Ceramics International 44 (2018) 1420–1424

Contents lists available at ScienceDirect

Ceramics International

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

The effect of pH control on synthesis of Sr doped barium titanate nanopowder by oxalate precipitation method

Jae Eun Jeon[a,1], HyukSu Han[b], Kyeong Ryeol Park[a], Yu-Rim Hong[b,c], Kwang Bo Shim[a], Sungwook Mhin[d,1,*]

[a] Hanyang University, 222, Wangsimni-ro, Seongdong-gu, Seoul, Republic of Korea
[b] Korea Institute of Industrial Technology, 137-41 Gwahakdanji-ro, Gangneung-si, Gangwon 25440, Republic of Korea
[c] Department of Chemistry, Seoul Women's University, Seoul 01795, Republic of Korea
[d] Korea Institute of Industrial Technology, 156 Gaetbeol-ro, Yeonsu-gu, Incheon 406-840, Republic of Korea

ARTICLE INFO

Keywords:
Sr-doped barium titanate
Positive temperature coefficient
Oxalate precipitation
Nanopowder

ABSTRACT

Sr substituted $BaTiO_3$ (BST) nanopowders were prepared using oxalate co-precipitation methods. During synthesis, oxygen was applied to the oxalate solution in order to control the oxidation states of Ti. Control of pH in the solution results in different crystalline phases of the powders after calcination; pure perovskite BST was obtained in the powder prepared at pH 3 solution, while perovskite $BaTiO_3$ (BTO) and impurities were observed in powders prepared at pH 1 solution. Phase transformation from amorphous to crystalline BST during heat treatment was discussed by different analysis technique. Also, morphology and elemental distribution of the pure BST was investigated.

1. Introduction

Barium strontium titanate (BST) has attracted considerable attentions due to its high permittivity, low dielectric losses and good thermal stability [1,2]. Especially, positive temperature coefficient of resistivity (PTCR) is one of the attractive properties for the semiconducting $BaTiO_3$ (BTO), which has Curie temperature (Tc) at 120 °C where a phase transition occurs from the tetragonal to the cubic phase. Such a phase transition is accompanied by a remarkable change in electrical properties [1–3]. For example, BTO doped with donor ions such as Sr^{2+} exhibits a large and rapid increase of resistance just above the Tc [4]. The Tc of the BST can be controlled, depending on various conditions such as sintering temperature, composition and grain size electrical characteristics, which determines the electrical properties of the BST [4,5].

BST powders are commonly prepared by solid-state reaction which is one of the industrial processing technique owing to its simplicity and low cost [6,7]. Current tendency towards miniaturization of electronic components requires the nanomaterials with the dimension of typically less than 200 nm. However, solid-state reaction can provide large particle with presence of impurities and multi phases. In order to obtain high performance of the nanoparticles, various wet-chemical methods at low temperature for homogeneous BST powders have been reported such as co-precipitation, sol-gel synthesis, hydrothermal, spray pyrolysis, and modified citrate gel [6–9]. Among them, co-precipitation utilizing the oxalate precursors can be considered as an effective method for the preparation of ultrafine BST powders thanks to following advantages: low energy, short production time, low sintering temperature to avoid grain growth and environment friendly. Also, it is possible to produce stoichiometric crystalline powders with controlled particle size and shape.

$TiCl_4$ is usually used as a titanium precursor for oxalate method, but there is main drawback it may be oxidized and react violently with water in the air. Alternative processing method to prohibit the oxidation of $TiCl_4$ has been explored using the $TiCl_3$ [10]. However, since the oxidation state of Ti in $TiCl_3$ is different from that of the final phase BTO, further modification is required. O_2 flowing during co-precipitation can be possible to tune the oxidation state of the titanium from 3+ of $TiCl_3$ to 4+. According to Schrey et al., the pH value is also likely to be the key factor in the oxidation state of titanium in precipitation method. Therefore, O_2 flowing and stringent pH control for single phase BST is essential during the synthesis using $TiCl_3$ [11,12].

In this study, BST nanopowders were prepared using the oxalate method, combined with pH control and O_2 flowing. For obtaining single phase BST nanopowders, control of O_2 flow, pH and calcination temperature plays important roles during processing. Structural

* Corresponding author.
E-mail address: hyeleci@kitech.re.kr (S. Mhin).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.ceramint.2017.09.231
Received 3 September 2017; Received in revised form 25 September 2017; Accepted 29 September 2017
Available online 30 September 2017
0272-8842/