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Synthesis of $BaTiO_3$ by soft chemistry routes

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Abstract In this paper we report a comparison concerning the properties of $BaTiO_3$ (BTO) ceramics obtained by two soft chemical routes, modified Pechini method and thermal decomposition of oxalate-based precursor. XRD data show the formation of single phase $BaTiO_3$ with tetragonal symmetry when the polymeric citrate-based precursor was annealed at 850 °C, 2 h. In the case of oxalate based-precursor, longer thermal treatment is required to obtain $BaTiO_3$ free of any secondary phases. For $BaTiO_3$ powders prepared by modified Pechini method, TEM and SEM investigations revealed the obtaining of uniformly sized particles forming spherical agglomerates inside large, non-uniform and partially sintered aggregates. The powders synthesized via oxalate route show particles of various sizes, with the same tendency of spherical agglomerates formation, but unlike the modified Pechini synthesis, more uniform and smaller aggregates with well-defined hexagonal-like shape were noticed. The relative permittivity values of 6,478 and 5,088 at Curie temperatures of 127 and 130 °C and low dielectric losses (tan δ=0.012) at room temperature were obtained for ceramic samples synthesized via Pechini method and oxalate route, respectively.

Keywords Barium titanate · Nanopowder-synthesis · Modified Pechini method · Oxalate route

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1 Introduction

Barium titanate, $BaTiO_3$, finds many applications due to excellent dielectric, ferroelectric, and piezoelectric properties, in producing electronic devices such as multilayer ceramic capacitors, thermal sensors, resonators, memories, etc. Since electrical properties (relative permittivity, dielectric loss and the temperature dependence of dielectric constant) and therefore advanced applications of $BaTiO_3$ ceramics are sensitive to their microstructure, especially pore and grain sizes distribution, it is very important to investigate the nature of this relation.

Solid-state reactions at temperatures above 1000 °C used to prepare $BaTiO_3$ produce relatively coarse, agglomerated particles that are not suitable for the processing of dense ceramics with required microstructure for advanced applications. Soft chemistry routes are widely apply for producing stoichiometric $BaTiO_3$ nanopowders with narrow particles size distribution and low tendency of agglomeration. The uniform composition achieved by these methods due to finer scale mixing of barium and titanium cations implies lower temperature of ceramics obtaining [1–5]. Therefore, many efforts have been focused on the optimization of the BTO

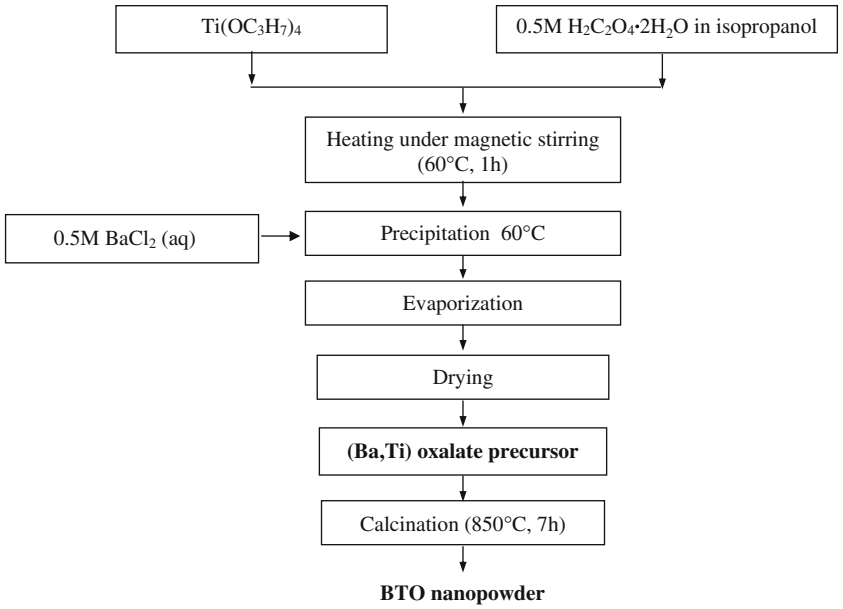

Fig. 1 Scheme of the synthesis of $BaTiO_3$ nanopowder by oxalate route

ceramics processing [6,7] in order to improve mainly their dielectric behavior.

The aim of this study is to investigate the influence of $BaTiO_3$ nanopowders preparation by two different routes (modified Pechini method and decomposition of oxalate-type precursor) on the microstructure evolution and the dielectric properties of BTO ceramics.

