Microwave-Hydrothermal Synthesis and Characterization of High-Purity Doped BaTiO₃ Nanocrystals

A. Khanfekr*, M. Tamizifar, R. Naghizadeh

Department of Metallurgical and Materials Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran

Abstract

The synthesis of Nb doped BaTiO₃ has been investigated under Microwave-Hydrothermal (MH) conditions in the temperature of 150°C for only 2 h using $C_{16}H_{36}O_4Ti$, $BaH_2O_2.8H_2O$ and $NbCl_5$ as Ba, Ti and Nb sources, respectively. Typical experiments performed on MH processing have not yet reported for Nb doped BaTiO₃. In the MH process, the formation of high purity nano tetragonal Nb-BaTiO₃ was strongly enhanced. New hydrothermal method was used instead of the previous solid state reaction for the $BaTiO_3 \pm Nb_2O_3$ system. The new method uses high pressure to create nano dimension particles in a lower time and temperature. In case of the phase evolution studies, the XRD pattern measurements and Raman spectroscopy were performed. TEM and FE-SEM images were taken for the detailed analysis of the particle size, surface and morphology. Synthesis of Nb doped BaTiO₃ with the Microwave-hydrothermal provides an advantage of fast crystallization and reduced crystal size when compared to existing methods.

1. Introduction

Perovskite-type oxides have general formula of ABO_3 in which A is a rare earth or alkaline earth metal and B is a transition metal and these oxides are typically *p*-type semiconductors. Their composition can be varied by a wide range with partial substitution of lower valent cation in A or B site yielding additional mobile anion vacancies. Their mixed conductivity by ions and electrons migration and their high nonstoichiometric composition have resulted from the basis of the applications for this group of materials in the areas of electrochemistry [1-2], oxygen separation membranes [3], chemical sensors in detection of humidity [4], alcohol [5], gases such as oxygen [6], hydrocarbon [7] and nitric oxide [8] in the past three decades. Microstructural control has become very important due to the strong

dependence of ferroelectric properties on grain size and its compositional aspects [9].

The understanding of the structural and physical features of the powders is essential in terms of synthesis parameters as well as their size from the practical and theoretical point of view. Barium titanate is one of the most important ferroelectric materials used in electronic ceramic's industry [10-12]. Numerous studies on developing synthesis methods for purer and finer $BaTiO_3$ powders have been reported in the literature. While a genuine hydrothermal method of low-temperature process has enjoyed success in preparation of high-purity homogeneous and ultrafine powders of $BaTiO_3$ under environmentally friendly conditions [13-15]. The microwave-assisted hydrothermal process is often found to be rapid, and has the potential to enhance the crystallization kinetics of hydrothermal process. The term microwave-hydrothermal process was coined by Komarneni and colleagues in 1992, and this process has been used for the rapid synthesis of numerous ceramic oxides, hydroxylated phases, porous materials, and metal powders [16].

Recently, an alternative microwave-hydrothermal (MH) process has been developed, which has shown some advantages over the conventional hydrothermal (CH) route in terms of rapid crystallization kinetics and enhancing energy efficiency [17]. A number of authors have synthesized $BaTiO_3$ by the MH method below the temperature of 200 °C; but MH processing has not been reported for Nb doped $BaTiO_3$. In this work, we investigated the effect of incorporating on the properties of $BaTiO_3$ doped with Nb with a new Microwave hydrothermal method; instead of previous solid state reaction for the $BaTiO_3 \pm Nb_2O_3$ system in high temperature.

2. Experimental procedure

The MH reactions were performed using a laboratory-made microwave-heating-autoclave system with a PTFE inner vessel which operates at a frequency of 2.45 GHz and can operate at full power range of 0–100% at 900W with a controlled temperature of up to 220 °C and An auxiliary cooling/heating device that is fitted to the system and enables it to operate at a fixed temperature for a prolong period of time, while maintaining the input power of the microwave radiation during reaction period.

