Obtaining the highly pure barium titanate nanocrystals by a new approach

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ABSTRACT

Purity and synthesis temperature of nanocrystals are key challenges facing the scientific community. Herein a novel solid-state approach to synthesize fine BaTiO$_3$ nanocrystals with narrow size distribution using a high-speed ball-milling process is reported. In order to improve the kinetics of this reaction, the starting materials, BaCO$_3$ and TiO$_2$, were milled for 10 h before mixing and initiating the synthesis reaction. The contribution of this step to the BaTiO$_3$ formation is analyzed by XRD diffractometry and FE-SEM techniques. It was found that the use of the mechanically activated starting materials favors the decomposition of BaCO$_3$ at low temperatures and improves the Ba^{2+} diffusion through the formed BaTiO$_3$ layer. In consequence, very fine BaTiO$_3$ nanocrystals free from the secondary phases were obtained at a lower temperature in contrast to the previous works.

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1. Introduction

Development of the electronic devices toward miniaturization requires reaching higher performances in smaller structures. In order to fabricate the high-quality volume efficient electronic devices, small particle size nanocrystals with narrow size distribution and high purity are needed. Barium titanate (BaTiO$_3$; BTO) is a well-known electroceramic material used in manufacturing the thermistors, dielectric ceramic capacitors, etc [1–3]. During the last decade, a large number of synthetic approaches have been developed for the preparation of barium titanate nanopowders [2–9], but large-scale production is frequently based on solid-state reactions of mixed oxides [10–12]. In this process, barium titanate is obtained from the reaction between TiO$_2$ and BaCO$_3$ at high temperatures (1100–1400 °C). The successful synthesis of BTO nanopowders for advanced electronic ceramics requires the control of the synthesis process. It is believed that mechanical activation alters the physicochemical properties of mixed polycrystalline oxides, and then the synthesis mechanism of BTO [2]. Therefore, seeking for new or modified approaches is of fundamental importance and current idea of new researches. In view of above, we present a novel synthesis process for obtaining the BTO nanopowders using mechanically activated starting materials that can be carried out at a relatively lower temperature in contrast to the literature to obtain BTO powder product free of secondary phases.

2. Experimental procedure

Barium titanate was obtained from solid-state reaction between BaCO$_3$ (Applichem; assay > 98 pct) and TiO$_2$ (Merck; assay > 99 pct) using a high-energy ball-milling process. Synthesis was performed in a planetary ball mill (Retsch PM 400) under a highly pure argon atmosphere (99.999%) for various times. In all milling runs, the ball-to powder weight ratio was kept at 10:1 and the bowl rotation speed was 300 rpm. In order to synthesize carbonate-free mono-sized BTO nanocrystals, the next steps were followed:

(i) in order to improve the kinetics of the synthesis reaction (the following reaction), the starting materials, BaCO$_3$ and TiO$_2$, were milled for 10 h before their mixing,

$$BaCO_3(s) + TiO_2(s) \rightarrow BaTiO_3(s) + CO_2(g)$$
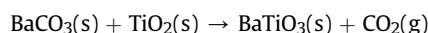
(ii) then, the mechanically activated BaCO$_3$ and TiO$_2$ were mixed in 1:1 relation at room temperature and milled for 4 h,

(iii) the powder mixture then was thermally treated at 900 °C for 2 h (sample BT1).

In order to analyze the role of the step 1, another sample was prepared following our approach in the absence of step 1 (sample BT2). Crystalline phases and the structural analysis were carried out by an X-ray diffraction (XRD) with a Phillips PW1830 diffractometer. The average crystallite size of the products was calculated using Scherrer's formula [13]. Functional groups in the product

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were detected using a FT-IR spectrophotometer (Hitachi 3140; Tokyo, Japan). FT-IR spectrum was recorded in the range of 400–4000 cm^{-1} and measured on samples in KBr pellets. The morphological features and microstructure of the products were observed by a field emission scanning electron microscope (FE-SEM; Hitachi S4160).

3. Results and discussion

FT-IR is known as a sensitive technique to carbonate phase identification. Fig. 1 shows FT-IR spectrum of the synthesized nanocrystals. FT-IR spectrum reveals the presence of absorption bands at around 541, 860, 1417, 1566 and 3444 cm^{-1}. The absorption bands at 3444 and 1566 cm^{-1} are assigned to O–H stretching and bending vibrations of water [13–17]. The absorption band at 1417 cm^{-1} can be considered as the alcoholic bending vibrations (C–OH functional groups) [13–17] implying the adsorption of small amount of alcohol on the surface of nanocrystals. This absorption is due to the use of ethanol in the washing process of the as-synthesized nanocrystals. Strong and wide band located between 850 and 466 cm^{-1} can be ascribed to BTO stretching vibrations and confirms the formation of BTO. This band is a combination of the following bands: a band at 692 cm^{-1} which is assigned to stretching vibrations of BaO and a band at 470 cm^{-1} which is assigned to stretching vibrations of TiO_2 [13–17]. Since the characteristic bands of the carbonates (1049, 1421 cm^{-1}) [13–17] have not been appeared in our spectrum, and only a little trace of the carbonate phases is seen at 860 cm^{-1} it can be stated that the synthesized nanocrystals are highly pure. This outcome is the significant advantage of the present method in contrast to other established methods [10–12].

