
Literature review: - bismuth layered structure ferroelectric compounds

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Abstract:

Bismuth layer-structured ferroelectrics (BLSFs), highlighting their synthesis, structural characteristics, and diverse applications. Initially synthesized in 1949 by Aurivillius, BLSFs have found commercial utility in various fields such as ferroelectric non-volatile random access memory (FRAM) storage devices, high-temperature piezoelectric applications, sensors, and photo-catalysts. Their advantageous electrical properties include excellent fatigue endurance, rapid switching speed, robust polarization retention, relatively high Curie temperature, low aging rate, and low operating voltage. Notably, BLSFs offer high fatigue resistance, a crucial requirement for FRAM applications, distinguishing them from lead-based perovskites. With a Curie temperature exceeding 400°C, BLSFs are particularly suitable for high-temperature piezoelectric applications, filling the gap left by lead-based materials due to environmental regulations.

Keywords

BLSF, memory device, electrical properties.

1. Introduction:

Bismuth layer-structured ferroelectrics (BLSFs) were initially synthesized by Aurivillius in 1949 [1]. These materials find diverse commercial applications such as ferroelectric non-volatile random access memory (FRAM) storage devices, high-temperature piezoelectric applications, sensors, and photo-catalysts [2-5]. BLSFs exhibit several appealing electrical properties, including excellent fatigue endurance, rapid switching speed, robust polarization retention, relatively high Curie temperature, low aging rate, and low operating voltage [6-9].

FRAMs, utilizing ferroelectric capacitors, are vital components in computers as they retain information even during power interruptions. Key requirements for commercial FRAM applications include high fatigue resistance, substantial remnant polarization, and low coercive field [2]. Unlike lead-based perovskites, which have high polarization but low fatigue resistance, BLSFs offer a significant advantage with fatigue resistance of up to $\sim 10^{12}$ switching cycles [2].

With a Curie temperature exceeding 400°C and a low temperature coefficient of dielectric, BLSFs are particularly attractive for high-temperature piezoelectric applications, especially under demanding conditions of high frequency and temperature [6-8, 10, 11]. While lead-based piezoelectric materials boast high coefficients, they are restricted due to environmental regulations banning lead-based materials. Lead-free alternatives like BaTiO_3 suffer from low Curie temperatures, limiting their utility in high-temperature applications. BLSFs, with their high Curie temperatures, emerge as strong contenders for the development of lead-free high-temperature piezoelectric materials.

The structure of BLSF consists of intergrown fluorite-like $(\text{Bi}_2\text{O}_2)^{2+}$ units and pseudo-perovskite slabs $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$, as depicted in Fig. 1.1. In this structure, A represents a relatively large monovalent, divalent, or trivalent cation occupying a 12-coordination site, such as Na^+ , K^+ , Ba^{2+} , Ca^{2+} , Sr^{2+} , Pb^{2+} , Bi^{3+} , etc. For instance, Sr^{2+} and Bi^{3+} are the A-type cations in the BLSFs shown in Fig.1.1 (a) and (b), respectively. B represents a small, highly charged tetravalent, pentavalent, or hexavalent cation in the octahedral coordination site of the pseudo-perovskite unit, typically occupied by Ti^{4+} , Ta^{5+} , Nb^{5+} , V^{5+} , W^{6+} , etc. For example, Ta^{5+} and Ti^{4+} are the B-type cations in the BLSFs shown in Fig.1.1 (a) and (b), respectively. The $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ perovskite slabs are sandwiched between Bi_2O_2 layers, resulting in a characteristic layered structure. Here, 'n' indicates the number of perovskite units stacked along the c-axis between

(Bi₂O₂)₂₊ layers, with $1 \leq n \leq 8$ [1, 13, 14]. Examples of BLSFs include Bi₂WO₆ ($n = 1$), SrBi₂Ta₂O₉ ($n = 2$), Bi₄Ti₃O₁₂ ($n = 3$), MBi₄Ti₄O₁₅ ($M = \text{Ca, Sr, Pb, Ba}$) ($n = 4$), and Ba₂Bi₄Ti₅O₁₈ ($n = 5$), among others. Fig.1.1 illustrates a typical two-layer (SrBi₂Ta₂O₉, $n = 2$) [15] and three-layer (Bi₄Ti₃O₁₂, $n = 3$) [16] BLSFs