Reagents of $C_{16}H_{36}O_4Ti$, $BaH_2O_2.8H_2O$, $NbCl_5$ and NaOH were used as raw materials. The molar ratio of Ti/Nb was kept at 0.09/0.01. Initial materials of $BaH_2O_2.8H_2O$, $NbCl_5$ and $C_{16}H_{36}O_4Ti$ were mixed in distilled water containing 1M NaOH at 70 °C to control the pH under stirring until it turned into a homogeneous solution. The solution was transferred into a sealed PTFE autoclave and followed by distilled water until the total volume has reached 100 ml, which was 80% of the capacity of the autoclave.

The system was heat treated at 150 °C for 2 h. The resulting powders were centrifuged and washed with distilled water and finally oven dried at 85 °C for 24 h. The obtained powders were characterized by X-Ray Powder Diffraction (XRD) (X'Pert PRO MPD) with Cu-Kα radiation in the 2θ range from 20° to 70° and Raman spectroscopy (BRUKER/ Spectral Range 80-3500 cm^{-1}) microstructural characterization was performed by the field emission scanning electron microscopy (FE-SEM/MIRAIITESCAN) and transmission electron microscopy (TEM, PHILIPS-EM-208).

3. Results and discussion

Fig. 1 shows the X-ray powder diffraction patterns for the microwave-hydrothermal Niobium doped barium titanate (MH - Nb doped $BaTiO_3$) powders

prepared at 150 °C for 2 h (The XRD result Compared with known standard JCPDS 01-075-2116). The nanoparticles were pure perovskite Nb doped $BaTiO_3$, without some intermediate carbonate phase that usually is observed in the 2θ equal to 24° or 42° in solid state method [18]. The presence of $BaCO_3$ can be attributed to either an incomplete reaction or due to the presence of carbonate in Ba alkali source or the reaction with CO_2 in air. The Nb doped $BaTiO_3$ sample crystallized in MH method is carbonate free; indicating that Microwave hydrothermal technique was successfully used to produce a pure crystalline nanoparticle [19].

The diffraction patterns are around 2θ equal to 45°, where there will be a characteristic splitting of the (200) reflection for the tetragonal form has been found. This is in contrast to a symmetric peak for the cubic form and no characteristic separation of the peak at 45° 2θ, which corresponds with the tetragonal structure. An eventual tetragonal peak splitting of the reflections cannot be resolved due to overlapping on the (0 0 2) and (2 0 0) planes. However XRD-peaks of the nano particles are wider than the largest one, thus the cubic structure cannot be totally excluded and often makes this splitting difficult to determine [20,21]. The tetragonal c/a ratios obtained from XRD patterns was 1.0023, for the MH - Nb doped $BaTiO_3$ powders.

For the lower Nb, it was deduced that Nb^{5+} could substitute Ti^{4+} in $BaTiO_3$ lattice because the small ionic radius of Nb^{5+} (0.064 nm) is close to that of Ti^{4+} (0.061 nm). It has been reported that the substitution of Nb^{5+} for Ti^{4+} decreased the tetragonality of $BaTiO_3$ ceramics [22-23]. The crystallite size of powder was calculated using the SCHERRER equation [24]:
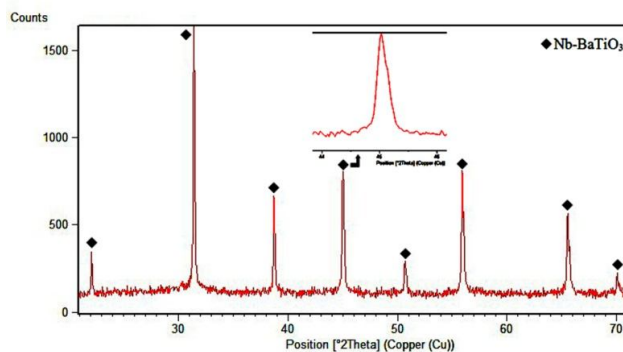

Fig. 1. X-ray diffraction pattern of Nb doped $BaTiO_3$ nanoparticles

$$(1) \quad D_v = \frac{K\lambda}{B_{size}\cos\theta}$$

where Dv is the crystallite size, K is a constant whose value is 0.9, λ is the X-ray wavelength, and the width peak B_{size} was determined as full width at half-maximum (FWHM). An average size of crystallites was estimated 50 nm from the broadening of diffraction peak using SCHERRER equation.

