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*Review paper*

# Aurivillius $BaBi_4Ti_4O_{15}$ based compounds: Structure, synthesis and properties

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## Abstract

*The discovery of some Aurivillius materials with high Curie temperature or fatigue-free character suggests possible applications in high temperature piezoelectric devices or non-volatile ferroelectric random access memories. Furthermore, increasing concerns for environmental issues have promoted the study of new lead-free piezoelectric materials. Barium bismuth titanate ($BaBi_4Ti_4O_{15}$), an Aurivillius compound, is promising candidate to replace lead-based materials, both as lead-free ferroelectric and high temperature piezoelectric. In this review paper, we report a detailed overview of crystal structure, different synthesis methods and characteristic properties of barium bismuth titanate ferroelectric materials.*

***Keywords***: *Barium bismuth titanate; structure; electrical, piezoelectric and ferroelectric properties; relaxors*

## Contents

## I. Introduction

Aurivillius oxides are family of materials first synthesized by Aurivillius in 1949 [1]. He described the structure as formed by bismuth oxide based layers interleaved with pseudo-perovskite-type layers. The terminology used to describe Aurivillius-type compounds is not standardized. In the literature they are mentioned as bismuth based layered compounds, perovskite-based layered structures, layered bismuth oxides, bismuth layered structure ferroelectrics (BLSFs) or other similar denominations [2]. Majority of Aurivillius compounds are ferroelectrics that are main subject of our research.

BLSFs are of technical interest due to their high-temperature ferroelectricity, in particular for high-temperature piezoelectric application. Lead zirconia titanate (PZT-based) materials also show high piezoelectric response and are incorporated into thousands of product including watches, ultrasonic equipment and hydrophones. However, PZT-based compounds can not be used at temperatures greater than 250 °C because of depoling and finally the loss of ferroelectricity at Curie temperature. Moreover, there is an increasing concern regarding recycling and disposal of the devices due to the toxicity lead. The majority of BLSFs have Curie temperature higher than 400 °C. Thus, those compounds are promising candidates for replacing lead-based materials, both as lead-free ferroelectric and high temperature piezoelectrics [3,4].

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BLSFs are commercially applicable in ferroelectric non-volatile random access memory (FRAM) storage devices, high temperature piezoelectric devices applications and sensor applications [5–7]. They possess some attractive electrical properties such as excellent fatigue endurance, fast switching speed, good polarization retention, relatively high Curie temperature, low aging rate and low operating voltage. FRAMs are non-volatile memory devices which employ ferroelectric capacitors. They can retain information even when the power supply is interrupted, making them an important component in the computers. FRAM circuit includes a capacitor where information is stored in binary form. The commercial application of FRAM requires high fatigue resistance, large remanent polarization and low coercive field. Though lead based perovskites have high polarization they have low fatigue resistance [8]. In this respect, BLSFs like $Bi_4Ti_3O_{12}$ (BiT), $SrBi_2Ta_2O_9$ (SBT) and $BaBi_4Ti_4O_{15}$ (BBT) have an advantage over the lead-based ones, as they possess fatigue resistance up to ~$10^{12}$ switching cycles [9,10].

A feature of the Aurivillius compounds resides in their compositional flexibility of the perovskite block which allows the incorporation of various cations. It is thus possible to modify the dielectric and ferroelectric properties by the substitution of A-site and to some extent the B-site of Aurivillius oxides with various iso- and aliovalent. Most of the BLSFs have a relatively high electrical conductivity which makes it difficult to pole. Doping with donor cations, like $Nb^{5+}$ to $Ti^{4+}$ site, can reduce the conductivity and, therefore, enable the existence of higher piezoelectric response. Also, the incorporation of trivalent $La^{3+}$ ions for divalent $Ba^{2+}$ ions in BBT ceramics could effectively stabilize the oxygen ions in the lattice and lead to reduction in the conductivity and dielectric loss. The compositional modification is broad topic which will not be discussed in this paper.

This article reviews in detail the crystal structure of Aurivillius compounds and existing knowledge about processing and properties of $BaBi_4Ti_4O_{15}$ compounds as one of the relaxor type of ferroelectric materials.