2 Experimental

All the chemicals were purchased from Merck and were GR grade (≥99%). The synthesis of BTO nanopowders by modified Pechini method [8] was carried out starting with titanium (IV) isopropoxide, barium citrate (obtained from barium carbonate dissolved in 4 M aqueous solution of citric acid), citric acid as chelating compound and ethylene glycol as esterification agent. The molar ratio, $BaCO_3$: $Ti(OC_3H_7)_4$:$C_6H_8O_7$:$C_2H_4O_2$, in the reaction mixture was 1:1:2:20 and more details on this procedure were presented elsewhere [9]. In the oxalate route, titanium isopropoxide and barium chloride were used as raw materials, oxalic acid as chelating agent, in a molar ratio, $Ti(OC_3H_7)_4$: $BaCl_2{\cdot}2H_2O$:$H_2C_2O_4{\cdot}2H_2O$=1:1:2 and isopropanol as solvent. Both oxalate and polymeric precursors were annealed at 850 °C for obtaining single phase, $BaTiO_3$ nanopowders. Figure 1 shows the obtaining steps of $BaTiO_3$ nanopowders by oxalate route.

Barium titanate samples were analyzed by X-ray diffraction, SEM and TEM. XRD data were collected using a Shimadzu XRD 6000 diffractometer with CuKα radiation with a scan step of 0.02° and a counting time of 1 s/step in the range of 2θ=20–80°. To estimate the structural characteristics a counting time of 10 s/step, for 2θ between 20° and 120° was used. The calculation of unit cell parameters is based on the least squares procedure (LSP) using the linear multiple regressions for several XRD lines. A Hitachi S2600N scanning electron microscope was used to analyze the microstructure of the samples. TEM investigations for determining the morphology and the average particle size of BTO nanopowders were performed with a Philips CM 120 microscope.

Ceramic samples were obtained by uniaxial pressing of BTO nanopowders at 160 MPa into pellets of 15 mm diameter that were sintered in air, at different temperatures. The electrical measurements were performed on parallel-plate capacitor configuration, at 1 kHz, by applying Pd–Ag

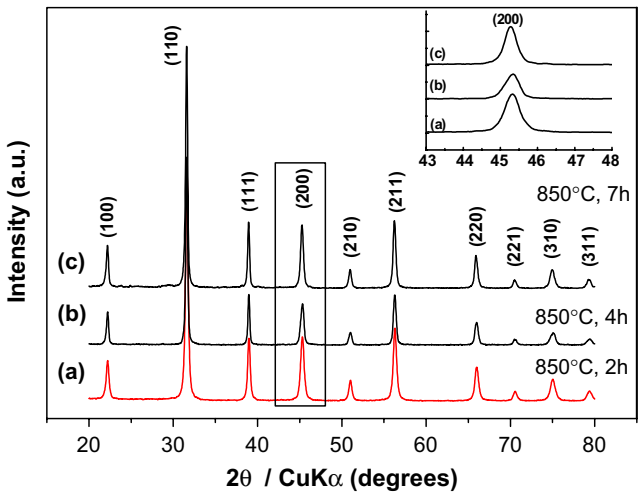

Fig. 2 Room temperature XRD patterns of $BaTiO_3$ nanopowders obtained by (*a*) modified Pechini method and (*b*), (*c*) oxalate route

Table 1 Structural characteristics of $BaTiO_3$ samples.

Sample	Type of precursor	Annealing/sintering conditions	Cryst. system	*a* (Å)	*c* (Å)	*c*/*a*	Unit cell volume (Å^3)
Powders	Polymeric	850 °C/2 h	T	3.9920 (16)	4.0091 (44)	1.0043 (15)	63.89 (12)
	Oxalate	850 °C/4 h	T	3.9977 (21)	4.0121 (34)	1.0036 (14)	64.12 (12)
	Oxalate	850 °C/7 h	T	3.9935 (19)	4.0155 (32)	1.0055 (13)	64.04 (11)
	Polymeric	1200 °C/3 h	T	3.9979 (16)	4.0242 (44)	1.0066 (15)	64.32 (12)
Ceramics	Polymeric	1300 °C/3 h	T	3.9981 (11)	4.0282 (32)	1.0075 (11)	64.39 (9)
	Oxalate	1300 °C/3 h	T	3.9883 (12)	4.0291 (20)	1.0102 (8)	64.09 (7)

T Tetragonal

electrodes on the polished surfaces of the ceramic pellets sintered at 1300 °C/3 h.

3 Results and discussion

The thermal analysis data of both precursors have shown, in agreement with the literature data [1], that the decomposition processes take place in several exothermic steps with different intermediate compounds formation including $BaCO_3$ and partially amorphous TiO_2 from polymeric precursor and barium titanium oxycarbonate, $Ba_2Ti_2O_5CO_3$, from oxalate-type precursor, respectively.

