size and its distribution in the ceramic bulk. For small grain size with low grain size distribution, the permittivity at room temperature is large and the curie temperature is 135 °C. For large grain sizes in very small grains matrix, the permittivity at room temperature is slightly larger and the phase transition occurs at 110°C.

References

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

Ti precursor	Synthesis temperature (°C)	Dwell time (h)	% d_{th}
TiCl ₃	150°C	10	98.8
		20	97.3
	250°C	10	94.5
		20	95.6
TiO ₂	150°C	10	94.2
		20	99.8
	250°C	10	92.2
		20	94.3

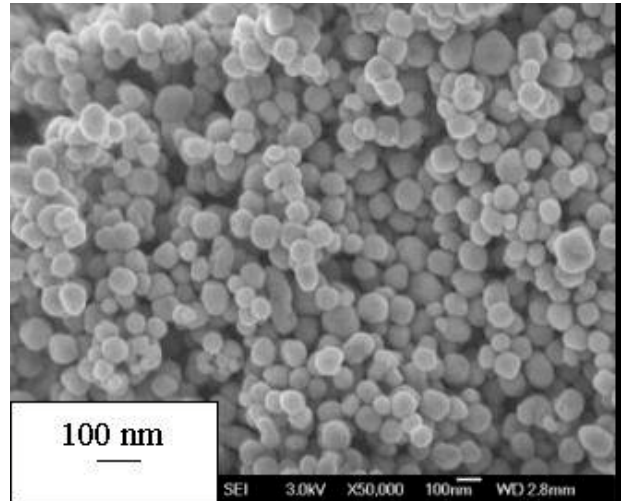
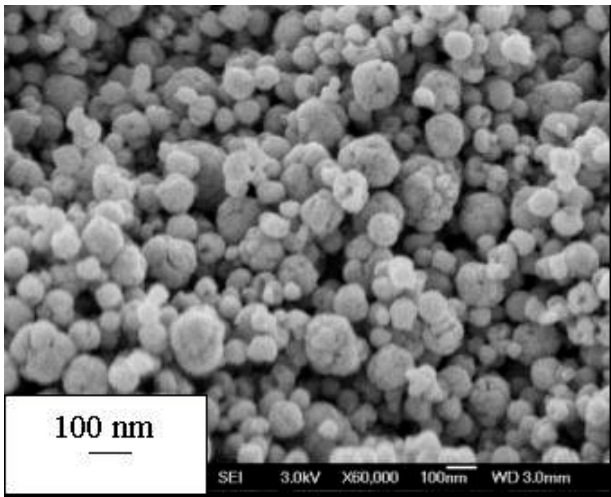
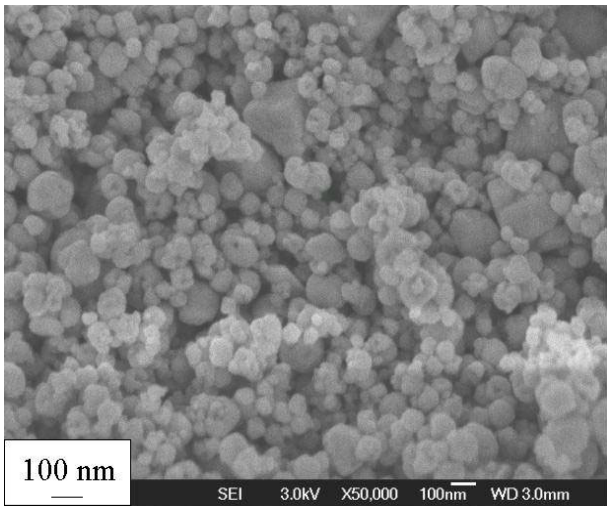
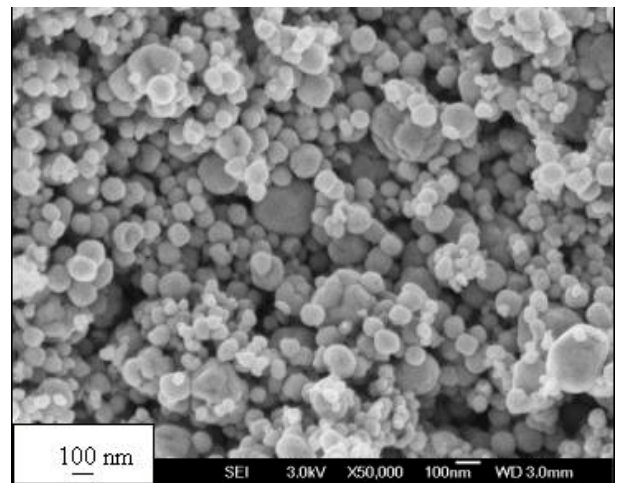