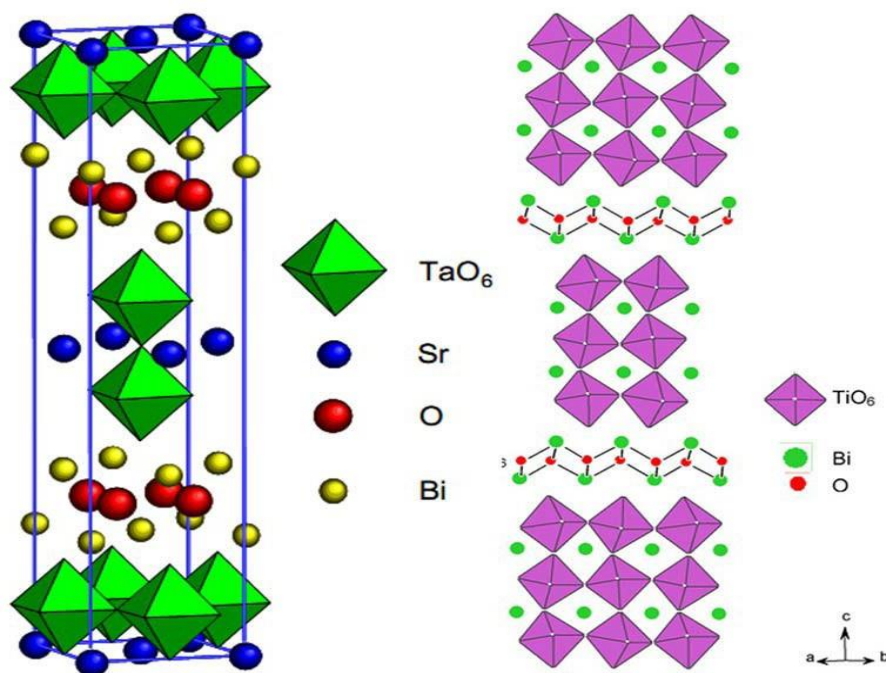


Figure. 1:

The majority of BLSFs exhibit a non-centrosymmetric orthorhombic structure at room temperature. Their ferroelectric properties stem from three main distortions in this orthorhombic structure during the transformation from the high-temperature paraelectric tetragonal phase as it cools through the Curie temperature. These distortions involve tilting of oxygen octahedra around the a-axis, around the c-axis, and a shift of A and/or B-cations along the polar a-axis [17, 18]. The ferroelectric behavior primarily originates from the perovskite blocks within BLSF [19]. Bi₂O₂ layers act as insulating layers, influencing the compound's electrical response, such as electrical conductivity and band gap [20, 21]. The insulating behavior of Bi₂O₂ layers results from their self-regulated positioning in the lattice to compensate for the space charge arising from oxygen vacancies.

One of the most notable advantages of BLSF compounds is their compositional flexibility, allowing properties to be tailored according to chemical composition. Different properties are exhibited by various members depending on the cations occupying the A and B-sites of BLSF.

While most member's exhibit normal ferroelectric behavior, a few, such as BaBi₂Nb₂O₉, BaBi₂Ta₂O₉, BaBi₄Ti₄O₁₅, display relaxor behavior [9, 14, 22, 23]. Even a slight alteration in the composition of a relaxor like BaBi₄Ti₄O₁₅, such as CaBi₄Ti₄O₁₅ and SrBi₄Ti₄O₁₅, can induce normal ferroelectric behavior. Additionally, variations in composition can modify the ferroelectric and piezoelectric properties of different BLSFs [24, 25]. Donor substitution improves the resistivity of BLSFs, which typically exhibit oxygen vacancies due to bismuth volatilization during high-temperature processing. Acceptor and donor co-substitution at A and/or B-sites effectively change relaxor behavior by forming localized charged polar pairs.

