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A review of the structure-property relationships in lead-free piezoelectric $(1-x)Na_{0.5}Bi_{0.5}TiO_3$–$(x)BaTiO_3$

Ryan R. McQuade, Michelle R. Dolgos *

Oregon State University, Department of Chemistry, Corvallis, OR 97331, United States

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ABSTRACT

Piezoelectric materials are increasingly being investigated for energy harvesting applications where $(1-x)Na_{0.5}Bi_{0.5}TiO_3$–$(x)BaTiO_3$ (NBT-BT) is an important lead-free piezoelectric material with potential to be used as an actuator in energy harvesting devices. Much effort has been put into modifying NBT-BT to tune the properties for specific applications, but there is currently no consensus regarding the structure-property relationships in this material, making targeted, rational design a major challenge. In this review, we will summarize the current body of knowledge of NBT-BT and discuss contradicting studies, unresolved problems, and future directions in the field.

1. Introduction

Piezoelectric materials are used in an astonishing number of actuator and sensor applications in electronic devices. One of the newer applications of piezoelectrics that has surfaced over the past decade is energy harvesting. The main drives for developing piezoelectric energy harvesting materials are for powering small electronic devices to reduce the waste generated by replacing batteries, and remote sensing for applications such as structural health monitoring. Other creative uses for energy harvesting that have been put into practice include several European dance clubs that power their lights and stereos from the force of people stepping and dancing on piezoelectric lined dance floors [1,2]. Also, a gym in Portland Oregon harnesses the power of piezoelectric devices in specially designed stationary bikes to generate electricity for the gym's TVs and stereo system [3]. This technology has also been demonstrated in commercial products such as wrist watches, tennis rackets, and wireless sensor nodes with many applications that have yet to be realized. For example, the armed services are interested in putting piezoelectric devices into soldier's boots to power their portable electronic equipment, but the current technology is too cumbersome, so further development is necessary. The field is in its infancy and scientists and engineers have yet to discover all of the ways in which human kinetic energy can be transformed to electrical energy. Piezoelectric energy harvesting devices hold an incredible amount of potential as a new energy source that will become part of the solution for creating a diverse supply of clean and sustainable energy sources, allowing our society to become completely independent of fossil fuels.

Piezoelectric energy harvesting devices are advantageous over other mechanical devices because they have a higher power output density, are easily scalable, and the devices require very simple circuitry [4,5]. These devices utilize the direct piezoelectric effect where an electric field is created in response to a mechanical stress. In the case of energy harvesting, this direct piezoelectric effect is caused by repeated vibrations. These devices are typically designed using a cantilever beam structure that is resonant matched to the physical vibrations present, allowing the maximum power to be generated at low frequencies. The most obvious piezoelectric material to be used in such devices is $Pb(Zr,Ti)O_3$ (PZT) due to its excellent piezoelectric response. However, due to the toxicity of lead, alternative materials are being studied for all piezoelectric applications to replace PZT.

$(1-x)Na_{0.5}Bi_{0.5}TiO_3$–$(x)BaTiO_3$ (NBT-BT) was first discovered in 1991 by Takenaka et al. as a very promising lead-free piezoelectric material [6]. At the time, one of the parent compounds, NBT, displayed above average ferroelectric properties, but reliable piezoelectric data was difficult to obtain due to the difficulty in poling this material. In Takenaka's study, $BaTiO_3$ was added to NBT to mirror the rhombohedral-tetragonal morphotropic phase boundary (MPB) similar to that found in PZT. The experiment was successful and showed that NBT-BT has a high piezoelectric response due to the existence of an MPB. The solid solution not only has an MPB, but is also easier to pole than NBT, and is much easier to densify compared to the other leading lead-free piezoelectric $K_{0.5}Na_{0.5}NbO_3$ (KNN). Despite its promise as a lead-free alternative,

* Corresponding author.
E-mail address: Michelle.Dolgos@oregonstate.edu (M.R. Dolgos).

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the use of NBT-BT has remained limited in practical applications. This slow progress stems from a lack of understanding of how to rationally tune the properties which results from an unclear picture of both the short- and long-range crystal structure. While careful, detailed structural studies of PZT have led to a rich body of literature that has resulted in a deep understanding of the high piezoelectric response in PZT [7–20], the structure at the MPB in NBT-BT has remained elusive and no true consensus developed regarding their structure-property relationships. Understanding the atomic structure of NBT-BT at the MPB is necessary to achieve a fundamental understanding of the processes that promote high piezoelectric properties and to effectively engineer specific functionality and tunability for a wide-range of applications.

This review focuses on summarizing the current state of knowledge of the structure-property relationships in NBT-BT. While we cannot report on every single study of NBT-BT, we will provide a broad overview of the present body of literature, point out any trends or contradicting ideas, and discuss specific studies of high importance along with future directions.

2. $BaTiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$

NBT-BT exists as a solid solution between $BaTiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$ end members. Barium titanate, $BaTiO_3$, (Fig. 1a) is the classic ferroelectric perovskite and at room temperature has a *P4mm* tetragonal structure. Twelve-coordinate barium ions occupy the perovskite *A*-site while titanium ions are found in the *B*-site, coordinated to six oxygen atoms. The Ti^{4+} cation is displaced along the $[001]_C$ direction giving rise to ferroelectric behavior. It has also been found that over a very short range, the local structure of $BaTiO_3$ has rhombohedral distortions where the Ti displaces towards the face of the octahdera along the $[111]_C$ direction where the averaging of these displacements results in the long-range tetragonal symmetry [21].

