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Enhancing the formation of tetragonal phase in perovskite nanocrystals using an ultrasound assisted wet chemical method

Abdolmajid Moghtada [a], Rouholah Ashiri [b,*]

[a] Department of Materials Science and Engineering, Sharif University of Technology, P.O. Box 11365-9466, Tehran, Iran
[b] Department of Materials Science and Engineering, Dezful Branch, Islamic Azad University, P.O. Box 313, Dezful, Iran

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ABSTRACT

Synthesis of highly-pure tetragonal perovskite nanocrystals is the key challenge facing the development of new electronic devices. Our results have indicated that ultrasonication is able in enhancing the formation of tetragonal phase in perovskite nanocrystals. In the current research, multicationic oxide perovskite ($ATiO_3$; A: Ba, Sr, $Ba_{0.6}Sr_{0.4}$) nanopowders are synthesized successfully by a general methodology without a calcination step. The method is able to synthesize high-purity nanoscale $ATiO_3$ ($BaTiO_3$, $SrTiO_3$, $Ba_{0.6}Sr_{0.4}TiO_3$) with tetragonal symmetry at a lower temperature and in a shorter time span in contrast to the literature. To reach an in-depth understanding of the scientific basis of the proposed methodology, in-detail analysis was carried out via XRD, FTIR, FT-Raman, FE-SEM and HR-TEM. The effects of the sonication time and sonication (bath) temperature on the tetragonality of nanoscale products were examined. Furthermore, Raman spectroscopy provides clear evidence for local tetragonal symmetries, in particular when a band is observed at 310 cm^{-1}.

1. Introduction

Ternary Perovskite materials include a wide group of compounds used in various electroceramic device applications such as electronic, electro-optical and electromechanical devices. Perovskites have a cubic structure with general formula of ABO_3, where A is usually an alkaline-earth or a large lanthanide, and B is usually a transition metal or a smaller lanthanide [1]. Perovskite structure has capability to host ions of different size. Focusing on parent compounds, in ABO_3 series, only barium titanate ($BaTiO_3$; BTO) is most studied and well explored compound in both bulk and thin film shapes. Although this compound shows a noteworthy range of interesting properties, however till now, only few studies have been reported on the sonochemical synthesis of perovskite-type materials. Sonochemistry uses the ultrasonic irradiation for inducing the formation of very fine powder products with high surface area in contrast to other synthesis methods [2]. It has been employed extensively for the synthesis of the nanostructured materials due to its rapid reaction rate, controllable reaction conditions, simplicity and safety. Moreover, powder particles synthesized through this method normally have uniform shape with narrow size distribution [1–4]. The crystal structure of BTO is typically observed by X-ray diffraction (XRD) and it appears to change from a tetragonal ferroelectric phase to a cubic paraelectric phase, which is inappropriate and is not very sensitive for transitions involving oxygen/titanium displacements [5]. However, vibrational spectroscopy is sensitive to this type of transformations, especially for Raman spectroscopy, which can detect local lattice distortions and crystallographic defects at the molecular level [6]. Chemical bonds vary widely in their sensitivity to scrutinizing by infrared techniques. Thus, the capability of infrared spectrophotometry (IR) is a function of the chemical bond, rather than being applicable as a general probe. FT-IR analysis was carried out for detecting the presence of the functional groups. Using this analysis, the reaction mechanisms in the sonochemical process can be detected. Raman and IR spectra are important in studying the ferroelectric materials, since ferroelectricity and lattice dynamics are closely related. Raman spectra give information on local symmetry and has been used by many researchers to study the relaxor behavior [7], the phase transitions [8], as well as in order to study other aspects like stress, strain [9] and grain size effect [10] of the ferroelectrics.

In the present work, we have tried to develop an innovative method in order to synthesize a variety of ceramic nanoparticles with perovskite symmetry which has no by-products. This method is able to prepare the powder products at a low temperature of 333 K (60 °C) under the irradiation of the ultrasonic waves. Our approach provides a unified methodology for the synthesis of the perovskite materials which is a rapid one-step method with no

* Corresponding author.
E-mail address: ro_ashiri@yahoo.com (R. Ashiri).

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need for calcination the products. On the other side, an elaborated explanation regarding mechanism of synthesis and phase development in sonochemical synthesis is not available in the literature. Few publications have studied the path of synthesis and characterized the phase formation, evolution and tetragonality of BTO powder. The goal of the present work is to study and characterize the structure and tetragonality dependences of the synthesized $ATiO_3$ nanopowders using X-ray diffraction (XRD), Raman and IR spectroscopy which are able to identify the phase formation and evolution in the obtained nanopowders.