The complex precursors were annealed at the same temperature, but with different annealing plateaus to obtain single phase $BaTiO_3$. In the case of modified Pechini method, XRD data (Fig. 2—pattern (a)) show that single phase $BaTiO_3$ was obtained after annealing at 850 °C for 2 h. In these conditions, the crystallite average size (calculated by convolutional model from XRD data) is $\overline{d} = 432(25)$ Å. Longer plateaus were required in order to transform the amorphous oxalate-type precursor into well-crystallized, single phase $BaTiO_3$ powders (Fig. 2—patterns (b) and (c)). In this case, the crystallite average size seems to remain almost constant when the annealing plateau increases ($\overline{d} = 547$ (77) A and $\overline{d} = 548$ (72) Å for nano-powders obtained by annealing the precursor at 850 °C for 4 h and 7 h, respectively), but a rise of the tetragonality degree has to be pointed out. It has to be mentioned that even if the almost symmetric profile of the (200) peak seems to indicate a "pseudocubic" structure (Fig. 2—inset), the deconvolution and the fitting technique allowed establishing for the powders produced by both method, a tetragonal symmetry, with low values of tetragonality degree (expressed by *c*/*a* ratio). The lattice parameters for $BaTiO_3$ powders are summarized in Table 1.

The SEM image (Fig. 3(a)) of $BaTiO_3$ powder prepared via modified Pechini method and annealed at 850 °C/2 h, shows large, partially sintered and non uniform aggregates consisting of spherical agglomerates of ~120–130 nm (Fig. 3(a)—inset). The TEM analysis has confirmed that the powder is well crystallized and has indicated that the agglomerates observed in the SEM image actually contain nanoparticles with an average size of 44 nm, very close to the crystallite size calculated from XRD data. This proves the single crystal nature of the BTO particles (Fig 4(a)).

A different morphology was observed for $BaTiO_3$ powder obtained from oxalate-type precursor, calcined at 850 °C/7 h. Unlike the polymeric precursor-derived powders, the SEM image revealed in this case, more uniform, smaller (of an average size of only ~3.7 μm) and hexagonal-like shape aggregates (Fig. 3(b)). The same

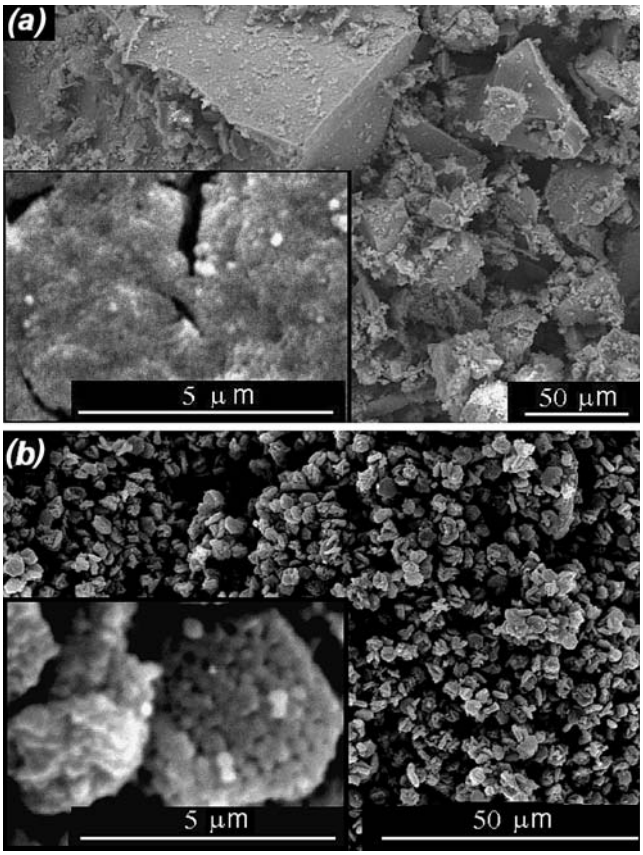

Fig. 3 SEM images of $BaTiO_3$ nanopowders obtained by (**a**) modified Pechini method at 850 °C/2 h and (**b**) oxalate route at 850 °C/7 h