Sodium bismuth titanate, NBT, also gives rise to ferroelectricity but has a more complicated structure. It was originally thought that NBT had the rhombohedral space group *R3c* (Fig. 1b) where the Na^+ and Bi^{3+} ions are disordered, sharing the same crystallographic site with a displacement of both the *A* and *B* sites in the $[111]_C$ direction. However, recent studies indicate that the structure is actually much more complex [22–27]. Single crystal structural determination by Gorfman and Thomas [22] as well as powder diffraction refinements by Aksel et al. [23,27] have shown that the average structure of NBT at room temperature can be described in the monoclinic space group *Cc* (Fig. 1c) which is a subgroup of the previously designated structure *R3c*. The main difference between the two space groups is that the symmetry in the *Cc* space group is lower as the octahedral tilting changes from $a^-a^-a^-$ in *R3c* to $a^-a^-c^-$ in *Cc* where the magnitude of the tilting in the $[001]_C$ direction is unique. Several experiments have probed the local structure of NBT and found the short-range ordering to be significantly different from the long-range order [27–30]. Studies showed that at the local level, the Bi^{3+} and Na^+ can be found at different positions with the bismuth atom in a more distorted environment than the average due to the lone pair effect. This arrangement allows for different *A–O* bonding environments, where each cation can better satisfy its preferred bond valence sum (BVS). This new and more accurate structural representation of both parent compounds is an important discovery as it will lead to a greater understanding in NBT-BT, which has an incredibly complicated structure that has been often disputed in the literature.

3. NBT-BT properties

NBT-BT has been heavily studied, as the addition of $BaTiO_3$ to the parent compound NBT, significantly improves the piezoelectric and ferroelectric properties. At the MPB at room temperature (RT) the piezoelectric response, d_{33}, of NBT-BT has been measured at 120–180 pC/N, the coupling constant, k_p, ranges from 21.2% to 36.7%, and the dielectric constant at RT is 600–825 [31–37]. While the existence of an MPB in NBT-BT improves piezoelectric properties as in PZT, that is where the similarities end between the two materials in regards to their macroscopic properties.

The temperature dependent dielectric properties of NBT-BT indicate that it is a relaxor ferroelectric, meaning that it has a broad, frequency and temperature dependent dielectric permittivity maximum (Fig. 2a). Relaxor ferroelectrics are a distinct class of materials from ferroelectrics and originate from the presence of polar nanodomains, resulting in an average structure that is cubic or nearly cubic (pseudocubic). The dielectric behavior along with the pseudocubic structure of NBT-BT contradicts the enhanced piezoelectric properties and the existence of an MPB, complicating any direct comparisons of NBT-BT with PZT. This peculiar structure-property relationship led to an intense focus on electric-field dependent studies to investigate the possibility of field-induced structural changes causing the enhanced piezoelectric properties at the MPB.

NBT-BT samples were studied under poled conditions to determine the exact nature of the MPB. Dielectric permittivity measurements of the poled sample are strikingly different from the unpoled samples (Fig. 2b). In the poled sample, there is an abrupt transition around 110 °C. Below this temperature, the frequency dispersion observed in the unpoled sample has completely disappeared. Above the transition, relaxor ferroelectric dispersion is observed as in the unpoled samples. This data clearly shows that

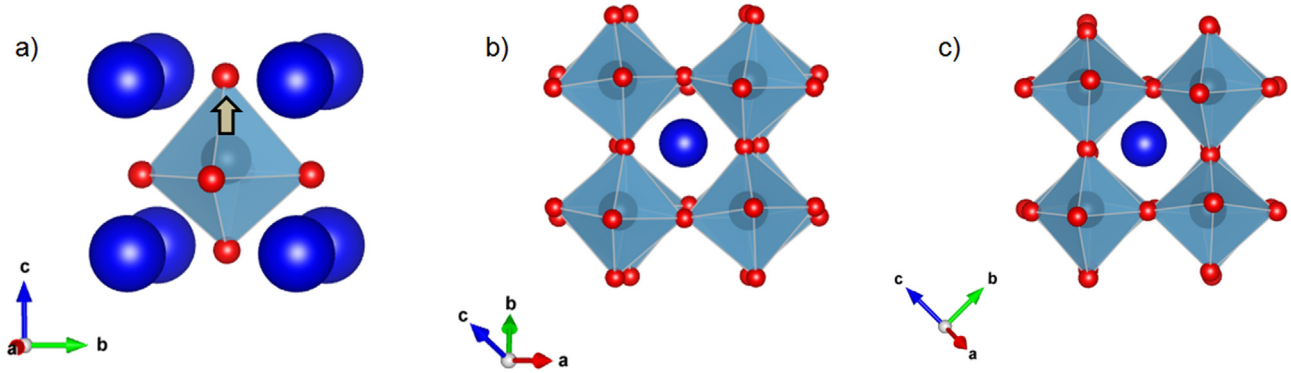

Fig. 1. (a) *P4mm* structure of $BaTiO_3$ showing displacement of the Ti atom along the $[001]_C$ direction, (b) *R3c* structure of NBT with *A* and *B*-site cation displacements and $a^-a^-a^-$ octahedral tilting, and (c) *Cc* structure of NBT which is similar to the *R3c* structure but with $a^-a^-c^-$ octahedral tilting.