## II. Crystalline structure of $BaBi_4Ti_4O_{15}$

BLSFs have a highly anisotropic structure which is composed of $n$ number of perovskite $(A_{n-1}B_nO_{3n+3})^{2-}$ unit cells sandwiched between $(Bi_2O_2)^{2+}$ slabs along pseudo tetragonal $c$-axis ($n$ is an integer between 1 and 5). The 12 coordinate perovskite-like A-site is typically occupied by a large cations (from 1.34 to 1.61 Å) such as $Na^+$, $K^+$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Pb^{2+}$, $Bi^{3+}$ or $Ln^{3+}$ and the 6-coordinate perovskite-like B-site by smaller cations (from 0.59 to 0.65 Å) such as $Fe^{3+}$, $Cr^{3+}$, $Ti^{4+}$, $Nb^{5+}$ or $W^{6+}$. The crystal structure of BBT is shown on Fig. 1. BBT, as the $n$ = 4 member of the Aurivillius fam-

ily, has Ba and Bi ions at the A sites and Ti ions at the B sites of the perovskite block $[(Bi_2O_2)^{2+} ((BaBi_2)Ti_4O_{13})^{2-}]$ [11]. Almost all BLSFs have orthorhombic symmetry at room temperature (that of $Bi_4Ti_3O_{12}$ is strictly monoclinic).

The first studies of symmetry of Aurivillius compounds showed that the structure of these compounds is tetragonal or pseudo-tetragonal [11,12]. Subsequent researches have shown that the structure of most Aurivillius compounds at room temperature are orthorhombic due to slight distortion from the high symmetry tetragonal (*I4/mmm*) parent structure. Some compounds ($Bi_2WO_6$, $Ba_2Bi_4Ti_5O_{18}$) belong to the *B2cb* space group at room temperature, while others belong to the *A21am* space group ($Bi_2BaNb_2O_9$, $Bi_2SrNb_2O_9$) [13]. Obviously, the symmetry of the low temperature polar phase depends not only on the high-symmetry paraelectric phase, but also on the number and way of the shifting of perovskite layers. In the Aurivillius family, the compounds with an odd number of perovskite layers crystallize in *B2cb*, while even-layered members prefer *A21am*. Changes in the structure during the phase transition in bismuth layered compounds happen in two ways that are taking place simultaneously: (1) there is a rotation of the $BO_6$ octahedron and formation of additional chemical bonds between the cations of bismuth in the $(Bi_2O_2)^{2+}$ layer and oxygen anions of the end fragments of perovskite block at lower temperatures, (2) displacement of the B cation from centre of octahedron to one of
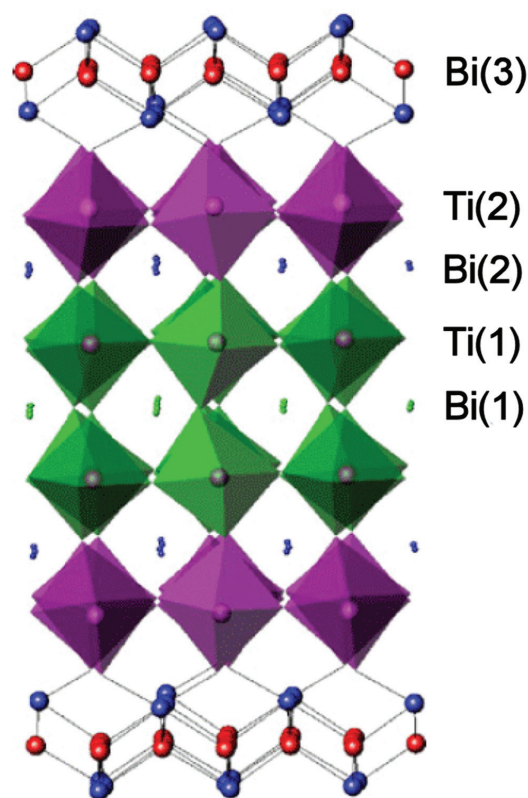


**Figure 1. Crystal structure of $BaBi_4Ti_4O_{15}$**

the equatorial edges of the octahedron $BO_6$, on the basis of which the spontaneous polarization occurs in low-temperature phase [14,15].

