G Model
JECS-11042; No. of Pages 7

ARTICLE IN PRESS

Journal of the European Ceramic Society xxx (2017) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Anisotropic electrical and magnetic properties in textured $Bi_5Ti_3FeO_{15}$ ceramics

Xiaoyi Gao, Lianmeng Zhang, Chuanbin Wang*, Qiang Shen

State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, 430070, PR China

ARTICLE INFO

Article history:
Received 7 December 2016
Received in revised form 27 January 2017
Accepted 30 January 2017
Available online xxx

Keywords:
Texture
$Bi_5Ti_3FeO_{15}$
Anisotropic
Electrical and magnetic properties

ABSTRACT

Textured $Bi_5Ti_3FeO_{15}$ (BTFO) ceramics were prepared by molten salt synthesis at 850 °C followed by plasma activated sintering at 800 °C. The structure and the anisotropic electrical and magnetic properties of the ceramics were investigated. The textured BTFO ceramics exhibited [001] preferred orientation with a high degree of texture fraction (Lotgering factor is 0.82), as confirmed from XRD patterns, FE-SEM and TEM micrographs. The anisotropic dielectric relaxation and conduction characteristics along the parallel and perpendicular directions were investigated using the dielectric and impedance spectroscopies. The grain boundary along the parallel direction had a similar value of capacitance to that of grains, whereas the grain boundary along the perpendicular direction dominated the resistive component. The magnetic performance along the perpendicular direction ($H_c \sim 32.5$ Oe) was better than that along the parallel direction ($H_c \sim 17.6$ Oe). These results could be useful for enhancing the electrical and magnetic properties of BTFO by texturization.

1. Introduction

Multiferroic materials that exhibit simultaneous magnetic and ferroelectric properties have attracted interest in recent years because of their special phenomena, promising applications and especially due to the associated electric/magnetic polarization coupling between the two different orders [1,2]. Important potential applications of these multiferroic materials include multi-state storage, non-volatile memory, and transducers. To expand the range of possible applications of multiferroics, researchers have investigated a wide variety of multiferroic materials, including $BiFeO_3$ [3], $BaFe_{12}O_{19}$ [4] and $BiMnO_3$ [5], among others. Nevertheless, these materials are still limited by the coupling intensity, application temperature, and application suitability. Recently the Aurivillius phase materials $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ have attracted much attention because of their potential applications in multifunctional devices, stemming from their large spontaneous polarization, and fatigue-free behaviours [6].

$Bi_5Ti_3FeO_{15}$ (BTFO) is an Aurivillius-phase material. Extensive efforts have been devoted to enhancing the properties of BTFO studying its structure and its magnetic and electrical properties [7–9]. Newnham reported that BTFO can be considered a solid solution of $Bi_4Ti_3O_{12}$ and $BiFeO_3$ and thus has a four-layered perovskite unit of $(Bi_3Ti_3FeO_{13})^{2-}$ between by two $(Bi_2O_2)^{2+}$ layers along *c*-axis [10]. Previous research has demonstrated a large spontaneous polarization of BTFO with a high Curie point [7], as well as ferromagnetism at room temperature [12]. Therefore, BTFO is a promising candidate for possible applications involving magnetoelectric coupling and piezoelectric. However, an important characteristic of BTFO is its remarkable anisotropy properties due to its anisotropic structure, which has implications for its possible applications. Nevertheless the anisotropic electrical and magnetic properties of BTFO ceramics have not been studied extensively, and most of the investigations into its anisotropic properties have focused only on its anisotropic ferroelectric behaviour [11]. Scientific understanding of the anisotropic properties of BTFO ceramics is desirable to improve their functional performance and could be used to design nominal compositions and optimize processing conditions to enhance the ferroelectric, magnetic and magnetoelectric properties of multiferroic BTFO materials. Thus, studies of the electrical and magnetic properties of BTFO ceramics with highly textured structures are important.

