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RESEARCH ARTICLE

Solid state synthesis of $BiFeO_3$ occurs through the intermediate $Bi_{25}FeO_{39}$ compound

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Abstract

The solid-state synthesis of perovskite $BiFeO_3$ has been a topic of interest for decades. Many studies have reported challenges in the synthesis of $BiFeO_3$ from starting oxides of Bi_2O_3 and Fe_2O_3, mainly associated with the development of persistent secondary phases such as $Bi_{25}FeO_{39}$ (sillenite) and $Bi_2Fe_4O_9$ (mullite). These secondary phases are thought to be a consequence of unreacted Fe-rich and Bi-rich regions, that is, incomplete interdiffusion. In the present work, in situ high-temperature X-ray diffraction is used to demonstrate that Bi_2O_3 first reacts with Fe_2O_3 to form sillenite $Bi_{25}FeO_{39}$, which then reacts with the remaining Fe_2O_3 to form $BiFeO_3$. Therefore, the synthesis of perovskite $BiFeO_3$ is shown to occur via a two-step reaction sequence with $Bi_{25}FeO_{39}$ as an intermediate compound. Because $Bi_{25}FeO_{39}$ and the γ-Bi_2O_3 phase are isostructural, it is difficult to discriminate them solely from X-ray diffraction. Evidence is presented for the existence of the intermediate sillenite $Bi_{25}FeO_{39}$ using quenching experiments, comparisons between Bi_2O_3 behavior by itself and in the presence of Fe_2O_3, and crystal structure examination. With this new information, a proposed reaction pathway from the starting oxides to the product is presented.

KEYWORDS
ferrites, ferroelectricity/ferroelectric materials, perovskites, synthesis, X-ray methods

1 | INTRODUCTION

$BiFeO_3$ is a scientifically and industrially interesting ferroic oxide because it can exhibit both antiferromagnetic and ferroelectric properties. The synthesis of $BiFeO_3$ is typically undertaken by solid-state reaction of the starting oxides of Bi_2O_3 and Fe_2O_3 in the region of 750°C,[1] although techniques such as wet chemical and sol–gel methods have been explored with some success.[2,3] Although the solid-state reaction of $BiFeO_3$ from Bi_2O_3 and Fe_2O_3 is simple in chemical formula, significant complications and challenges have been reported.

A description of solid-state synthesis was outlined by Bernardo et al.[4] in which it was proposed that the Bi_2O_3 diffuses into the Fe_2O_3 particle, which then forms $BiFeO_3$. This schematic diagram is reproduced in Figure 1. In Figure 1, the idealized final stage of the reaction is shown with the arrow toward the top-right of the figure, a process