Journal of the European Ceramic Society 35 (2015) 3437–3443

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Facile route to prepare grain-oriented multiferroic $Bi_7Fe_{3-x}Co_xTi_3O_{21}$ ceramics

Xiaoning Li[a], Zhu Zhu[a], Feng Li[a], Ranran Peng[a,b], Xiaofang Zhai[b], Zhengping Fu[a,b,*], Yalin Lu[a,b,c,d,**]

[a] CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China
[b] Synergetic Innovation Center of Quantum Information and Quantum Physics & Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, PR China
[c] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230026, PR China
[d] Laser Optics Research Center, US Air Force Academy, Colorado 80840, USA

ARTICLE INFO

Article history:
Received 14 April 2015
Received in revised form 27 May 2015
Accepted 28 May 2015
Available online 10 June 2015

Keywords:
Grain-oriented
Aurivillius phase
Hydrothermal method
Pressureless sintering
Doping

ABSTRACT

A facile route was developed to fabricate $Bi_7Fe_{3-x}Co_xTi_3O_{21}$ (BFCTO) ceramics in which the micrometer sized grains were highly [0 0 1] oriented. The preparation involved dry pressing nanoplates with high aspect ratio under low axial pressure (10 MPa), and subsequently sintering the green compact at high temperature without applied pressure. The formation mechanism and the effects of Co doping on the orientation were investigated. The results indicated that the orientation degree of BFCTO grains was depended on the aspect ratio of nanoplate powder, which increased with the increase of doping amount of Co. The degree of orientation was achieved as high as 0.91 in $Bi_7Fe_2CoTi_3O_{21}$ ceramic. The saturation magnetization (2 Ms) values were larger when surfaces of the oriented grains were perpendicular to the direction of applied magnetic field, indicating obvious anisotropic magnetism. This fabrication method provided an economical yet convenient approach to manufacture grain-oriented complex oxide ceramics with improved magnetic property.

1. Introduction

Multiferroic materials combining two or more of the primary ferric orderings, such as ferroelectricity (FE) and ferromagnetism (FM) have great significance in fundamental physics, as well as in practical applications in sensors, actuators, multiple state memory elements, etc [1,2]. Aurivillius compounds, with a general formula of $Bi_4Bi_{n-3}Fe_{n-3}Ti_3O_{3n+3}$ (BFTO, n denotes the number of perovskite-like layers within a unit cell), are a family of potential single-phase multiferroic materials. The properties of Aurivillius compounds are feasible to be manipulated by changing the layer number or by doping foreign elements. Previous researches show that BFTO can present much elevated Curie temperature and unusual dielectric behavior, but the FM is very weak [3–5]. Groundbreaking work has been performed on a 4-layer $Bi_5Fe_{0.5}Co_{0.5}Ti_3O_{15}$ ($n = 4$) with a remarkable coexistence of FE and FM well over the room temperature (RT), which suggest an efficient method to improve BFTO's multiferroic properties by doping cobalt [6]. Subsequently, we have reported that the cobalt-doped 6-layer $Bi_7Fe_3Ti_3O_{21}$ presented much enhanced multiferroic properties too, together with the analogous morphotropic transformation (AMT) effect [7–9]. Especially, low magnetic field response magnetoelectric (ME) coupling well above the room temperature has been realized in single phase $SrBi_5Fe_{0.5}Co_{0.5}Ti_4O_{18}$ [10].

Comparing to randomly oriented ceramics, grain-oriented ceramics have attractive anisotropic properties. This could deliver an additional freedom in designing functional devices respective to electric or magnetic polarizations, as well as the oriented multiferroic coupling [11,12]. It is worth to study properties of multiferroic Aurivillius phase ceramics with highly oriented structures. In the past, various approaches have been developed to produce anisotropic ceramics: (1) hot working techniques, for instance, hot-forged, hot pressed or superplastic deformation [13–15]; (2) aligning seed crystals by screen printing, tape-casting or pressing

* Corresponding author at: CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China. Tel.: +86 551 63603194.
** Corresponding author at: CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China. Tel.: +86 551 63603004.
E-mail addresses: fuzp@ustc.edu.cn (Z. Fu), yllu@ustc.edu.cn (Y. Lu).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.05.032
0955-2219/

