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Tailoring of perovskite oxides nanopowders: particles size and morphology control to produce nanocrystalline dense ceramics

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The current trend in advanced ceramics is to realize grain size below a few hundred of nanometers. This aim can be attained if high quality nanopowders (≈100 nm) with narrow particle size distribution are available for which also relatively low-temperature sintering is also required to reach high densification whilst preventing grain growth. An original and innovative approach in producing high quality perovskite non-agglomerated nanopowders, with a strict control of stoichiometry, narrow particle size distribution by soft chemistry methods is presented. Ultra-fine, non-agglomerated $BaTiO_3$ and $SrTiO_3$ nanopowders with sharp particle size distribution were prepared by direct precipitation of the relevant metal chlorides dissolved in a strong alkaline aqueous solution by considering the thermodynamic conditions stated for these aqueous syntheses. Since the preparation of nanopowders is very sensible to the synthesis parameters, critical points such as nuclei formation, crystallite growth and aggregation of crystallites were strictly controlled. Particularly a strict control of supersaturation and temperature strongly reduces the heterogeneity conditions of the reactor and makes possible to control the cations concentration which determines the final particle size. We succeeded in tailoring $BaTiO_3$ and $SrTiO_3$ nanopowders in the range 15 ÷1500 nm, with a narrow particle size distribution and a high stoichiometry control.

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Keywords: Nanocrystalline powders, Perovskite, Particle size distribution

1. Introduction

Many ceramics with perovskite-like structure, such as $BaTiO_3$ (BT), are ferroelectric materials, also showing piezoelectric and pyroelectric properties in their polar phase [1], *i.e. multifunctionality*. Due to their very high permittivity (normally ε =1500-4000, according to the grain size) and low losses, they are extensively used in the electronic industry where they find manifold applications. Although they can be employed for underwater acoustic sensors, actuators, PTCR (Positive Temperature Coefficient of Resistivity) resistors, ferroelectric memories, and embedded capacitance in Printed Circuit Board (PCB) [2], the main application is in the field of communication and microelectronics (Multilayer Ceramic Capacitors, MLCCs and tunable elements).

Presently, continuous advances toward component miniaturisation lead the high-technology ceramics on the way of grain size reduction below a few hundred of nanometers or even below 100 nm in order to improve the performance of the devices and possible to reduce their costs. In the case of MLCCs, the current trend is to increase the number of dielectric layers above 500 and to decrease their thickness below 1 μm. This objective can be achieved under two conditions:

(i) production of high quality nanopowders (≤ 100nm) with narrow particle size distribution,

(ii) use of relatively low sintering temperature that prevents grain growth whilst leading to high densification.

Recently, an increasing interest has been focused on the soft chemistry methods for preparing such nanopowders with applications in electroceramics. In the present paper, our innovative approach in producing high quality perovskite non-agglomerated nanopowders, with a strict control of stoichiometry and narrow particle size distribution for a few perovskite systems is presented.

2. Powder preparation approach

Ultra-fine, non-agglomerated $BaTiO_3$ and $SrTiO_3$ nanopowders were prepared according to the direct precipitation reaction (T<100°C; p=10^5 Pa; pH ≈14):

$$(Ba/Sr)Cl_2(aq) + TiCl_4(aq) + 4NaOH(aq) \rightarrow (Ba/Sr)TiO_3(s) + 4NaCl(aq) + 3H_2Ol(l) \quad (1)$$

where *(aq)* indicates the salts dissolved in aqueous solution [3,4]. The thermodynamic conditions for the hydrothermal synthesis of BT stated by Łenka and Riman [5] were taken into consideration. The reaction was carried out either in batch or mini-tubular reactors.

For larger amount of powders, a Segmented Flow Tubular Reactor (SFTR) was firstly designed and employed [6, 7]. An excess of Ba over the $BaCl_2/TiCl_4$ stoichiometry ratio (R=1.11) was always used to compensate depletions due to the washing step. The STFR

system (Fig. 1) essentially is composed by a *micromixer*, where the reactants are efficiently mixed and a *segmenter* in which the supersaturated solution is separated by an organic immiscible fluid into micro-batch volumes (≈60 mL) in a continuous mode. Each micro-volume is fed into the tubular reactor (Ø 4mm, length 20m) kept in a thermostatic bath, and meets exactly the same residence time and the same reaction conditions all throughout the length of the tubular reactor. As a result, the formation of practically identical nano-particles is observed, as each micro-volume behaves like a microreactor. Eventually the powder dispersion, separated from the immiscible fluid by decantation, is collected, washed and finally dried.