Aurivillius originally described $BaBi_4Ti_4O_{15}$ as tetragonal at room temperature, while his analogues ($ABi_4Ti_4O_{15}$, where A = Ca, Sr, Pb) are shown as orthorhombic. Nalini and co-authors [16] confirm the tetragonal structure of BBT with space group *I4/mmm*, while Irie and co-authors [17] suggested that in fact $BaBi_4Ti_4O_{15}$ is orthorhombic, although not presented details of the structure of this compound. An accurate determination of the structure of the ferroelectric phase is complex, given the large number of atoms
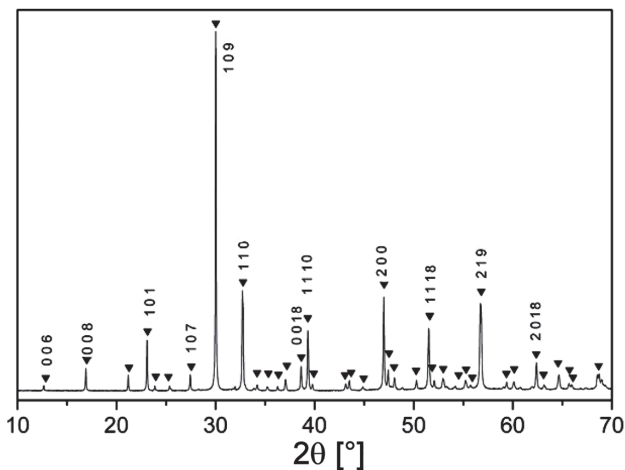


**Figure 2. XRD pattern of BBT ceramics obtained by solid state method, sintered at 1130 °C for 1 h [23]**
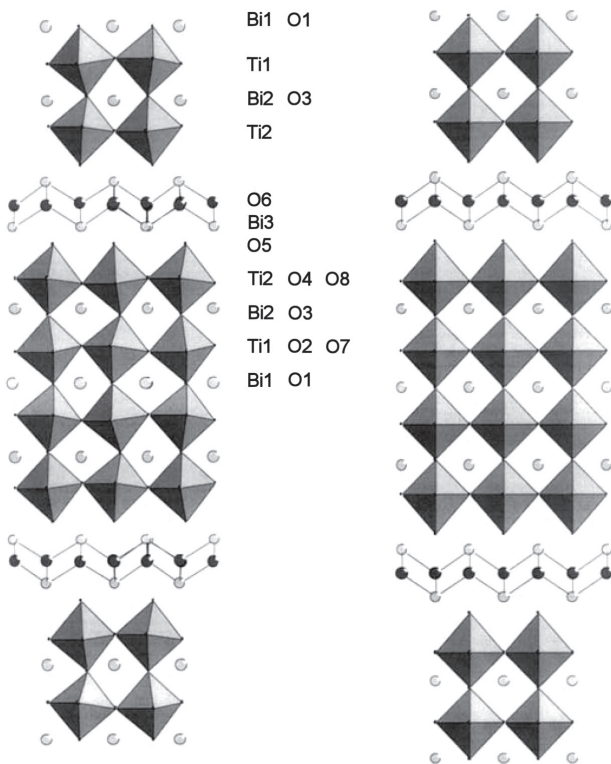


**Figure 3. Ortorombic *A21am* and tetragonal *I4/mmm* structure of $BaBi_4Ti_4O_{15}$ [21]**

per unit cell. So far, only a few authors have examined the crystal structure of BBT based on diffraction patterns obtained from different sources: laboratory X-ray (conventional diffractometer), high resolution synchrotron diffraction (High-Resolution Synchrotron X-ray Powder Diffraction - HRSXRPD) and neutron powder diffraction patterns (Neutron Powder Diffraction - NPD). Tellier *et al.* [18,19] and Lightfoot *et al.* [20], based on their examination of X-ray diffraction data indicated the orthorhombic structure of BBT at room temperature, with *F2mm* space group. The structure proposed by Kennedy [21,22] is different from the structure that was given by Tellier and co-authors. Using both the NPD and HRSXRPD diffractometer, Kennedy confirmed the same crystal structure but different space group - *A21am*. The structures in *F2mm* and *A21am* differ in that the latter allows for rotation of the $TiO_6$ octahedral as a consequence of displacement of the oxygen atoms. XRD of BBT ceramics was shown in Fig. 2 [23].