XRD results (Fig. 2a) indicate that the current method has led to formation of the BTO nanoscale crystals with perovskite symmetry. BTO nanocrystals are characterized by well-resolved peaks at around 22.16, 31.56, 38.96, 45.24, 50.96, 56.24 and 65.88° corresponding to the (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), (2 1 1) and (2 2 0) planes. All peaks of the XRD patterns match well with standard cubic BTO perovskite phase JCPDS No. 31-174 confirming the formation of BTO with perovskite symmetry. The XRD patterns of the synthesized products are consistent with other reports [1–7]. Sample BT2 (without application of the milling step on the starting materials ($BaCO_3$ and TiO_2)) exhibits more intense peaks than BT1 sample indicating its crystallites have grown in contrast to those of BT1 sample. Considering the prominent (1 1 0) peak located at 31.56° and using the Scherrer formula given in Ref. [4], we estimate the average crystallite size of BT1 and BT2 samples to be 26.66 and 45.44 nm, respectively. These results indicate that our approach has led to a significant reduction in the size of the synthesized BTO crystallites. On the other hand, the peaks of carbonate phases are
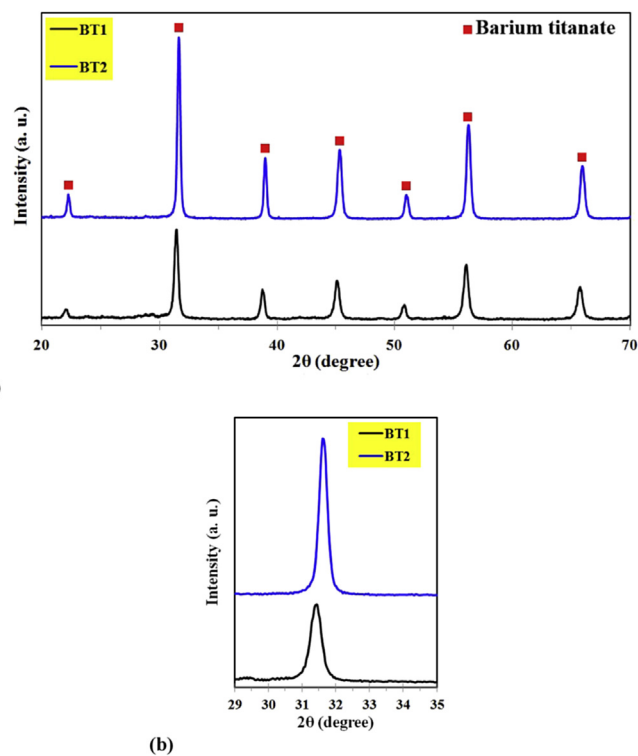
(a)

(b)

Fig. 2. XRD patterns of BTO nanocrystals synthesized in this work.

not found in the pattern of Fig. 2a, therefore, it can be said that the product is carbonate-free, if any, are below the XRD detection limit. The above results indicate that very fine BTO nanocrystals free from any by-product have been obtained through the present synthesis pathway. As can be seen in Fig. 2b, the location of XRD peaks in BT1 sample has shifted about 0.2° to lower 2θ in contrast to those of BT2 sample due to stored energy in the material during the milling stage of the starting materials.

Fig. 3 shows FE-SEM images at different magnifications of BTO powder products synthesized in this work. As can be seen in this figure, the powders seem to be agglomerated caused primarily by the processes occurring during milling the powder mixtures. Moreover, the small particles embedded in each agglomerated cluster correspond to the BTO nanocrystals. All the FE-SEM micrographs exhibit crystal size consistent with the average crystallite size determined by the analysis of XRD. The morphological properties and size distribution characterization of the BT1 sample indicate that the products consist of somewhat regularly shaped and relatively spherical particles with a narrow size distribution.
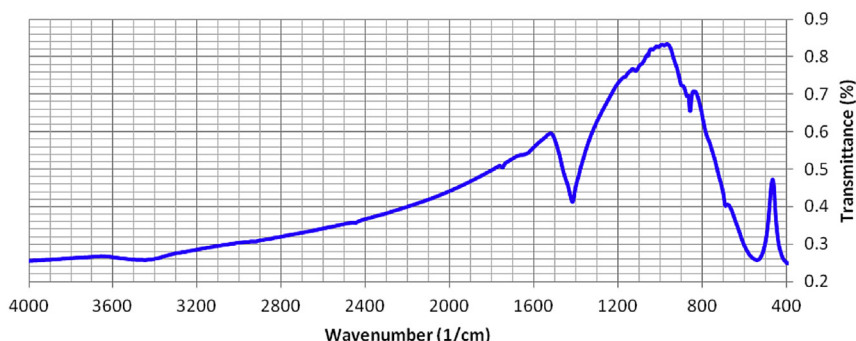
Fig. 1. FT-IR spectrum of BTO nanocrystals synthesized through our established method.