Highly textured, dense ceramics are required for studies of the anisotropic properties of BTFO. Molten salt synthesized Aurivillius powders have been reported to exhibit a plate-like morphology with a developed *ab*-plane [13]. Thus, for the plate-like BTFO particles with a laminated distribution in the direction parallel to the *c*-axis, we can design and fabricate textured ceramics to investi-

* Corresponding author.
E-mail address: wangcb@whut.edu.cn (C. Wang).

http://dx.doi.org/10.1016/j.jeurceramsoc.2017.01.037
0955-2219/© 2017 Elsevier Ltd. All rights reserved.

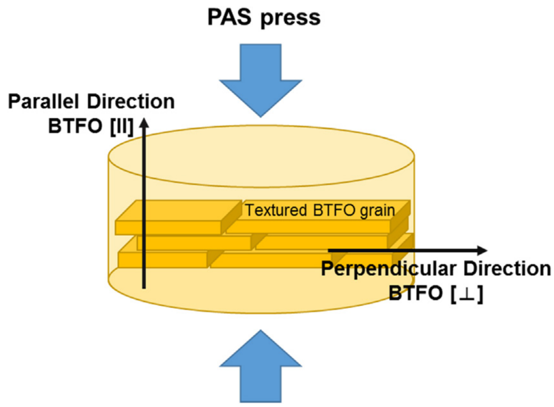

Fig. 1. Diagrammatic sketch of the parallel and perpendicular directions of BTFO.

gate their anisotropic properties. Therefore, we used the molten salt synthesis (MSS) method to produce a BTFO powder and then used plasma activated sintering to fabricate textured BTFO ceramics. The anisotropic dielectric relaxation behaviours and the effects of grain and grain boundaries were investigated using a combination of impedance and modulus analyses. In addition, the conductivity and magnetism were characterized along the parallel and perpendicular directions. Therefore, the aim of the present work is to elucidate the relationship between the orientation and properties of BTFO ceramics to help enhance their properties.

2. Experimental procedures

$Bi_5Ti_3FeO_{15}$ powders were obtained by the MSS method. Stoichiometric quantities of Bi_2O_3 (99.0%), TiO_2 (99.0%) and Fe_2O_3 (99.9%) powders, purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd, were mixed in an agate mortar for 1 h. An equimolar mixture of NaCl (Sinopharm group Co., Ltd, 99.5%) and KCl (Sinopharm group Co., Ltd, 99.5%) was then added and ball-milled in ethanol for 24 h. The chlorides-to-oxides mass ratio was kept at 1/1. After drying, the powders were calcined at 850 °C for 2 h. The reaction products were thoroughly washed several times until the addition of the supernatant fluid to silver nitrate solution did not result in precipitation.

Compaction of BTFO powders was performed using a plasma activated sintering (PAS) system (ED-PAS III, Elenix Ltd, Japan). First, the precursor powders were loaded into a graphite die with an inner diameter of 20 mm. Graphite foils were used to avoid any reaction between the samples and the pressing tool. After an initial pressure of 80 MPa was applied, the loaded powder was heated at 100 °C/min under vacuum to 800 °C and was sintered at this temperature for 5 min. The samples were then cooled down to room temperature. The graphite paper was then removed from the outside surface to obtain the sample with diameter of 20 mm. Finally, the sintered BTFO disc was annealed in air at 720 °C for 15 h.

The density of the BTFO ceramics was measured via Archimedes' method using deionized water immersion. To more conveniently study the crystallographic anisotropy of the sintered body, we carried out measurement perpendicular and parallel to the PAS pressing direction, defined as the perpendicular [⊥] and parallel directions [//], respectively (Fig. 1). The crystal phases of the BTFO ceramics were established by X-ray diffraction (XRD, Rigaku Ultima III, Cu Kα radiation, scanning range from 5° to 60° (2θ) at a step size of 0.05°). The microstructures of both samples were observed by field emission scanning electron microscopy (FESEM, FEI Quanta FEG250) and high-resolution transmission electron microscopy (TEM, Jeol JEM-2100F). The dielectric and electrical properties were tested using a dielectric/impedance analyser (Novocontrol, Germany). The magnetic hysteresis loops of the samples were measured by a vibrating sample magnetometer (Quantum Design MPMS3, USA).

