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Influence of reactant type on the Sr incorporation grade and structural characteristics of $Ba_{1-x}Sr_xTiO_3$ ($x=0-1$) grown by sol–gel-hydrothermal synthesis

S. Fuentes[a,f,*], E. Chávez[b,c], L. Padilla-Campos[d], D.E. Diaz-Droguett[e]

[a]*Departamento de Ciencias Farmacéuticas, Facultad de Ciencias, Universidad Católica del Norte, Casilla 1280, Antofagasta, Chile*
[b]*Department of Physics, Universitat Autònoma de Barcelona, Campus de la UAB, 08193 Bellaterra (Barcelona), Spain*
[c]*Catalan Institute of Nanotechnology (ICN-CIN2), Campus de la UAB 08193 Bellaterra (Barcelona), Spain*
[d]*Departamento de Química, Facultad de Ciencias Básicas, Universidad de Antofagasta, Casilla 170, Antofagasta, Chile*
[e]*Departamento de Física, Facultad de Física, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile*
[f]*Center for the Development of Nanoscience and Nanotechnology, CEDENNA, Santiago, Chile*

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Abstract

The influence of barium and strontium starting reactants used in different mole ratios, $BaCl_2$ and $Ba(OH)_2$, $SrCl_2$ and $Sr(OH)_2$, on the chemical and structural properties of $Ba_{1-x}Sr_xTiO_3$ ($x=0-1$) (BST) nanoparticles prepared via sol–gel-hydrothermal synthesis in an oxygen atmosphere is discussed. The effect of the type of reactant on the relative amount of Sr incorporated in BST compound was also analysed. The synthesised BST nanoparticles showed differences in their structural and chemical characteristics, which were attributed to the presence of Cl^- or OH^- anions during the synthesis of the compound. The structure, morphology and oxidation state of the samples were studied by X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy, respectively. In addition, theoretical calculations using cluster models were carried out to understand the possible phases formed of BST, the effect of the Sr incorporation and the possible presence of oxygen vacancies inside the BST structure.

Keywords: A. Sol–gel processes; B. Defects; B. Spectroscopy; C. Ferroelectric properties; D. $BaTiO_3$ and titanates

1. Introduction

Ferroelectric materials are used in many modern devices, such as piezoelectric actuators and electro-optic modulators. Materials of the ABO_3 family (A and B are cations and O is oxygen), such as $BaTiO_3$, $PbTiO_3$ and $SrTiO_3$, have received a significant amount of attention due to their ferroelectric and electro-optic properties [1–3]. The properties and behaviour of macroscopic ferroelectric materials are well known.

More recently, the investigation of properties has been extended to the electronic structures of the impurities, surfaces, and electron-doped $SrTiO_3$ (ST) or $BaTiO_3$ (BT) [4,5]. However, the atomic structure and the electronic properties of the grain boundaries in $BaTiO_3$ or $SrTiO_3$ are the subject of great interest due to their technological implications. There are various reports on the effects of impurity doping on the properties of this interesting system [6].

Among other materials, barium strontium titanate, $BaSrTiO_3$ or BST, is the most extensively studied perovskite ferroelectric oxide. This material is invaluable for the electronics industry, due to its high dielectric constant, low dielectric loss, good thermal stability and high frequency characteristics [7,8]. BT and BST are commonly used in a number of electronic devices such as transducers, piezoelectric actuators, thermal switches, passive memory storage devices and dynamic random access memories (DRAMs) [9,10]. The properties of BST strongly depend on the composition and characteristics of its constituent materials; therefore, efforts are still in progress to synthesise BST compounds with excellent properties.

*Corresponding author at: Universidad Católica del Norte, Departamento de Ciencias Farmacéuticas, Facultad de Ciencias, Av. Angamos 0610, Antofagasta, Chile. Tel.: +56 55 355383; fax: +56 55 355632.
E-mail address: sfuentes@ucn.cl (S. Fuentes).

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Barium strontium titanate, $Ba_xSr_{1-x}TiO_3$, is a solid solution of $BaTiO_3$ and $SrTiO_3$. At room temperature, $BaTiO_3$ and Ba-rich $Ba_xSr_{1-x}TiO_3$ compounds have a tetragonal lattice and are ferroelectric, whereas $SrTiO_3$ and Sr-rich $Ba_xSr_{1-x}TiO_3$ compounds are cubic and paraelectric. The substitution of Ba by Sr will result in a decrease of the Curie temperature and an increase in the dielectric constant of the material [11].

Several methods have been considered for the preparation of BST in powder form, including the sol–gel method [12], a solid-state reaction [13], spray pyrolysis [14], combustion synthesis [15], a microwave method [16] and a hydrothermal method [17,18]. The latter method is advantageous due to low temperature processing, the non-vacuum requirement and a low cost compared with others.