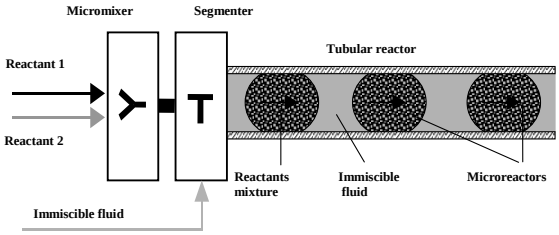
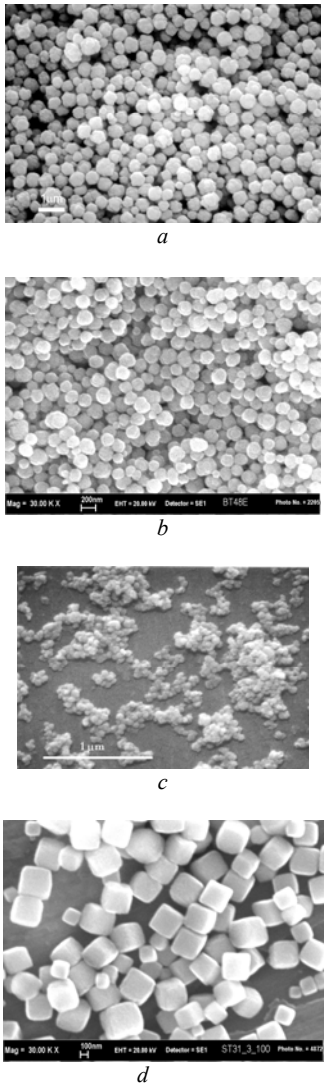


Fig. 1. *Operating schema of SFTR showing the formation of segmented micro-batch volume.*

3. Results and discussions

It is known, that to obtain high-quality powders, some critical points such as nuclei formation, crystallite growth and aggregation of crystallites must be controlled because the preparation of nanopowders is very sensible to all these parameters. In particular a strict control of the supersaturation and temperature strongly reduces the heterogeneity conditions of the reactors, and in turn, makes possible the control of cations concentration that determines the final particle size. In fact, the particle size decreases when the concentration increases. We showed that these requirements are successfully achieved by employing our SFTR technology and we succeeded in tailoring BT nanopowders in the range 15÷1500 nm, with a satisfactory stoichiometry control (Fig. 2 a-c and 3).

The authors proved [3,4] that the reaction (1) represents an easy way to obtain well defined, no agglomerated, stoichiometric and equiaxed BT and ST nano-powders with a very narrow Particle Size Distribution, as shown in Fig. 4, where the dimensional volume distribution is reported.



a

b

c

d

Fig. 2. *Micrographs of perovskite nanopowders with tailored particle size distribution: (a) $BaTiO_3$ of 500-700 nm, (b) $BaTiO_3$ of 150-200 nm, (c) $BaTiO_3$ of 30-50 nm, (d) $SrTiO_3$ nanopowders with average particle size of 400 nm. Note the similar particle size of each powder and the non-aglommeration.*

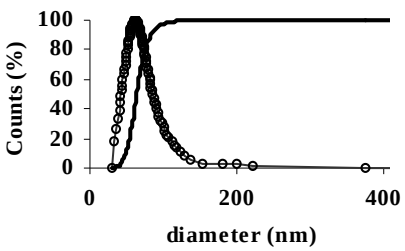
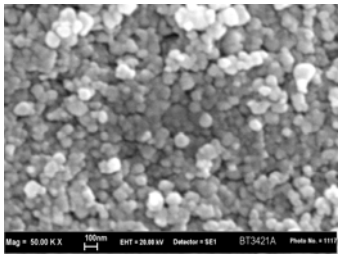
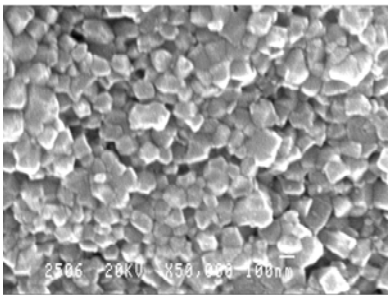


Fig. 3. Dimensional volume distribution (— cumulative; ❍ frequency). Note the very sharp particle size distribution (logarithmic scale is commonly used in literature).