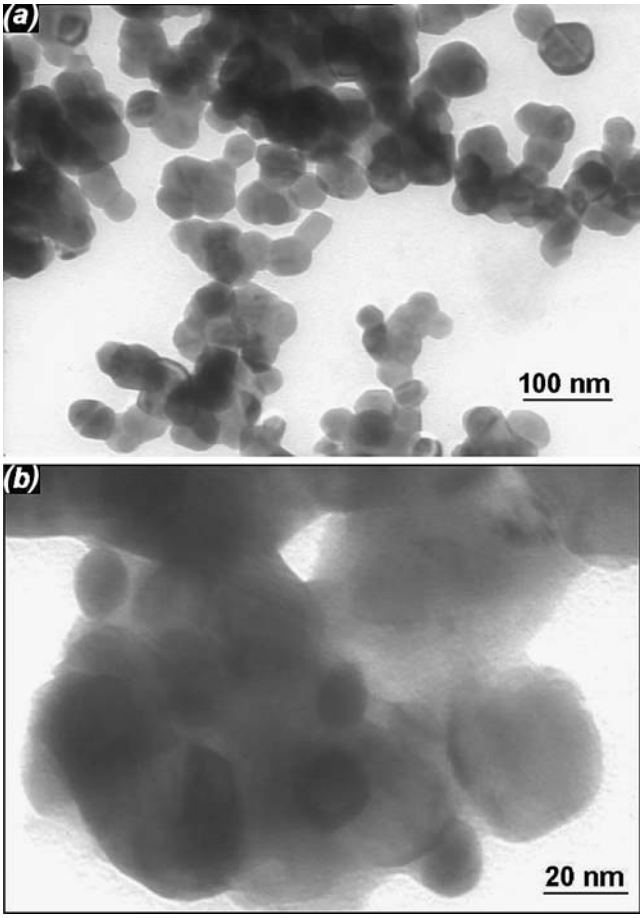

Fig. 4 TEM micrographs of $BaTiO_3$ nanopowders obtained by (**a**) modified Pechini method at 850 °C/2 h and (**b**) oxalate route at 850 °C/7 h

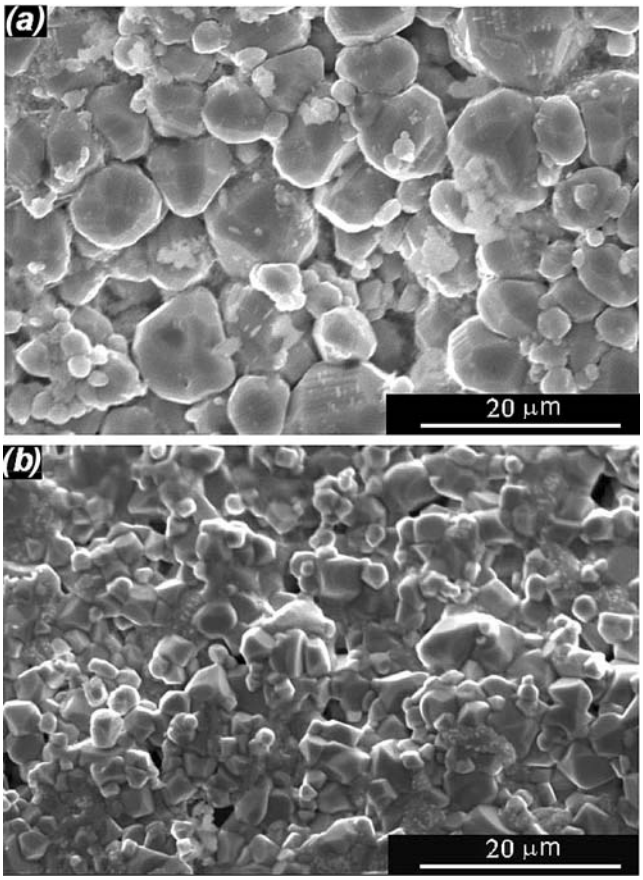

Fig. 6 Surface SEM images of $BaTiO_3$ ceramics sintered at 1300 °C/3 h from powders prepared by (**a**) modified Pechini method and (**b**) oxalate route

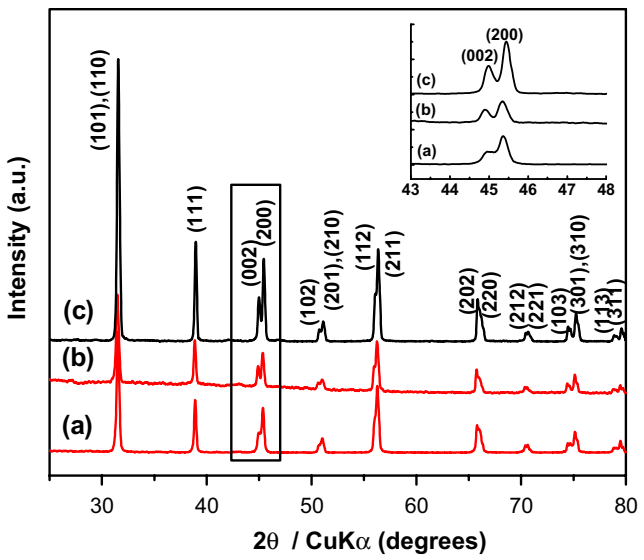

Fig. 5 Room temperature XRD patterns of $BaTiO_3$ ceramics obtained from powders synthesized by modified Pechini method ((*a*) 1200 °C/3 h and (*b*) 1300 °C/3 h) and (*c*) oxalate route (1300 °C/3 h)