On the other hand, based on Raman studies, particles were tetragonal rather than cubic for the occurrence of asymmetry of TiO_6 octahedra. Nb doped $BaTiO_3$ ceramic powder samples obtained in the Raman spectra are presented in Fig. 2. The peak at 518 cm^{-1} is assigned to the TO mode of A1 symmetry and the sharp peak at 305 cm^{-1} is attributed to the B1 mode, which is the characteristic of tetragonal $BaTiO_3$. The weak peak at 715 cm^{-1} is assigned to the highest-frequency longitudinal optical mode (LO) with A1 symmetry is for tetragonal $BaTiO_3$ as well [25-27].

The field emission scanning electron microscopy (FE-SEM) of the Nb doped $BaTiO_3$ powders prepared are shown in Fig. 3. It shows that the powder prepared for 2 h consists of ultrafine with well dispersed spherical morphology particles with average particle size of 75 nm.
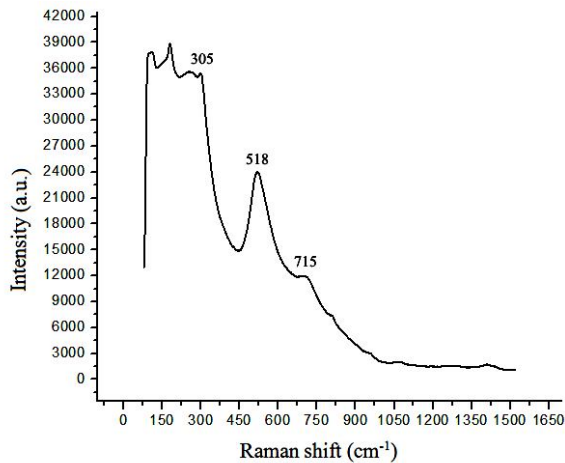
Fig. 2. Raman spectra of the hydrothermal nano-sized Nb doped $BaTiO_3$ powders.

In microwave-hydrothermal synthesis the heating is rapid and uniform and formation of Nb doped $BaTiO_3$ is via dissolution and recrystallization reaction [28]. During Microwave Hydrothermal (MH) synthesis leads to homogeneous nucleation of large number of tiny stable Nb doped $BaTiO_3$ particles which further grow uniformly, and makes the primary Nb doped $BaTiO_3$ particles form agglomerates.
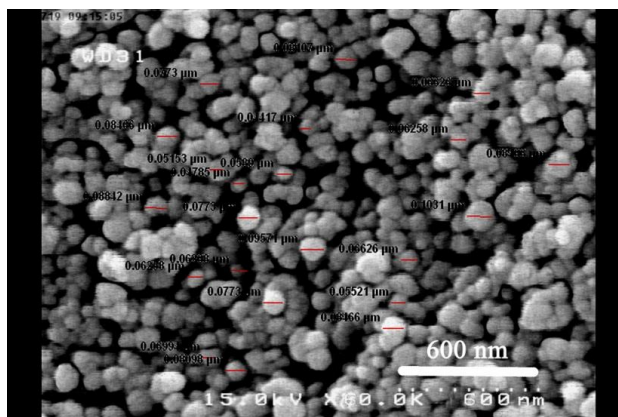
Fig. 3. Nb doped $BaTiO_3$ powders prepared at 150 °C for 2 h.

