



Structural properties of barium stannate



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ARTICLE INFO

Keywords:

Structure
Diffraction
Oxides
Semiconductor

ABSTRACT

BaSnO₃ has attracted attention as a transparent conducting oxide with high room temperature carrier mobility. We report a series of measurements that were carried out to assess the structure of BaSnO₃ over a variety of length scales. Measurements included single crystal neutron and x-ray diffraction, Rietveld and pair distribution analysis of neutron powder diffraction, Raman scattering, and high-pressure x-ray diffraction. Results from the various diffraction probes indicate that both the long-range and local structures are consistent with the cubic symmetry. The diffraction data under pressure was consistent with a robustly cubic phase up to 48.9 GPa, which is supported by density functional calculations. Additionally, transverse phonon velocities were determined from measured dispersion of the transverse acoustic phonon branches, the results of which are in good agreement with previous theoretical estimates and ultrasound measurements.

1. Introduction

Barium Stannate, BaSnO₃, is a wide bandgap semiconductor (experimental values of the gap vary from 2.95 to 4.05 eV [1–6]) that has attracted considerable recent interest, because when doped, BaSnO₃ possesses large carrier mobilities (μ) for n-type conduction at room temperature at relatively high carrier densities (n); for example, $\mu \leq 320 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $n \sim 8 \times 10^{19} \text{ cm}^{-3}$ [5–7]. Transparent conducting behavior has been demonstrated in various single crystals and epitaxial films through either rare earth (e.g., La³⁺ [5–9]) substitution on the A-site or via oxygen vacancies [6,10,11]. Density functional theory (DFT) calculations indicate that the lower conduction band consists of hybridized s and p-states of Sn and O atoms, which leads to a low electron effective mass [12]. The low effective mass of the charge carriers combined with the shallow donor level for La³⁺ in BaSnO₃ leads to the transparent conducting behavior [12].

Interestingly, although the structure of BaSnO₃ has been continually described in terms of the cubic perovskite structure (space group $Pm\bar{3}m$), some DFT calculations have suggested that there are phonon instabilities on the zone boundaries [12]. Liu *et al.* obtained imaginary

phonon frequencies at both the M ($\frac{1}{2}, \frac{1}{2}, 0$) and R ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) points of the cubic Brillouin zone. For perovskites, these instabilities often arise due to rotations of oxygen octahedra that allow the structure to adapt to a mismatch in (A+O) radii to (B+O) radii. Such distortions lead to a lowering of the symmetry and a larger unit cell that incorporates more than one formula unit [13]. Commonly, the resulting space group is orthorhombic ($Pnma$ or equivalently $Pbnm$) or rhombohedral ($R\bar{3}c$). In contrast, the phonon calculations of Stanislavchuk *et al.* showed no unstable modes on the zone boundaries [14], although their calculations yielded very similar formation energies for the cubic, orthorhombic, and rhombohedral structures. Moreover, they reported the presence of Raman peaks, which are forbidden as first-order scattering cross-sections for cubic symmetry. Based on this result, Stanislavchuk *et al.* suggested that BaSnO₃ may exhibit local orthorhombic lattice distortions [14]. The occurrence of oxygen tilt instabilities or local lattice distortions may have implications on the carrier mobility in BaSnO₃; for example, a soft optical phonon mode associated with a cubic-orthorhombic/rhombohedral distortion may induce electron-phonon scattering events, and local static structural distortions may serve as a source of electron scattering.

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It is therefore important to consider these possibilities as they could have implications on engineering compounds with higher mobilities.

We report the results of a variety of scattering experiments that were performed to assess whether BaSnO₃ possesses structural deviations from cubic symmetry on either long-range or short-range length scales. Rietveld refinements of powder neutron diffraction data are consistent with an average cubic structure between 100 K and 500 K. Pair density function analysis similarly is well-described by the cubic structure and shows no evidence of long-range or local structural distortions. Single crystal neutron diffraction and synchrotron x-ray diffraction measurements reveal neither sharp nor diffuse Bragg peaks at the M or R points, again providing no evidence of either local or long-range static lattice distortions. Raman measurements performed on single crystals suggest a likely defect-induced mode at 140 cm⁻¹ and a mode of uncertain origin at 247 cm⁻¹, but reveal neither of the strong first-order modes at ~408 cm⁻¹ or 724 cm⁻¹ which had been previously attributed to optical modes at the M-points allowed by local orthorhombic distortions [14]. High pressure x-ray diffraction measurements and calculations suggest that the cubic phase is stable to the highest measured pressure (~49 GPa). Furthermore, we have measured the transverse phonon velocity via inelastic neutron scattering along both the [110] and [100] directions.

2. Materials and methods

Polycrystalline BaSnO₃ was grown by standard solid-state reaction using BaCO₃ and SnO₂ as starting materials. Single crystals of BaSnO₃ were grown from Cu₂O flux using the method described by Kim *et al.* [10]. Consistent with previous reports, the single crystals showed n-type conductivity that most likely arises due to a low concentration of oxygen vacancies [6,8,10]. Crystals with masses of 30–70 mg were employed in the neutron scattering measurements.