Subbarao [24] excludes the possibility that the larger $Ba^{2+}$ ion (1.35 Å) can replace the smaller $Bi^{3+}$ ion (1.17 Å) in the $(Bi_2O_2)^{2+}$ layer. However, most researchers [16,21,25] still agreed with the fact that it is necessary to make the structure stable, that the $Ba^{2+}$ ions are found in the perovskite block, and in the structure of $[M_2O_2]^{2+}$ layer. Such redistribution creates a positively charge cation in the perovskite block where $Bi^{3+}$ ions are replaced by $Ba^{2+}$ ions, and negative charges in the $(Bi_2O_2)^{2+}$ layer, where $Ba^{2+}$ ions replace $Bi^{3+}$ ions. According to most authors, this gives the appearance of cation disorder wich could be an explanation of the specific electrical properties of barium bismuth titanate compared to other similar oxides $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Pb), where the disorder is not present. A detailed analysis of the diffraction pattern and refinement have shown that the structure of BBT at room temperature is orthorhombic (space group with lattice parameters and *A21am*: $a = 5.4697$, $b = 5.4558$ Å and $c = 41.865$). Above Curie temperature, the BBT structure changes to the pseudo-tetragonal (space group *I4/mmm* with the lattice parameters $a = 3.8624$ and $c = 41.851$ Å), as shown on Fig. 3 [21].

### III. Methods for synthesis of $BaBi_4Ti_4O_{15}$ powders

It is well known that physical properties of ceramics are greatly affected by the characteristics of powder, such as particle size, morphology, purity and chemical composition. The selected synthesis method depends on cost, but even more important is the final application of the obtained ceramics. BLSFs have been prepared through various methods like conventional solid state method, co-precipitation, sol-gel, auto-combustion, polymeric precursor method (Pechini, i.e. complex citrate), molten salt synthesis, metal-organic decomposition etc. Chemical methods have been confirmed to

efficiently control the morphology and chemical composition of prepared product. On the other hand, processing of BLSF compounds by the conventional solid-state reaction method demands careful optimization of the calcination and sintering characteristics because of the loss of $Bi_2O_3$ during heating which results in the formation of Bi-Ti-O compounds with different stoichiometry. Introducing a slight excess of $Bi_2O_3$ is found to act as a sintering aid to control the loss of volatile $Bi_2O_3$. In spite of this, there have been very limited reports on the bulk $BaBi_4Ti_4O_{15}$ ceramic powder synthesis using non-conventional techniques other than conventional solid-state method.

As miniaturization of electronic devices demand smaller particle size of powders with controlled morphology, the desired characteristics of the starting powder become a critical issue. Thus, the most frequently used method for synthesis of BBT powder will be presented in the next chapter.

### 3.1 Conventional solid state reaction method

The mostly commonly used method for the synthesis of $BaBi_4Ti_4O_{15}$ powder is **conventional solid state reaction**. This method involves mixing of oxides and carbonates of the required metals in stoichiometric amounts:

$$BaCO_3 + 2Bi_2O_3 + 4TiO_2 = BaBi_4Ti_4O_{15} + CO_2 \quad (1)$$

$$BaO + Bi_2O_3 + TiO_2 = BaBi_4Ti_4O_{15} + CO_2 \quad (2)$$
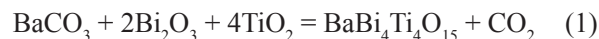
Repeated grinding and high temperature calcinations with long soaking periods are necessary to form a pure phase. Preparation of BBT ceramics by solid state reaction method shows variation in the reported processing temperatures from 750 °C to 950 °C [26–28]. Kumar *et al.* [27] proposed a two-step heat treatment, with the samples first calcined at 950 °C, and then at 1050 °C with intermediate grinding. Due to the high calcination temperature, such prepared powders contain large particles of average size from 2 to 5 μm, an inhomogeneous structure with a certain percentage of strongly agglomerated particles, a broad particle size distribution and also irregular particle morphology which is hard to control. Thus, it is important to use appropriate calcination temperature because Aurivillius powders calcined at high temperature possess a lamellar morphology, which makes it difficult to produce dense ceramics