Figure 1. FEG-SEM pictures of BaTiO₃ powders synthesized using TiCl₃ as titanium source at 150°C (a) and at 250°C (b)

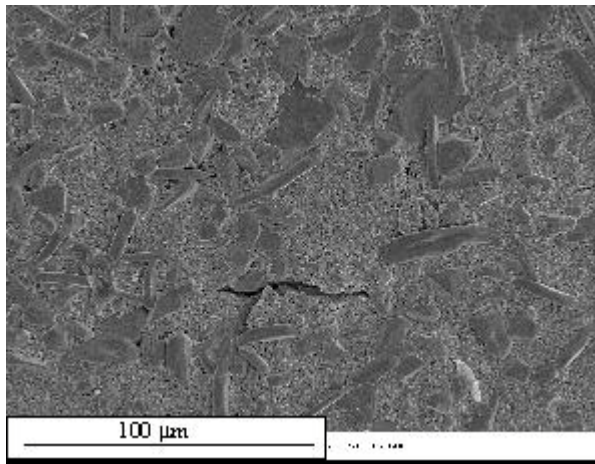


(a)

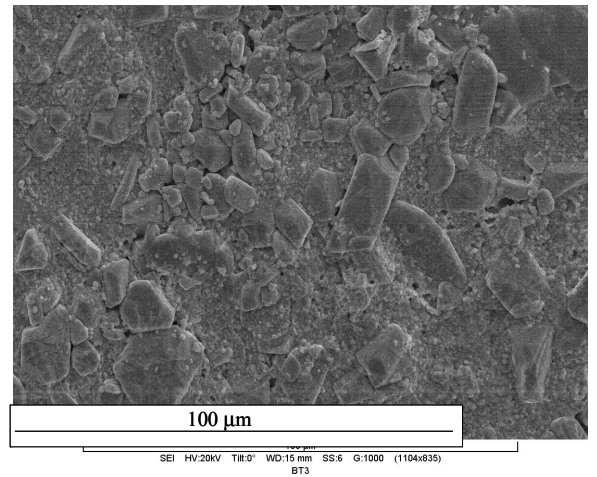


(b)

Figure 2. FEG-SEM pictures of BaTiO₃ powders synthesized using TiO₂ as titanium source at 150°C (a) and at 250°C (b)



(a)



(b)

Figure 3. SEM micrographs of BaTiO₃ ceramics synthesized using TiCl₃ as titanium source at 250°C, sintered **10h** at 1250 °C (a) and **20h** at 1250 °C 250°C (b)

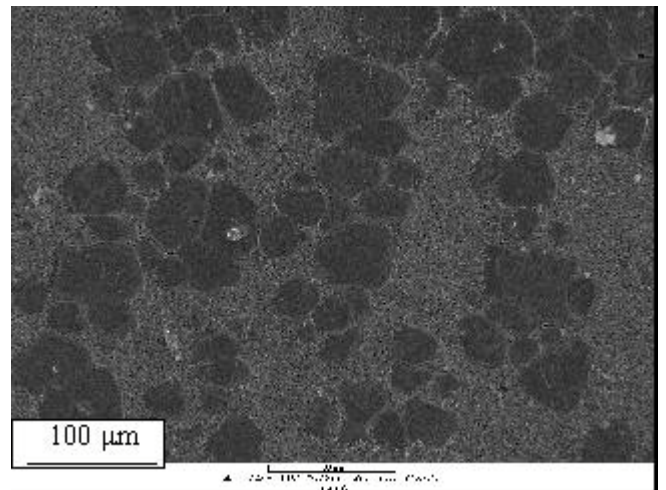
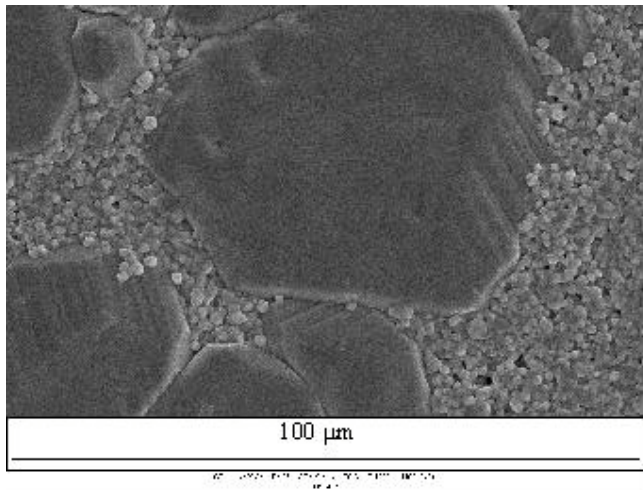