Time-of-flight powder neutron diffraction measurements were performed on the beamline NOMAD located at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory [15]. The sample was measured in a thin-walled quartz tube in a Cobra cryostat at various temperatures between 100 K and 500 K. Rietveld refinement was carried out using GSAS [16] with EXPGUI [17] interface for a *d*-spacing range from 0.420 < *d* < 1.505 Å. The structure function *S*(**Q**) was obtained by subtracting the background of the empty capillary and normalizing the data to the scattering from a solid vanadium rod. Pair distribution function (pdf) refinement was carried out using PDFgui/PDFfit2 [18], and termination ripples were simulated in the fit. Single crystal x-ray diffraction measurements were performed on 15-ID-B at the Advanced Photon Source (APS) at Argonne National Laboratory using λ = 0.413280 Å and an APEX II CCD detector. Elastic single crystal neutron scattering measurements were performed on the thermal triple-axis spectrometer, BT-7, located at the NIST Center for Neutron Research. The scan through the R-point discussed later in the paper (Fig. 4a) was performed on one single crystal aligned in the cubic (*hhl*) scattering plane. The other scans were performed on 3 co-aligned crystals aligned in the cubic (*hk0*) scattering plane. A fixed final neutron energy of *E_f* = 14.7 meV was employed, and beam harmonics were suppressed through use of pyrolytic graphite filters. Inelastic neutron scattering measurements were also performed on BT-7 using the 3 co-aligned crystals. The angle-dispersive XRD experiments under high pressure were performed at the HPCAT beamline 16-BM-D at the Advanced Photon Source, Argonne National Laboratory. A MAR345 image plate detector was equipped in the beamline and the diffraction was processed in transmission mode. The wavelength of X-ray for the experiments was set to 0.4246 Å. The application of high pressure was realized with a pair of 300 μm-cutlet diamonds mounted on a symmetric diamond anvil cell. A 301 stainless steel sheet was used as a gasket, and Neon was loaded into the gasket as a pressure-transmitting medium.

Temperature-dependent Raman scattering measurements were

performed using the 647.1 nm excitation line from a Kr⁺ laser and room temperature measurements were performed using a Nanophoton Raman microscope with a 532 nm laser. The 647.1 nm Raman system's incident laser power was limited to 5 mW, and was focused to a ~50 μm-diameter spot to minimize laser heating of the sample. The scattered light from the samples was collected in a backscattering geometry, dispersed through a triple-stage spectrometer, and then detected with a liquid-nitrogen-cooled CCD detector. The incident light polarization was controlled using a polarization rotator, and the scattered light polarization was analyzed with a linear polarizer, allowing the determination of excitation symmetry information. For the temperature-dependent measurements, the sample was inserted into a continuous He-flow cryostat, which allowed the sample temperature to be varied between 3 and 300 K.

The measurements using the Nanophoton Raman Microscope system were performed using a 532 nm excitation line with an imaging spatial resolution of 350 nm × 800 nm. The incident laser power was limited to 0.5 mW to minimize laser heating. The scattered light from the sample was collected in a backscattering geometry, through a confocal slit, dispersed through a triple-stage spectrometer and then detected with electrically cooled CCD detector cooled to -70 °C. For the room temperature measurement, the sample was kept on a microscope slide.

3. Results

3.1. Powder neutron diffraction

An example of a powder neutron diffraction pattern (100 K) and its Rietveld refinement is displayed in Fig. 1. Consistent with previous reports, all peaks in the pattern are described by cubic symmetry, with no unexpected splitting of fundamental peaks observed at any measured temperature (100 – 500 K). Furthermore, no superlattice peaks at either the M or R points were observed at any temperature. The obtained lattice parameters, thermal displacement parameters, and agreement factors at various temperatures are provided in Table 1.

Although the Rietveld refinements were consistent with an average cubic structure, they do not preclude the possibility of local distortions. We have therefore investigated the same data using pdf analysis which is a measure of the local structure that has been shown to be quite different than the average structure in a number of perovskites [19]. The pdf analysis is made possible by the time-of-flight diffraction in which data is collected up to large wave-vector transfers (**Q**) and Fourier transformed from reciprocal space up to |**Q**| = 31.4 Å⁻¹ to obtain a high-resolution pdf in real space. Essentially, the Fourier transform is performed on the measured structure function, *S*(**Q**), which yields a pair correlation function, *G*(*r*), defined by [20]:

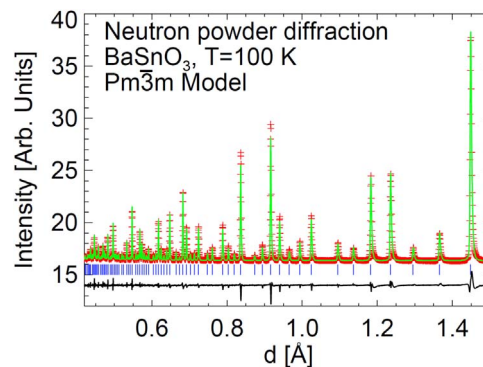


Fig. 1. Rietveld refinement of powder neutron diffraction data for BaSnO₃ at 100 K. Data points are shown by red + symbols and the fit is shown in solid red. Short blue lines mark the positions of Bragg reflections, and the difference curve is shown in solid black. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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