a)                                                                                           b)
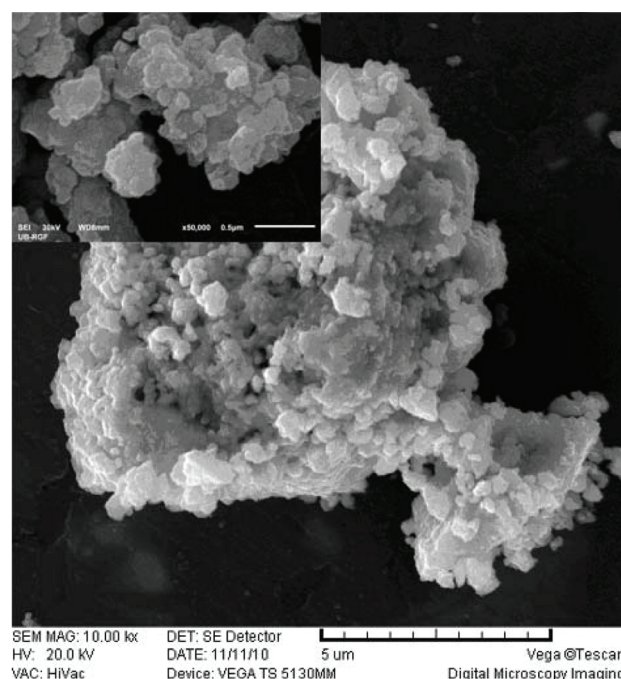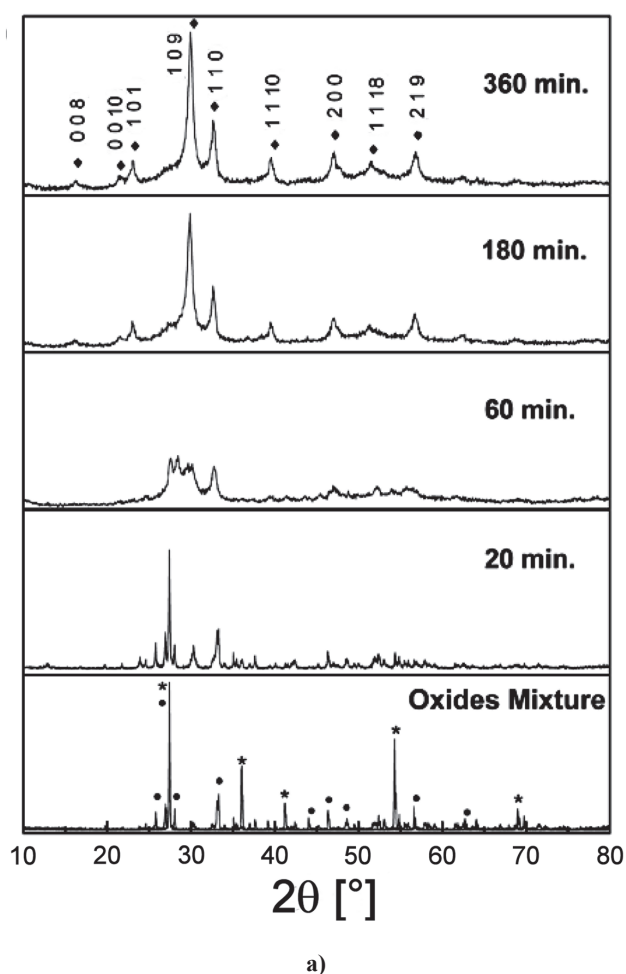
**Figure 4. XRD traces of homogenized starting oxide mixture of BaO, $Bi_2O_3$ and $TiO_2$ together with those mechanically activated for 20, 60, 180 and 360 min, respectively (a), SEM images of 360 min activated powder calcinated at 850 °C for 4 h (b) [23,31]**
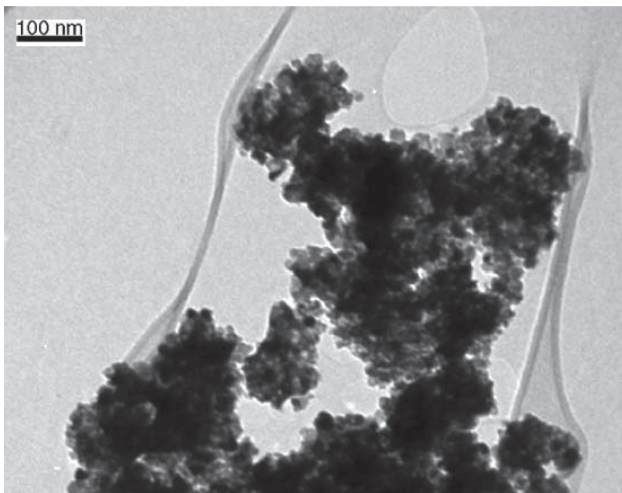
**Figure 5. TEM of BBT precursor powder obtained by Pechini method calcined at 600 °C [32]**

since a high degree of packing of the particles is not easy to achive by the normal cold-pressing. All mentioned characteristics of powders present disadvantages of this method. On the other hand, the advantage of solid oxide method is the use of simple oxide raw materials and easy processing steps. Despite all these shortcomings, the conventional method of synthesis of this type of material is economical and widely used for the production of large quantities of powder.