Figure 4. SEM micrographs of BaTiO₃ ceramics synthesized using TiO₂ as titanium source at 250°C, sintered **10h** at 1250 °C (a) and **20h** at 1250 °C 250°C (b)

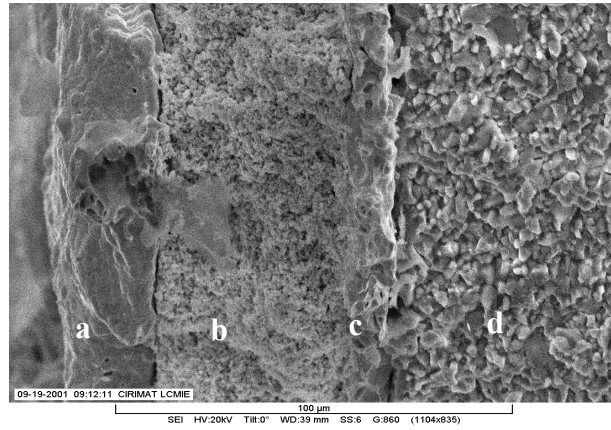


Figure 5. SEM micrograph of a cross section of our multilayers structure. (a) : Ag electrode, (b) : BaTiO₃,
(c) : Pt electrode, (d) : Al₂O₃