2. Experimental

Synthesis temperature and purity of perovskite materials are key challenges facing the scientific community. This work addresses the challenges by developing a method for synthesizing the perovskite nanopowders. Our new approach is based on an ultrasound-assisted wet chemical processing method. To show that the developed method can be used as a general strategy for synthesizing carbonate-free perovskite nanocrystals, first BTO, strontium titanate ($SrTiO_3$; STO) and barium strontium titanate ($Ba_xSr_{1\_}xTiO_3$; BSTO) nanocrystals were synthesized. Then, in order to study the tetragonality of the powder products, the second step of the study was focused on BTO as the most widely studied perovskite material. Titanium chloride (>99%), strontium chloride (>99%), barium chloride (>99%) anhydrous sodium hydroxide (>99%) and ethanol (99.8%) were obtained from Merck. The flowchart of the approach is shown in Fig. 1. The stoichiometric amounts of chloride salt and titanium chloride are dissolved in deionized water and ethanol, respectively. These solutions are added into a glass vessel containing NaOH solution. The concentration of the NaOH solution was required to guarantee a strong alkaline environment (pH = 14) during reaction. The glass vessel containing precursor solution is subjected to an ultrasonic bath (Soner 220H, 53 kHz, 500 W, New Taipei City, Taiwan). The advantages of the sonochemical method include green synthesis, no waste product and ease of synthesis. The solution mixture was placed at the center of the ultrasonic bath and then was sonicated at 25, 50 and 60 °C for 5, 10 and 20 min to see the effect of sonication time and temperature. The sonication was conducted without cooling so that the temperature of the solution increased gradually up to 60 °C during synthesis. Our previous results [1] have shown that in order to synthesize BSTO (with general formula of $Ba_xSr_{1-x}TiO_3$), first the corresponding molar ratios of the barium chloride (x) and strontium chloride (1 – x) should be mixed together, then their mixture should be dissolved in deionized water. The successive steps of the synthesis are similar to those for BTO synthesis. After the reaction is finished and the mixture is cooled down to room temperature, then the powder product is separated, washed, and dried in an oven. The crystal structure and average crystallite size of the powder products are determined using an X-ray diffractometer (Philips PW3710). Functional groups in the product are detected using a FT-IR spectrophotometer (Hitachi 3140). FT-IR spectrum are recorded in the range of 400–4000 cm^{-1} and measured on samples in KBr pellets. Raman spectrum was carried out with a FT-Raman 960 (Thermo Nicolet model) using a 5.5 mW laser with a wavelength of 636 nm. The morphological characteristics and microstructure of the nanoparticles were observed using field emission scanning electron microscopy (FE-SEM; Hitachi S4160, Tokyo, Japan) and high-resolution transmission electron microscopy (HR-TEM; ZEISS, LIBRA200, Oberkochen, Germany).

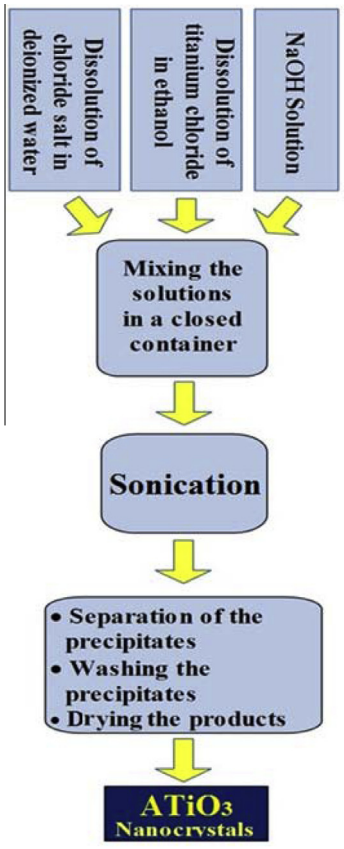

Fig. 1. Flowchart of the sonochemical method used in this work for the synthesis of the titanate-based perovskite nanocrystals.

3. Results and discussion

3.1. XRD characterization

It is known that advances in microelectronics and communication industries have led to substantial miniaturization of many electronic devices, while the performance requirements have increased [11]. As a result, smaller and more uniform particle sizes of ternary perovskite materials with tetragonal phase are required [12]. For instance, BTO powder with a narrow particle size distribution and high tetragonality is required for ceramic capacitors, self-controlled heaters, communication filters and non-volatile memories. Unfortunately, most of the methods used for the production of titanate-based (ATiO3; A: Ba, Sr, ...) powders, such as the conventional solid state reaction method, alkoxide-hydroxide route, solvothermal process, hydrothermal methods, etc. have not been fully successful in preparing perovskite nanopowders with a tetragonal phase. As a result, formation of tetragonal $ATiO_3$ nanopowders remains as a challenging issue for scientific community. XRD method is a powerful nondestructive tool that can provide information regarding crystal structure, plane of orientation, strain relaxation, etc. The aim of the present work is phase identification, evolution and tetragonality of BTO powders. $ATiO_3$-type ferroelectric (FE) compounds with perovskite structure often transform to a paraelectric (PE) phase when the temperature or pressure change [13,14]. For instance, $PbTiO_3$ tetragonal perovskite (*P4mm*) transforms to cubic perovskite (*PmN3m*) at a high temperature of 763 K or at a high pressure of 11.2 GPa [15,16]. $BaTiO_3$ also exhibits a tetragonal (*P4mm*) to cubic (*PmN3m*) phase transition at a high pressure of about 2 GPa or at 393 K [17]. XRD patterns of the sonochemically synthesized titanate-based ($ATiO_3$) particles show strong diffraction peaks as it can be seen in Fig. 2. X-ray diffraction patterns are in good accordance with JCPDS No. 31-0174 (BTO), JCPDS No. 35-734 ($SrTiO_3$; STO), JCPDS No. 34-0411 ($Br_{0.6}Sr_{0.4}TiO_3$;