The basic forces responsible for agglomeration process are van der Waals forces of attraction. If Van der Waals attractive forces dominate over repulsive forces at all distances, then the particles will agglomerate. If primary particles are colloidal in nature due to Brownian motion, the particles may come in contact and agglomerate. Larger particles may get settled under influence of gravitational force and form agglomerate. All the above mentioned processes contribute to the formation of agglomerates to lower the surface to volume ratio as a result of basic tendency of primary particles to reduce surface energy. Therefore, it is likely that in our case primary $BaTiO_3$ particles grow uniformly and form agglomerates [29, 31].

The transmission electron microscope (TEM) images were taken in order to estimate the size of the particles. The morphology of the particles of the sample is shown in Fig. 4. Most particles are spherical shaped crystals with an average size of 70 nm and this result is in good agreement with the XRD and SEM. The decreased crystal size in MH method might be related to the increased nucleation rate and the high energy which activate chemical reactions at low temperatures. The nucleation rate should be high because of high heating rate in microwave heating processes.

4. Conclusion

The present investigation shows that nano particle-sized Nb doped $BaTiO_3$ powders can be crystallized with rapid and cost-effective Microwave-assisted hydrothermal process. An eventual tetragonal peak splitting f the reflections cannot be resolved due to overlapping of the (0 0 2) and (2 0 0) planes. However XRD-peaks of the nano particles are wider than the larger one, thus the cubic structure cannot be totally excluded and often makes this splitting difficult to determine. But based on Raman studies, particles were tetragonal structures rather than cubic for the occurrence of asymmetry of TiO_6 Octahedra.

The Raman peak at 518 cm^{-1} is assigned to the TO mode of A1 symmetry and the sharp peak at 30 cm^{-1} is attributed to the B1 mode which is the characteristics of tetragonal BaTiO$_3$. The dependence of tetragonality on the particle size has been extensively investigated for BaTiO$_3$.
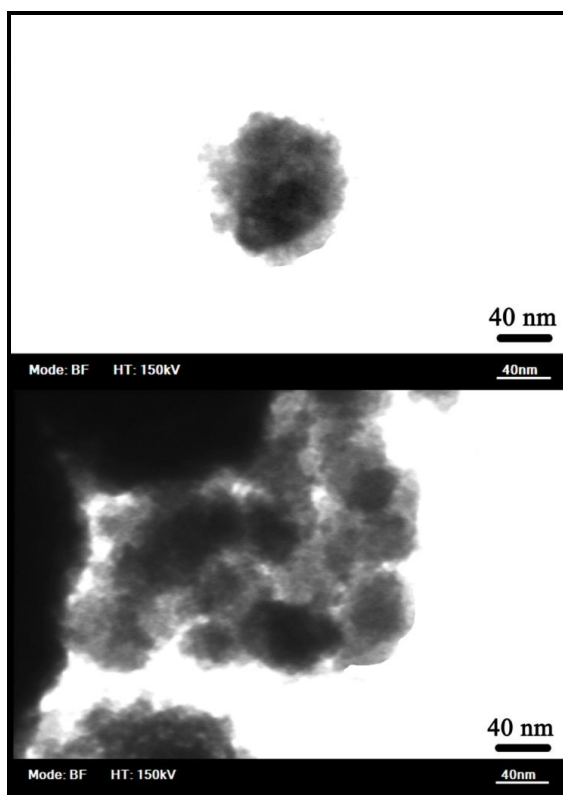
Fig. 4. TEM image of the Nb doped BaTiO$_3$ powders.

A variety of explanatory models were proposed and all have reported that tetragonal distortion decreased with decreasing particle size below 1 μm [23, 24]. Thus, a reasonable explanation for the larger tetragonality in sample synthesized at MH method is that the particles grow faster under MH conditions. In the MH process, microwave radiation can couple with and be absorbed by the dielectric material and thus the smaller BaTiO$_3$ will dissolve more quickly. According to the dissolution/recrystallization

mechanism, this will lead to larger particles growing faster.

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