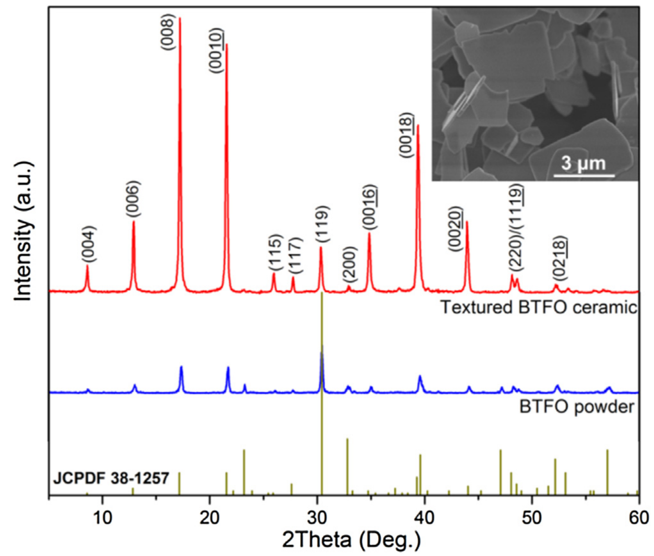

Fig. 2. XRD patterns of BTFO powders and the textured BTFO ceramic; the inset shows an SEM image of the BTFO powder obtained by MSS.

3. Results and discussion

3.1. Structural characterization

Fig. 2 shows the XRD patterns of the BTFO powder and the textured BTFO ceramic. All diffraction peaks of the samples are clear, with high signal-to-noise ratios. No other impurities or intermediate phases are observed; thus, all samples can be regarded as single-phase with a high degree of accuracy. The (119) peak is the most intense peak in the pattern of the BTFO powder with randomly oriented grains. In the case of the textured BTFO ceramic, the (008) peak is the most intense, and the (00$\underline{10}$) peak exhibits the second-highest intensity compared to that of the BTFO powder. These results indicate that the texture degree of the *c*-axis for BTFO ceramic was enhanced after the BTFO powder was consolidated into a ceramic. The Lotgering factor, [14] *f*, of the textured BTFO ceramics was calculated to be approximately 0.82. This Lotgering factor of the textured BTFO ceramic is larger than the factors ($f < 0.7$) previously reported for textured BTFO ceramics prepared by conventional pressureless sintering [15,16].

The morphology of the BTFO powders observed by FESEM is depicted in the inset of Fig. 2. The powders synthesized by MSS exhibit plate-like shapes with a thickness of 120 nm and a maximum diameter of 5 μm. The origin of the classic growth tendency is attributed to the BTFO crystalline particles preferentially growing along the *ab*-plane [15–17]. Fig. 3(a) and (b) shows SEM images of the polished surface of the BTFO viewed in the parallel and perpendicular directions, respectively. For better observation of grains and grain boundaries, the sintered samples were polished and then thermally etched at a temperature 100 °C below their sintering temperature. The textured BTFO ceramic consisted of rectangular plates with maximum dimensions of ~5.5 μm in length and 130 nm or less in thickness. Notably, the grain sizes of the BTFO ceramic sintered by PAS were similar to those of the powder. These results show that PAS can be used to fabricate BTFO ceramics with fine grain size because the uniaxial compression and high direct current used in the PAS process enable the rapid consolidation of the powder at lower temperatures [18,19].

Please cite this article in press as: X. Gao, et al., Anisotropic electrical and magnetic properties in textured $Bi_5Ti_3FeO_{15}$ ceramics, *J Eur Ceram Soc* (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.01.037