Author's Accepted Manuscript

www.elsevier.com/locate/jcrysgro

Exploring Reaction Pathways in the Hydrothermal Growth of Phase-Pure Bismuth Ferrites

Abby R. Goldman, Jeremy L. Fredricks, Lara A. Estroff

PII: S0022-0248(16)30557-7
DOI: http://dx.doi.org/10.1016/j.jcrysgro.2016.09.054
Reference: CRYS23612

To appear in: *Journal of Crystal Growth*

Received date: 30 July 2016
Revised date: 19 September 2016
Accepted date: 23 September 2016

Cite this article as: Abby R. Goldman, Jeremy L. Fredricks and Lara A. Estroff Exploring Reaction Pathways in the Hydrothermal Growth of Phase-Pur Bismuth Ferrites, *Journal of Crystal Growth* http://dx.doi.org/10.1016/j.jcrysgro.2016.09.054

Exploring Reaction Pathways in the Hydrothermal Growth of Phase-Pure Bismuth Ferrites

Abby R. Goldman[a], Jeremy L. Fredricks[a], Lara A. Estroff[a,b*]

[a]Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, United States

[b]Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York 14853, United States

[*]Corresponding Author. lae37@cornell.edu

Abstract

Phase-pure bismuth ferrites ($BiFeO_3$ and $Bi_2Fe_4O_9$) are grown using hydrothermal synthesis. In addition to varying the KOH, bismuth, and iron salt concentrations to tune which crystalline phases are formed, we identified that a 48 hour, pre-furnace, room temperature reaction is critical for the formation of phase-pure $BiFeO_3$. To understand the reaction pathways leading to the different bismuth ferrite phases, we investigate the changes in composition of the intermediate products as a function of reagent concentrations and room temperature reaction times. During the syntheses that included a room temperature reaction, $Bi_{25}FeO_{40}$ is formed in the intermediate products, and $BiFeO_3$ is the majority phase of the final products. The $BiFeO_3$ crystals grown using this method are clusters of faceted subunits. These results indicate that forming $Bi_{25}FeO_{40}$ is a productive route to the formation of $BiFeO_3$. $Bi_2Fe_4O_9$ is formed via an alternate reaction pathway that proceeded via an amorphous precursor. This improved understanding of how hydrothermal synthesis can be used to control the phase-purity and morphology of bismuth ferrites opens doors to explore the multiferroic properties of $BiFeO_3$ with complex morphologies.

Keywords

A1. Crystal growth reaction pathways, A1. Reaction intermediates, A2. Hydrothermal crystal growth, B1. Bismuth ferrite, B2. Multiferroic materials

1. Introduction

$BiFeO_3$ has gained much attention for its promise as the only known room-temperature, single-phase magnetoelectric multiferroic material [1,2]. One of the largest challenges to exploring the magnetoelectric properties of $BiFeO_3$ has been the phase-pure growth of $BiFeO_3$, as often other ternary phases such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ are also produced. Recently, it has been reported that $BiFeO_3$ is amenable to growth by hydrothermal synthesis, which allows for simultaneous control of phase and crystal morphology [3–6]. A plethora of experimental variables have been used to achieve phase-pure $BiFeO_3$ in the literature [7–14], however, further understanding of which variables control which phases are formed is needed to establish robust and tunable syntheses.

By systematically controlling multiple experimental variables, we developed a robust, tunable, additive-free synthesis that yields two different bismuth iron oxides in phase-pure form, dependent on well-defined parameters. We achieved phase-pure $BiFeO_3$ by adding a 48 hour room temperature reaction to the