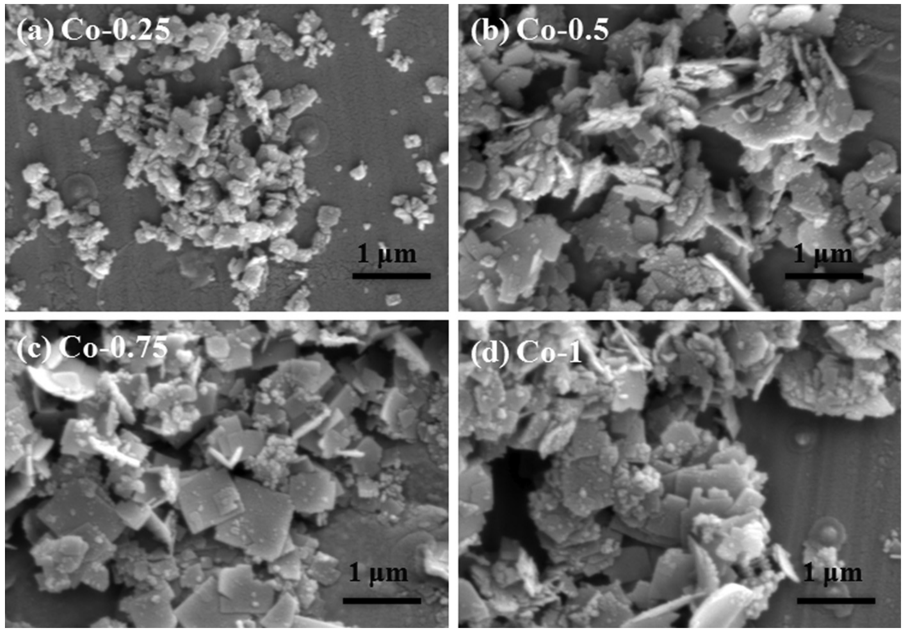

Fig. 1. SEM images of as-prepared BFCTO nanoplates with different cobalt content synthesized by hydrothermal method: (a) Co-0.25, (b) Co-0.5, (c) Co-0.75 and (d) Co-1, respectively.

plat-like crystals at high pressure, followed by pressureless sintering [16–19]; (3) sintering by applying an external magnetic field [20,21]; (4) providing a reactive template or reactive-templated grain growth (RTGG) method by using anisometric particles as reactive templates [22–26]. Nevertheless, these methods were less convenient or with low degree of orientation. Above all, the oriented microstructures can hardly be developed without the help of external motivation.

In this work, a new facile route was developed to fabricate highly grain-oriented BFCTO ceramics: dry pressing the BFCTO nanoplates at rather low pressure (10 MPa) and subsequently sintering the green compacts without applied pressure. The orientation degree of ceramic prepared by this convenient method could reach as high as 0.91. Our present work may point out a convenient and economical way for fabricating highly-oriented ceramics.

2. Preparation and characterization

All the chemicals are analytical grade reagents without further purification. In a typical hydrothermal synthesis route, $Ti(OC_4H_9)_4$, $Bi(NO_3)_3{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_3{\cdot}6H_2O$ according to the nominal stoichiometric ratio of $Bi_7Fe_{3-x}Co_xTi_3O_{21}$ (x = 0.25, 0.5, 0.75, 1) were dissolved into 4 M HNO_3 solution. After 20 min. of magnetic stirring, the homogeneous metal-ions solution was added into 2 M NaOH solution. Afterwards, the slurry was transferred into a Teflon-lined stainless steel autoclave up to 80% of the total volume. The autoclave was sealed and heated at 200 °C for 2 days, then allowed to cool to the room temperature naturally. The sediment was washed with water for several times and then dried at 60 °C. About 0.3 g obtained powders were dry pressed into green compacts with the diameter of 12 mm and the thickness of 0.5 mm under 10 MPa axial pressure on Disk-Tap Powder Presser (40T, MTI Corporation, USA). Then the green compacts were sintered at 880 °C (x = 0.25), 870 °C (x = 0.5), 860 °C (x = 0.75) and 850 °C (x = 1), respectively for 5 h at normal atmosphere in the Muffle furnace (MF-1100C-S, Anhui BEQ Equipment Technology Co., Ltd., China) with a heating rate of 4 °C/min. After that, the sintered ceramics were cooled down to the room temperature naturally. For convenience, the samples with the nominal cobalt content of 0.25, 0.5, 0.75 and 1 are named as Co-0.25, Co-0.5, Co-0.75 and Co-1, respectively.

Purity and crystallinity of all the samples were characterized by X-Ray powder diffraction (XRD) patterns recorded on a Rigaku-TTR III X-ray diffractometer with Cu-Kα radiation. Morphologies of the powders and microstructure of ceramics were observed by scanning electron microscopy (SEM, JSM-6700F). Magnetic properties were characterized by vibrating sample magnetometer (VSM) option of the Quantum Design physical property measurement system (PPMS) (Quantum Design, USA). The anisotropy of the magnetism of the grain-oriented ceramics was studied by changing the relative orientation between the magnetic field and the ceramics.

3. Results and discussion

All the as-prepared powder samples synthesized by the hydrothermal method were plate-like with a thickness of about 50 nm (Fig. 1), and the average width was increased from 250 nm (Co-0.25), 700 nm (Co-0.5), 750 nm (Co-0.75), to 800 nm (Co-1) and the corresponding aspect ratio is 5, 14, 15 and 16, respectively. It should be noted that all the samples were prepared at the same conditions except for the stoichiometry. In the hydrothermal synthesis, concentration of hydroxyl radical usually plays key role in the growth of crystals [27]. Co ion could be bonded with different amount of hydroxyl radical in the solution compared with Fe ion, which resulted in different concentration of residual hydroxyl radical for samples with different amount of doping Co. The abundant residual hydroxyl radical in the solution enlarged the nanoplates and increased the aspect ratio, which was very important for synthesizing the highly oriented ceramics afterwards.

SEM images of ceramics which were prepared by dry pressing nanoplates at 10 MPa followed by being sintered at atmospheric pressure are presented in Fig. 2. It is obvious that the grains of prepared ceramics are highly oriented with sharp crystal boundary, except that Co-0.25 sample is less ordered. From Fig. 2(a–d), we observed that the ceramics are with high relative density and the values determined by the Archimedes method ranges from 85.3%, 81.8%, 82.6% to 79.5% for the samples with the increase of Co. To better appreciate grain morphology and orientation,