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Synthesis of BF–PT perovskite powders by high-energy ball milling

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Abstract

$0.7BiFeO_3$–$0.3PbTiO_3$ (BF–PT) powders were synthesized from a mixture of the oxides Bi_2O_3, Fe_2O_3, PbO and TiO_2 using a Fritsch P4™ vario-planetary ball milling system. The perovskite structure of the BF–PT powder can be obtained well and the crystallite size of the powders was greatly reduced to 20–35 nm after milling for 8 h. The pre-calcined course shows a rhombohedral–tetragonal phase transition with the increasing temperature and shows the structure transition near the Curie temperature T_c.

Keywords: BF–PT; High-energy ball milling; Morphotropic phase boundary

1. Introduction

For many years, ceramics based on the perovskite $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) have been the best choice for various piezoelectric applications [1]. Recently, bismuth perovskites have been attracting attention as a family of piezoelectric ceramics in place of the widely used PZT system. $BiFeO_3$–$PbTiO_3$ is a solid solution of bismuth ferrite and lead titanate, which displays ferroelectric behavior and has the potential to be utilized in high-temperature piezoelectric applications. Ferroelectric bismuth ferrite $BiFeO_3$ exhibits a rhombohedral perovskite structure below 850 °C, while $PbTiO_3$ has a tetragonal perovskite structure below 490 °C [2–4]. There is a morphotropic phase boundary (MPB) separating the tetragonal and rhombohedral phase around $x=0.3$, similar to other ceramics of $Bi(Me)O_3$–$PbTiO_3$.

High-energy ball milling was originally developed for the production of alloys and intermetallic compounds in 1966 [5]. The major advantage is that the solid-state reaction is activated by the mechanical energy rather than the calcination at elevated temperatures. It has been shown to be possible to synthesize a variety of ferroelectric materials with perovskite structure, such as $PbTiO_3$ (PT) [6], $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [7], and $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) [8], $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) [9], using a single-step mechanochemical technique and starting from oxide precursors because they effectively alleviate the loss of PbO. At the same time, the high-energy ball milling equipment has been developed in order to meet high-powered synthesis. Great efforts have been made in order to understand the basic principles and the mechanisms involved.

Furthermore, $Bi(Me)O_3$–$PbTiO_3$ were mechanochemically synthesized recently. We have prepared nano-crystalline $BiScO_3$–$PbTiO_3$ by high-energy ball milling [10], and the two materials Bi_2O_3 and PbO were volatilized simultaneously. The $BiFeO_3$–$PbTiO_3$ system had been prepared by Mikael A. Khan et al. [11], however, perovskite phase formation as a result of mechanical activation alone was not observed in their work. They put into effort to investigate whether the reduced powder size and the modification in the phase of the powder mixtures had an impact on the temperature required to form the perovskite phase. In contrast to their work, in this paper, the perovskite phase of BF–PT has been obtained clearly and the powder characteristics during the milling process were investigated in detail.

2. Experimental

Solid solutions of $0.7BiFeO_3$–$0.3PbTiO_3$ (BF–PT) were prepared using high-energy ball milling. Reagent grade oxides Bi_2O_3 (98.5%), Fe_2O_3 (99.9%), PbO (99.9%) and TiO_2 (99.6%) were used as the starting materials. 100 g mixed oxides were ball milled for 4 h with stabilized zirconia balls in alcohol then the mixture was dried and sieved.

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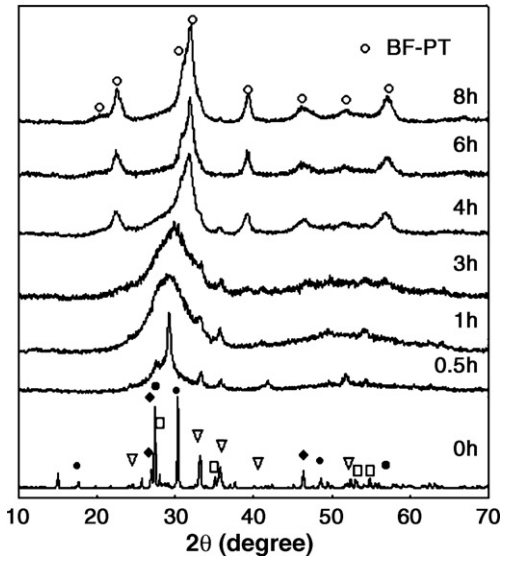

Fig. 1. XRD patterns of $x=0.3$ powder mixture treated for various times ranging from 0 to 7 h: (●) PbO, (□) TiO_2, (♦)Bi_2O_3, (▽) Fe_2O_3, and (○) BF–PT.