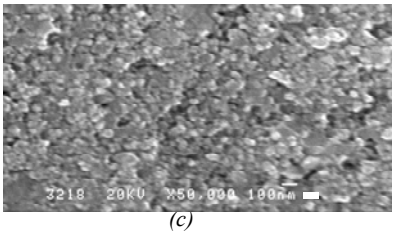
The production of high-quality nano-powders is a necessary but not sufficient condition to obtain dense nanocrystalline ceramics unless innovative sintering procedures are applied to prevent grain growth below a few tenth of nm. Spark Plasma Sintering (SPS) allows a rapid densification of powders that we used [8-10] to prepare dense, bulk nanocrystalline BT ceramics in the range of grain size (GS) of 30-100 nm and a high relative density: ≥97% (Fig. 5 a-c). The dense structure represented in the Fig. 6 represented at the moment of publication [9] the finest dense $BaTiO_3$ structure ever reported, still preserving local ferroelectricity. The obtaining of such dense samples with a large range of well controlled grain size, including sizes below 100nm allowed a complex investigation in which: (i) grain size effects on the structural and macroscopic properties were observed, this giving important data for the MLCC applications and (ii) the estimation of the critical grain size for the existence of ferroelectricity in dense $BaTiO_3$ ceramics was realized, this being of high importance from the fundamental point of view [9, 10].



(a)

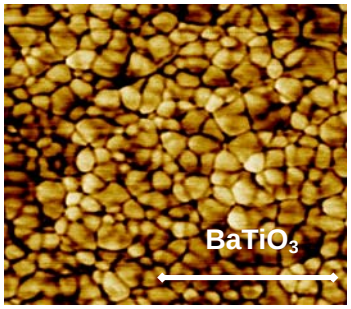


(b)

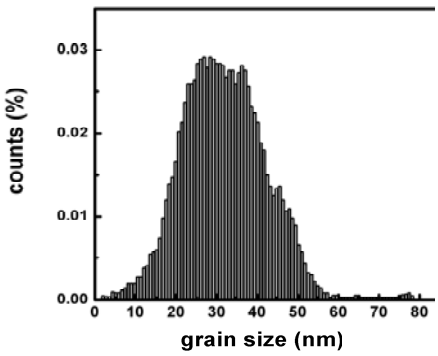


(c)

Fig. 4 *$BaTiO_3$ nanocrystalline ceramics: (a) GS ≈100 nm; bar 100 nm, (b) GS ≈ 50 nm; bar 100 nm, (c) GS ≈ 30 nm; bar 100 nm.*



(a)



(b)

Fig. 5 *(a) AFM surface image of the 30 nm $BaTiO_3$ ceramic (bar: 250 nm) and (b) the corresponding grain size distribution.*

The structural and functional properties showed a progressive reduction of the tetragonal distortion, heat of transition, Curie temperature, and relative dielectric constant with reduction of grain size. The critical size for disappearance of ferroelectricity has been estimated from these data as being in the range of (10–30)nm [10]. The finest dense structure produced by this procedure (Fig. 5) demonstrated to present local ferroelectricity in spite of almost zero macroscopic polarization (frozen polarization). In the authors' opinion, the functional properties of these ceramics are ascribed to a combination of the intrinsic grain size effect and of the size-dependent role of the grain boundary (so-called "dead" layer).

4. Conclusions

A new soft chemistry method for producing high quality perovskite nanopowders is presented. Ultra-fine, non-agglomerated $BaTiO_3$ and $SrTiO_3$ nanopowders with sharp particle size distribution were prepared by direct precipitation of the relevant metal chlorides dissolved in a strong alkaline aqueous solution. Critical parameters of the synthesis such as the nuclei formation, crystallite growth and aggregation of crystallites were strictly controlled.

By using these powders and Spark Plasma Sintering method, dense nanocrystalline ceramics with excellent dielectric properties (high permittivity, low losses, almost non-hysteretic P(E) dependence and high thermal stability) were obtained, these ceramics representing valuable alternative as Pb-free materials for the electroceramics industry.

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