**Mechanochemical activation** is another method for synthesis of BLSF. Solid-state reaction that normally requires high temperatures can occurs at lower temperatures during milling, without any externally applied heat. Intensive milling increases the contact area between the reactant powder particles due to the reduction of particle size allowing fresh surface to come into contact [29,30]. Synthesis of $BaBi_4Ti_4O_{15}$ utilizing mechanochemical activation was performed by Bobic *et. al*

[31]. Appropriate mixture of oxides: $BaO$, $TiO_2$ and $Bi_2O_3$ is milled using a Fritsch Pulverisette 5 type planetary mill with zirconia balls. Fig. 4a shows the XRD of homogenized starting oxide mixture of $BaO$, $Bi_2O_3$ and $TiO_2$ together with those mechanically activated for 20, 60, 180 and 360 min. Aurivillius phase was obtained after 360 min of milling. After calcination of this powder at 850 °C for 4 h, obtained BBT powder was consisted of particles agglomerates of varying size and morphology, with particles of a mostly rounded shape in the range of 100–130 nm (Fig. 4b) [23].

### 3.2 Chemical methods for BBT powder synthesis

Chemical route produces homogeneous powders with finer particle size. However, these chemistry-based routes require high purity inorganic or organometallic reactants that are sensitive to light or humidity and more expensive than the widely available oxides and carbonates. Therefore, a combined method having advantages of solid oxide and chemical route will be more effective for industrial applications.

The **Pechini process** involves creating metal complexes with polyfunctional carboxylic acids, such as citric acid or tartarate acid with one hydroxyl group. The synthesis of polymeric precursors of $BaBi_4Ti_4O_{15}$ was performed by Murugan *et al.* [32]. Titanium (IV) chloride, bismuth (III) nitrate, barium chloride, and citric acid were used as starting materials. $TiCl_4$ was diluted with ice-cold distilled water to form a known concentration of $TiOCl_2$ solution. A stoichiometric amount of $BaCl_2 \times 6H_2O$ was dissolved in distilled water and required quantity of $Bi(NO_3)_3 \times 5H_2O$ was dissolved in minimum amount of dilute $HNO_3$ to avoid precipitation of Bi ions. All the above cations solution and citric acid was mixed well in the stoichiometric ratio. The ratio of the total metal cations to citric acid was 1. Since there
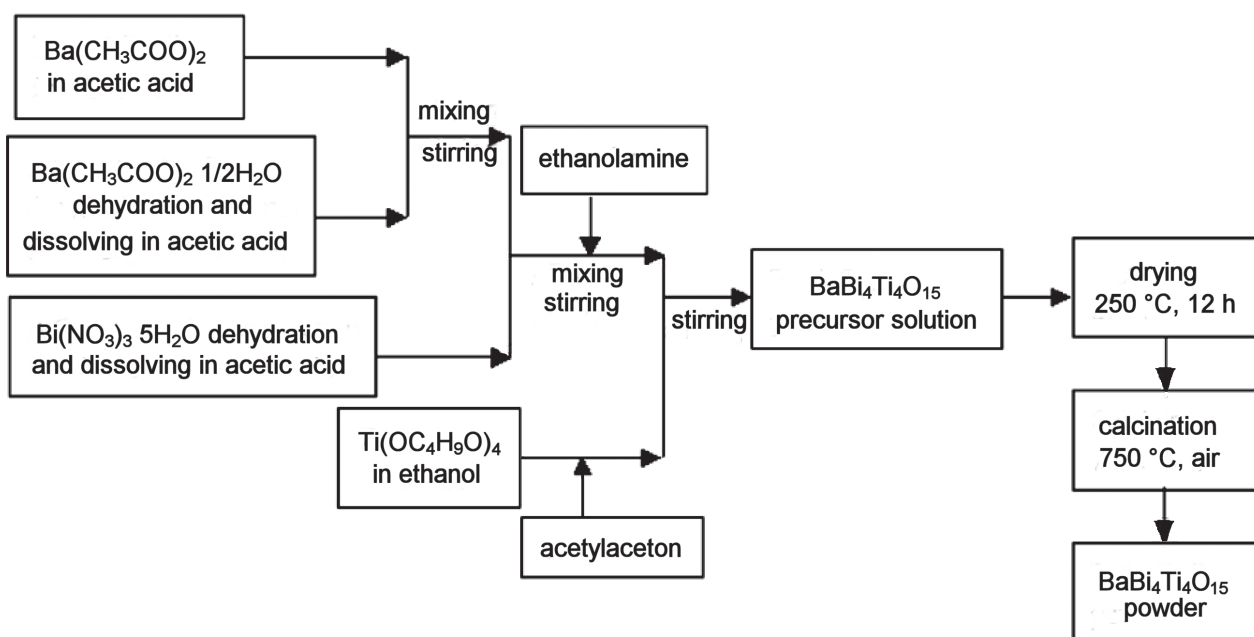


