



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

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ABSTRACT

Sr substituted BaTiO₃ (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 BaTiO₃ (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 BaTiO₃ (BTO), which has Curie temperature (T_c) 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 Sr²⁺ exhibits a large and rapid increase of resistance just above the T_c [4]. The T_c 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.

TiCl₄ 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 TiCl₄ has been explored using the TiCl₃ [10]. However, since the oxidation state of Ti in TiCl₃ is different from that of the final phase BTO, further modification is required. O₂ flowing during co-precipitation can be possible to tune the oxidation state of the titanium from 3+ of TiCl₃ 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, O₂ flowing and stringent pH control for single phase BST is essential during the synthesis using TiCl₃ [11,12].

In this study, BST nanopowders were prepared using the oxalate method, combined with pH control and O₂ flowing. For obtaining single phase BST nanopowders, control of O₂ flow, pH and calcination temperature plays important roles during processing. Structural

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