In ferroelectric fine particles, ferroelectricity decreases with decreasing particle grain size and disappears below a certain critical size [19,20]. Other physicochemical factors, such as the density, shape, presence of impurities and structural defects, also affect this property [21,22]. Moreover, Dutta et al. [23] have proposed that a relationship exists between the tetragonality in BT and the type of counter ion used in the synthesis. Although the exact mechanism of this process is not yet known, the authors suggested that most soluble salts can promote the dissolution of BT, disturbing the dissolution–recrystallisation process. Thus, a better understanding of the structure-property relationship of perovskite nanocrystals is highly desirable, which is also necessary for developing high-performance electronic devices.

The structural and morphological characteristics of sol–gel-hydrothermal BST powders often vary as a function of the synthesis parameters, such as reaction time, reaction temperature, and composition. Thus, the study of how these parameters influence the BST composition is considered important, first to explain the fundamental crystallisation process and second to optimise the material properties for potential technological applications.

In the present study, we prepared barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$, $x=0-1$) powders of nanoparticle size using the sol–gel-hydrothermal method with tetrachloride titanate and two sources of barium and strontium salts as the starting material at a typical temperature of 180 °C and 24 h of reaction time in an oxygen atmosphere. The effect of the synthesis conditions (presence of chloride ions and alkali metal ions) and the different mole ratios and on the characteristics of the resulting compound is analysed. Finally, theoretical calculations were carried out to help with the interpretation of the experimental results.

2. Experimental

$Ba_{1-x}Sr_xTiO_3$ powders prepared using a different Ba:Sr mole ratio ($x=0$, 0.3, 0.5, 0.8 and 1) were synthesised using the sol–gel-hydrothermal process with tetrachloride titanate ($TiCl_4$, 1 M) and two different salts of barium ($BaCl_2$, $Ba(OH)_2$) and strontium ($SrCl_2$, $Sr(OH)_2$) as the starting materials using two methods of synthesis.

Table 1
The preparing parameters of BST powders synthesized at 180 °C and 24 h.

Samples Method 1 (M1)	Ba:Sr in reactant	Samples Method 2 (M2)	Ba:Sr in reactant
B1	1:0	S1	1:0
B2	0.7:0.3	S2	0.7:0.3
B3	0.5:0.5	S3	0.5:0.5
B4	0.2:0.8	S4	0.2:0.8
B5	0:1	S5	0:1

In method 1 (M1), a typical synthesis of sample (B2) used $BaCl_2{\bullet}2H_2O$ (99.999%, Aldrich) and $SrCl_2{\bullet}6H_2O$ (99.995%, Aldrich) as the reactants (Table 1). A 1.1 mL solution (A) of $TiCl_4$ (1 M, Aldrich) was diluted in 2.3 mL of 2 M HCl to form a yellowish solution. The aqueous solution (B) was prepared by dissolving 0.52 g of $BaCl_2{\bullet}2H_2O$ and 0.4 g of $SrCl_2{\bullet}2H_2O$ in 20 mL of deionised water. For preparing the $BaSrTiO_3$ precursor, solution (B) was added into solution (A) with vigorous stirring for 1 h. Under stirring and N_2 bubbling, 13 mL of 6 M NaOH were added to the barium strontium titanium solution and a white homogeneous colloidal slurry (barium strontium titanium) was formed.

The mixed solution was transferred into a 100 mL Teflon-lined stainless steel reactor; the reactor was sealed and then heated for 24 h at 180 °C under a partial oxygen pressure of 60 psi. At the end of the reaction, the autoclave was naturally cooled to room temperature. The as-formed white solid powder that was attached to the bottom and inner wall of the Teflon container was collected, centrifuged, washed with distilled water and ethanol to remove the remaining ions, and dried at 60 °C for 6 h in vacuum.

In method 2 (M2), similarly, $Ba_{1-x}Sr_xTiO_3$ powders using the same Ba:Sr mole ratio were prepared using $Ba(OH)_2$ and $Sr(OH)_2$ as the starting materials (Table 1).

2.1. Characterisation

X-ray diffraction (XRD) data were acquired using a Siemens Advanced D-8 diffractometer with CuK_α radiation at 40 kV and 30 mA. Transmission electron microscopy (TEM) studies were performed in a Jeol JEM-2011 operated at 200 kV under diffraction and phase contrast modes. The surface chemical information of the samples was obtained by the X-ray photoelectron spectroscopy (XPS; Physical Electronics system model 1257) using an AlK_α emission. The binding energies and oxidation states were obtained from high-resolution scans. The energy scale was calibrated by assigning 284.8 eV to the C 1s peak, corresponding to adventitious carbon.

3. Results

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of the BST sample synthesised by the two methods (M1 and M2). As shown in Fig. 1a (M1) and c (M2), the sharp and well-defined peaks revealed high crystallinity