**Figure 6. Flow chart of the fabrication process of BBT powder utilizing sol-gel method [33]**

was no precipitation during mixing of citric acid and these metal salts, the pH of the solution was not varied. On heating in water bath at 100 °C a gel was formed after evaporation of water. Subsequently, the gel is decomposed at various temperatures ranging from 400 to 800 °C. The gel initially started to swell and filled the beaker producing a foamy precursor. This foam was consisted of very light and homogeneous flakes of very small particle size. Single phase BBT powder was obtained after calcination at 600 °C, and the average size of the resulting powder is 60 nm. Particles of calcined powder prepared by the citrate process were irregular in shape; a TEM image of this powder is presented in Fig. 5 [32].

Xie and Pan [33] successfully synthesized $BaBi_4Ti_4O_{15}$ powders utilizing **sol-gel process**. The flow chart of the process is shown in Fig. 6. Barium acetate, bismuth nitrate and tetrabutyl-titanate were used as starting materials. Glacial acetic acid and ethanol were selected as solvents, ethanolamine ($H_2NCH_2CH_2OH$) as complexation reagent, and acetylacetone ($CH_3COCH_2COCH_3$) as reagent to stabilize tetrabutyl titanate. In order to prevent the excessive hydrolysis of $Ti(OC_4H_9)_4$, the 99% pure $Bi(NO_3)_3 \times 5H_2O$ was vacuum-dried at 60 °C for 96 h, and then dissolved in glacial acetic acid. Acetylacetone was added to Bi-Ba acetum mixed solution. To adjust viscosity, surface tension of the precursors and to prevent the hydrolysis of bismuth nitrate in acetic acid, ethanolamine was added to the solution under ultrasonic agitation. The pH value was adjusted to remain approximately 3.5. The re-

sultant solution was filtered to form the stock solution, which was transparent, yellow and clear. After drying, BBT powder was formed when heated at 750 °C for 1 h. The average particle size of BBT powder obtained by this method is around 60 nm.