pronounced tendency to form spherical agglomerates, but of higher equivalent average size (of ~250 nm) as compared to those ones resulted by modified Pechini method it has to be emphasized (Fig 3(b)—inset). The TEM analysis shows particles of various sizes, the smallest having around 13 nm

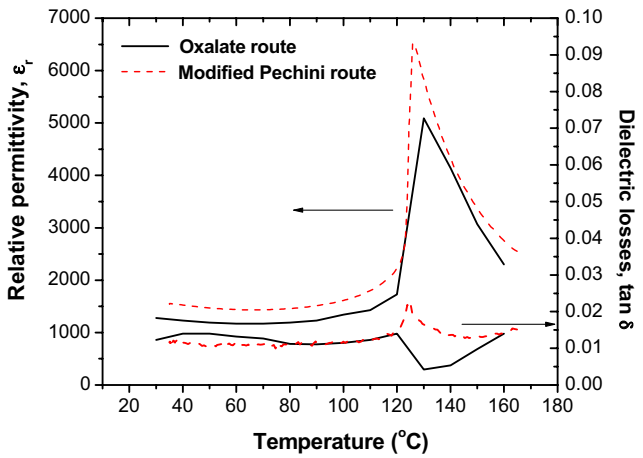

Fig. 7 Relative permittivity and dielectric losses vs. temperature measured at 1 kHz for $BaTiO_3$ ceramics sintered at 1300 °C/3 h

(Fig. 4(b)). Since it was very hard to disperse this powder and because of the strongly bonded agglomerates, it was difficult to estimate the particle average size by TEM investigation. However, the crystallite average size of 54.8 nm obtained from XRD data suggests that larger particles (of several tens of nanometers) should prevail in this powder.

Figure 5 shows the room temperature XRD patterns of BTO ceramics obtained via both modified Pechini method and oxalate route and sintered at different temperatures for 3 h. The XRD patterns were indexed as single phase $BaTiO_3$ perovskite, with a clear tetragonal symmetry characterized by high values of c/a ratio (Table 1) and proved by the visible splitting of the peak located at $2\theta = 45.3°$ (Fig. 5—inset).

The ceramic sample obtained via Pechini method and sintered at 1300 °C for 3 h has presented well-defined, pore-free microstructure, with bimodal grain distribution, consisting of both polyhedral, faceted, large grains of ~9 μm and small grains of ~3.5 μm (Fig. 6(a)). SEM investigation of $BaTiO_3$ ceramic obtained by oxalate route and sintered at 1300 °C for 3 h (Fig. 6(b)) has shown a homogeneous microstructure consisting of fine polyhedral grains of 2–3 μm with a monomodal grain distribution and intergranular pores. These fine grain appear from a matrix with no well-defined grain boundaries, specific to ceramics in the early stages of the sintering process. Therefore, one can conclude that the ceramic produced by modified Pechini method shows a better densification than the one obtained by oxalate route (relative density values are 90% and 79%, respectively).

The microstructure features clearly influenced the electrical behavior of the ceramics, so higher relative permittivity values were recorded for the highly sintered sample produced by the modified Pechini method. Phase transition temperatures of 127 and 130 °C with relative permittivity values of 6,478 and 5,088 recorded at 1 kHz, were obtained for ceramic samples synthesized via modified Pechini method and oxalate route, respectively (Fig. 7). However, in both cases, sharp dependence $\varepsilon_r(T)$ at the Curie temperature and low dielectric losses (tan δ=0.012) at room temperature were recorded.

4 Conclusions

$BaTiO_3$ nanopowders present various structural and morphological features depending on the type of raw materials and processing route. $BaTiO_3$ nanopowders with tetragonal symmetry were obtained after annealing the complex precursors at 850 °C by two soft chemistry routes. In the case of oxalate based-precursor, a longer thermal treatment is required in order to prepare barium titanate free of any secondary phase.

The higher dielectric performance of the ceramic obtained by the modified Pechini method in comparison with the sample prepared by the oxalate route may be related to its dense and pore-free microstructure induced by the presence in the oxide nanopowder of large, non-uniform aggregates, already partially sintered.

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