BaBi₄Ti₄O₁₅, the focus of this study, is a four-layer relaxor ferroelectric compound proposed for capacitor applications with broad temperature stability and piezoelectric applications following appropriate compositional adjustments. Relaxor ferroelectrics are desirable for a range of applications due to their excellent high dielectric and piezoelectric responses across a wide temperature range [26, 27]. BaBi₄Ti₄O₁₅ adopts an orthorhombic structure at room temperature with space group A21am, transforming into a tetragonal structure with space group I4/mmm above its Curie temperature (~400°C) [22, 28]. Fig. 1.2 illustrates these structures, with four perovskite blocks sandwiched between the Bi₂O₂ layers. Fig. 1.2(a) highlights the tilting of TiO₆ octahedra, which, along with the shifting of A-type Bi³⁺ cations along the a-axis, contributes to the ferroelectricity of BaBi₄Ti₄O₁₅. The degree of off-center displacement of the TiO₆ octahedral chain correlates with the remnant polarization, which can be altered through A and/or B-site substitutions. Fig. 1.2(b) illustrates the absence of tilting in the tetragonal structure, rendering it paraelectric. Recent studies have revealed partial occupancy of Ba²⁺ in the Bi₂O₂ layer, known as cationic disorder, which contributes to the relaxor behavior of BaBi₄Ti₄O₁₅ by creating local charge centers within its macro-domain, forming polar clusters responsible for its relaxor behavior [22, 29].

As mentioned, BLSFs have been extensively explored for use in piezoelectric devices suitable for high frequencies and temperatures. However, their piezoelectric activities are typically lower (~20 pC/N) compared to lead-based piezoelectrics (~200 pC/N). Various approaches have been proposed to enhance the piezoelectric activities of BLSFs, including grain orientation techniques like hot forging, template grain growth, and spark plasma sintering [8, 10, 30-34]. While these techniques significantly improve the piezoelectric coefficients (d₃₃), they are not commercially viable. Hence, there's a need to develop high d₃₃ BLSF ceramics through conventional sintering

methods for commercial viability. Approaches such as A-site rare-earth substitutions, B-site substitutions, and A-site vacancy modifications have been suggested for conventional sintering [35-37]. However, the piezoelectric activities of modified BLSF compounds remain low, warranting further research into these substitution approaches. For instance, BaBi₄Ti₄O₁₅ exhibits a piezoelectric d₃₃ coefficient of ~12 pC/N, whereas a similar lead-based four-layer PbBi₄Ti₄O₁₅ exhibits ~23 pC/N. Different substitutions and microstructural engineering through conventional sintering could play a significant role in enhancing the piezoelectric activities of the compound.

(a) Synthesis of BLSF Compounds BLSFs have been synthesized through various methods, including conventional solid-state methods, co-precipitation, sol-gel, auto-combustion, polymeric precursor methods (such as Pechini, i.e., complex citrate), molten salt synthesis, and metal-organic decomposition. Conventional solid-state methods involve mixing oxides and carbonates of required metals in stoichiometric amounts, followed by repeated grinding and high-temperature calcinations with extended soaking periods to achieve a pure phase. Dense samples are obtained at a high sintering temperature of ~1150°C, although volatilization of bismuth can occur due to the high sintering temperature. Chemical synthesis routes can mitigate bismuth volatilization, providing homogenized fine powders at lower formation temperatures due to molecular-scale mixing of precursors. Various wet-chemistry routes can synthesize ultra- fine and nano-sized powders, with co-precipitation being successful in producing ultrafine powders with a narrow particle size distribution. For instance, tantalum fluoride, bismuth nitrate, and strontium chloride have been used to synthesize SrBi₂Ta₂O₉ through co-precipitation. Polymeric precursor methods based on the Pechini process have also been employed, offering precise stoichiometric control and resulting in a pure phase with a grain size of ~1µm for BaBi₄Ti₄O₁₅. Sol-gel methods, though capable of producing nanopowders in the range of 150 to 180 nm, require a water-free atmosphere for synthesis and may encounter issues with solution aging that alter microstructure. Mechanochemical activation, involving milling barium oxide, titanium dioxide, and bismuth oxide in a planetary ball mill, has also been utilized for synthesis. Literature suggests BaBi₄Ti₄O₁₅ has been prepared by solid oxide routes, sol-gel methods, Pechini methods, mechanochemical activation, etc. While solid oxide methods offer simplicity and easy processing steps, chemical routes produce homogeneous powders with finer particle sizes, albeit with higher costs. Therefore, a combined method incorporating advantages of solid oxide and chemical routes would likely be

more effective for industrial applications

2. References:

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