The milling operation was carried out in a Fritsch Pulverisette ™ vario-planetary high-energy ball milling system in air at room temperature for different times (0–8 h respectively). A 225-ml tungsten carbide vial and 50 tungsten carbide balls with diameter (D_B) of 10 mm were used as the milling medium. The milling speed of the main disk was set at 400 rpm and the speed of each pair was set at −800 rpm, which means that the rotation speed ratio (R-ratio) was −2.0. The ball mass to powder mass ratio (M_B/M_P) varied between 10:1 and 20:1. The milling was stopped for 20 min for every 30 min of milling to cool down the system and was interrupted after each hour to decant the samples for analysis. The powders milled for 8 h were calcined from 500 °C to 750 °C to analyze the structure change with the calcined temperature rising. The milled powders were pressed into disks 12 mm in diameter and 1–2 mm in thickness at 200 MPa, and sintered in sealed crucibles at temperatures between 1000 and 1040 °C for 2 h.

The milled powders, calcined powders and ceramics were analyzed by Rigaku D/MAX-2400 X-ray diffraction with Cu K_α radiation at room temperature. Microstructures were analyzed by scanning electron microscopy (JEOL JSM-6460). TEM images of the powders were conducted using a JEOL JEM3010 transmission electron microscopy.

3. Results and discussion

The XRD pattern of the milled powder mechanochemically treated is shown in Fig. 1. For the powder mixture without being subjected to any mechanochemical treatment, only sharp peaks of the oxides are presented in the XRD pattern, indicating that no reaction was triggered during the mixing milling by the conventional ball mill. The powder mechanochemically treated for 3 h, in contrast, almost all the sharp peaks have vanished, and replaced by a few broadened ones. The time from 4 h to 6 h is the period of the growing of crystallite, while the size steadily increased and the perovskite phase is visible. Up to 8 h, the tetragonal phase can be detected because there is a low intensity peak at $2\theta=19.76$ ° and 30.72 ° which is in accordance with the XRD pattern of the powders by heat treatment.

Fig. 2 shows the SEM images of the uncalcined BF–PT powder with 1 h and 6 h high-energy milling. After 1 h, the particle size ranges from 500 nm to 4 μm. The size is not in a relatively small range because the milling was at the beginning of a dramatic refinement. The larger size particles partially had not broken down. After 6 h, a particle size ranging from 50 nm to 600 nm was observed. The formation of agglomerates was also observed with a size range from 40 nm to 2 μm.

Fig. 3 shows the bright field electron micrograph of the 8 h milled sample. In TEM studies, it was observed that when the electron beam

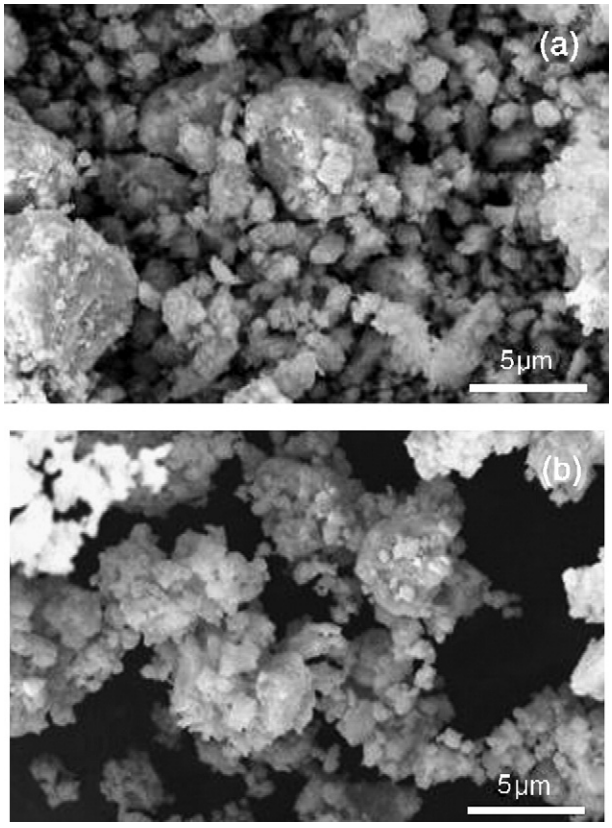

Fig. 2. Uncalcined BF–PT powder with high-energy milling: (a) 1 h and (b) 6 h.

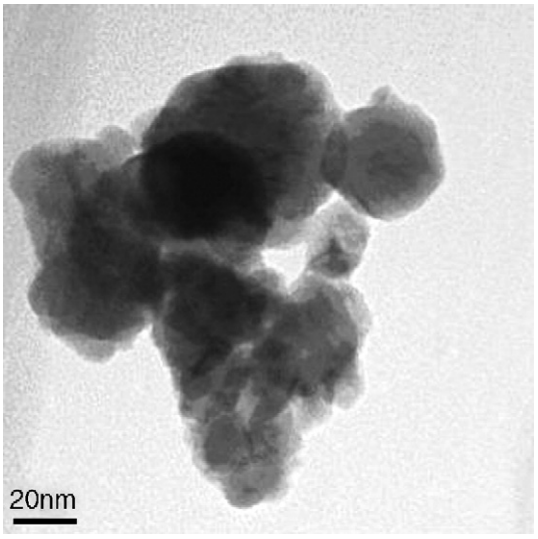

Fig. 3. The bright field electron micrograph of the 8 h milled sample.