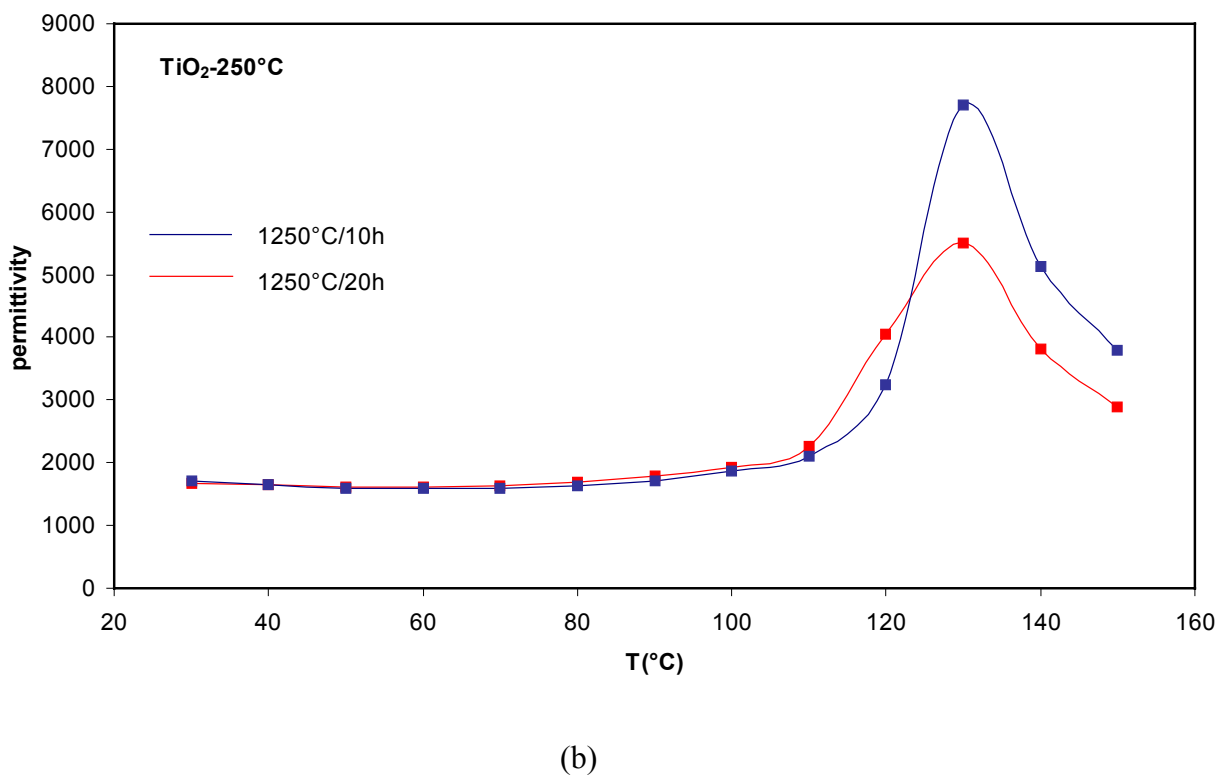
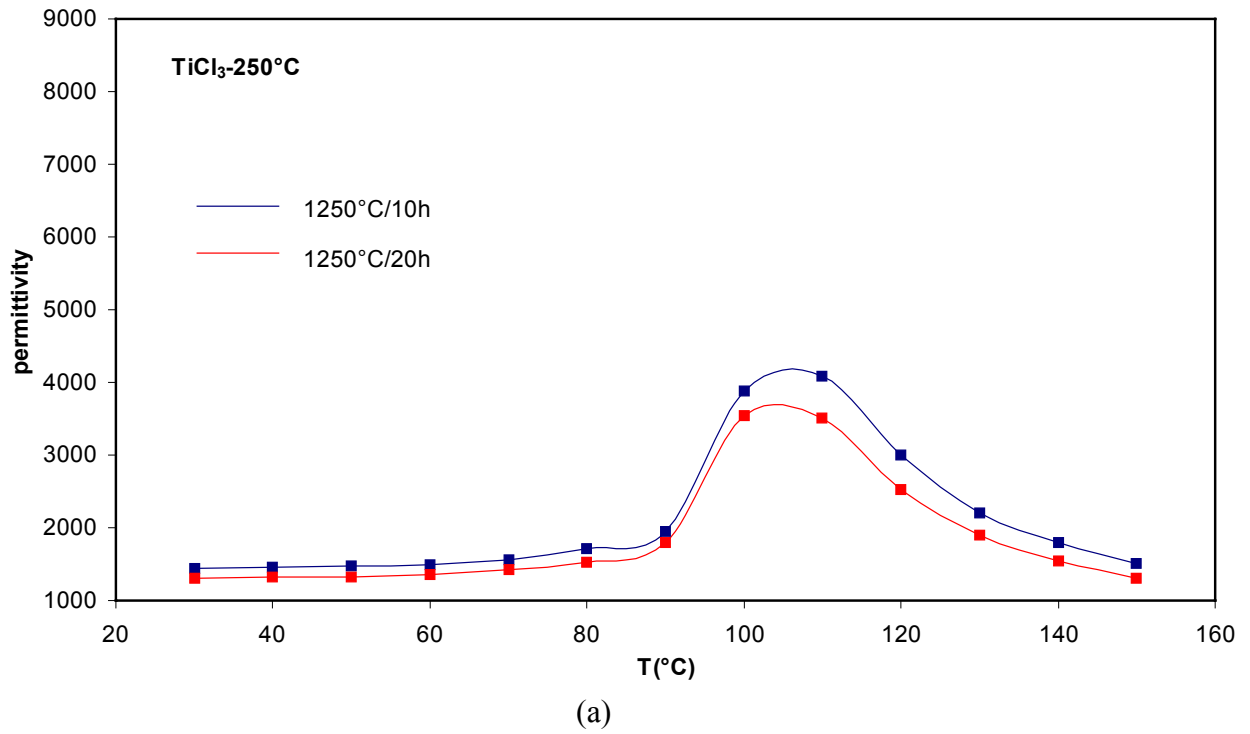


Figure 6. Permittivity vs temperature of BaTiO₃ ceramics synthesized sintered 10h and 20h at 1250 °C, using **TiCl₃** as titanium source at 250°C (a) and using **TiO₂** as titanium source at 250°C