



Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

The effect of the A-Site cation on the structural transformations in $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}, \text{Sr}$): Raman scattering studies

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ARTICLE INFO

Keywords

$\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}, \text{Sr}$)
Raman scattering
Temperature dependence
Structural transformation
Ionic radii of A-site cation

ABSTRACT

The effect of the type of A-site cation on the structural transformations of $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}, \text{Sr}$) was studied by a comparative analysis of the Raman scattering of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ in the temperature range 120–850 K. The results are also compared with those previously reported on $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$. Similar to $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$, $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ exhibit an additional structural transformation at $T_a < T_c$ and T_a decreases with the increase in the ionic radius of the A-site cation. This structural alteration consists of rearrangements of the A-site cations, which for $A = \text{Ba}$ is accompanied by readjustment of the octahedral tilting and a change in the BO_6 geometry. The results presented here confirm that the development of spontaneous polarization in four-layer Aurivillius-type ferroelectrics is triggered by the rigid-layer phonon mode, i.e., vibrations of the Bi_2O_2 planes relative to the perovskite-like blocks, rather than by cationic vibrations only within the perovskites blocks.

1. Introduction

$\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ are members of the four-layer Aurivillius-type family. These compounds have recently gained much attention as environmentally friendly lead-free ferroelectrics with the potential to be used in ferroelectric random access memories (FRAMs) [1, 2]. The structure of Aurivillius oxides consists of a regular stacking of perovskite blocks $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$ and bismuth layers $[\text{Bi}_2\text{O}_2]^{2-}$, where $A = \text{Na}, \text{K}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{etc.}$ $B = \text{W}, \text{Ta}, \text{Nb}, \text{Ti}, \text{etc.}$ and n is integer representing the number of octahedral BO_6 layers within a single perovskite block [3,4]. The ferroelectricity of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ was firstly found by Subbarao and the Curie temperature (T_c) of the ferroelectric-paraelectric (FE-PE) transition was reported to be 668 K for $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and 803 K for $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ [5]. The origin of ferroelectricity in the Aurivillius structure has been suggested to be related to several displacive mechanisms such as (a) A- and/or B-site cation displacements, (b) displacements of the Bi_2O_2 planes relative to the perovskite-like blocks (rigid layer (RL) mode), and (c) octahedral BO_6 tilting [6,7].

The structure of four-layer Aurivillius-type materials is orthorhombic below T_c and tetragonal above T_c . Kennedy et al. reported space

group symmetry of $A2_1am$ for the ferroelectric phase of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ and $I4/mmm$ for the paraelectric phase [8]. On the other hand, Lightfoot et al. (2003) reported neutron diffraction data of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ at 298 K and suggested that the $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ structure refines in a space group $F2mm$ [9]. This indicates that there may be an additional phase transition that changes the space group symmetry from $F2mm$ to $A2_1am$. For $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$, Hervoches et al. (2002) found an intermediate paraelectric orthorhombic phase in the temperature range 550–650 K, which relates to space group $Amam$ [10]. So far, the structural changes in $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ were investigated mainly by X-ray diffraction (XRD) analysis. This method probes the average structure and can hardly provide information about atomic rearrangements within a few unit cells. Such local-scale structural transformations could be however critical to understand the atomistic origin of the ferroelectric properties in complex materials. Furthermore, a comprehensive analysis of the atomic dynamics is important to reveal the mechanism of development of the ferroelectric state.

Previous studies have demonstrated that Raman spectroscopy is a suitable method to study the local structure and dynamics of Aurivillius compound [11–14]. It has been proposed that Raman scattering at $\sim 40 \text{ cm}^{-1}$, which originates from the A-site cation displacement mode, is

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<https://doi.org/10.1016/j.jssc.2019.121131>

Received 5 September 2019; Received in revised form 12 December 2019; Accepted 13 December 2019

Available online 14 December 2019

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