Also, $BaBi_4Ti_4O_{15}$ can be successfully synthesized utilizing the cost-effective **oxalate method** [34,35]. Barium nitrate ($BaNO_3$), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \times 5H_2O$), titanium dioxide ($TiO_2$) and oxalate acid (($COOH)_2 \times 2H_2O$) were used as precursors. Barium nitrate solution (0.02 M) was prepared by dissolving $Ba(NO_3)_2$ in distilled water. Required amount of $Bi(NO_3)_3 \times 5H_2O$ was separately dissolved using minimum quantity of concentrated nitric acid. Bismuth nitrates solution was then drop-wise added to the barium nitrate solution under constant stirring. A low concentration of barium nitrate solution (0.03 M) must be used in order to avoid precipitation during this addition. $TiO_2$ was dispersed in 0.4 M oxalic acid solution in a separate vessel. The suspension was ultrasonicated for 15 min to break the soft agglomerates of $TiO_2$. Then, the barium- and bismuth-nitrate mixed solution was added drop-wise into the $TiO_2$-oxalic acid suspension under vigorous stirring. Barium- and bismuth-oxalate hydrates were precipitated inside the suspension by heterogeneous nucleation. Finally, the pH of the suspension was adjusted to 7 by adding ammonium hydroxide solution. The precipitated mixture of $TiO_2$ and barium- and bismuth-oxalates was separated by filtration and washed thoroughly using deionized water, followed by drying at 50 °C for 24 h.
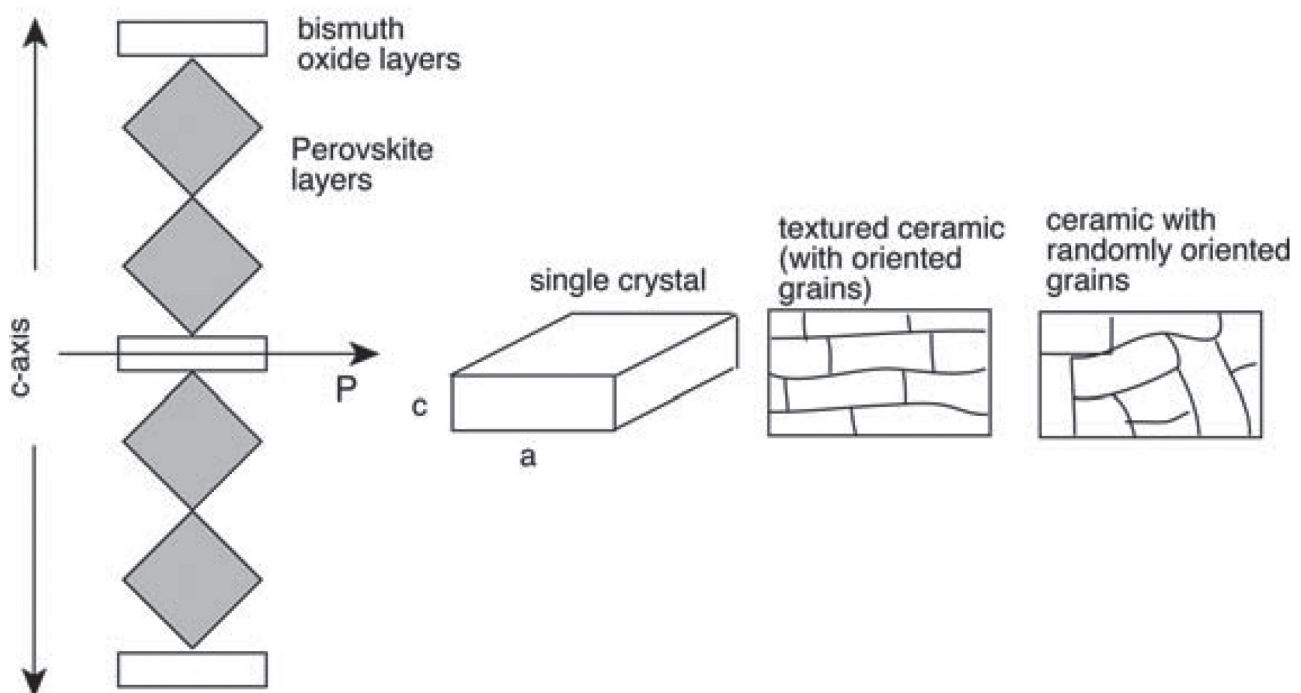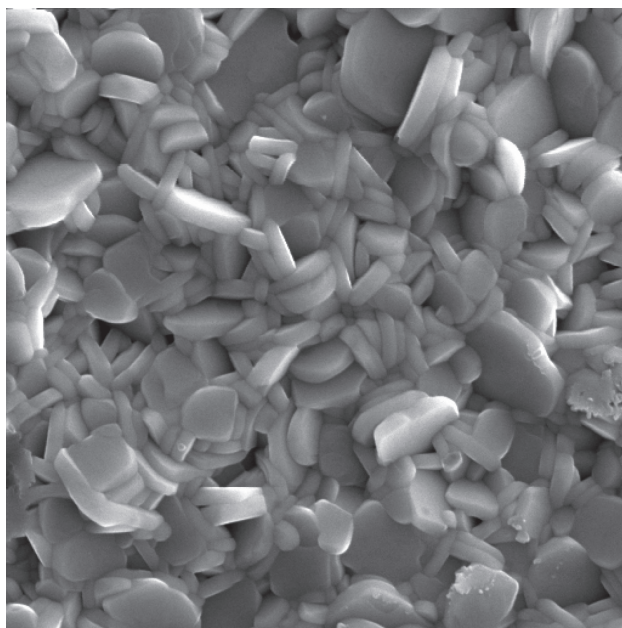


**Figure 7. Schematic presentation of: a) Aurivillius layer structure, b) single crystals with platelet form, c) textured ceramics with plate-like grains, d) ceramics with randomly oriented plate-like grains [36]**

The advantage of this method is reflected in the low cost due to the use of aqueous solutions, and the preparation of precursors at room temperature. Additionally, this method offers a good homogeneity and control of the composition. The dispersion of the constituent components in liquid precursor gives the opportunity to synthesize powders with submicron particles.

## IV. Modern approach to the processing of ceramics $BaBi_4Ti_4O_{15}$

According to the requirements of the different applications, the piezoelectric materials with Aurivillius type of structure were fabricated in different forms: bulk ceramics, single crystal and thick or thin film. Schematic presentation of single crystal, textured ceramics and ceramics with randomly oriented plate-like grains is shown in Fig. 7 [36]. The main difficulty for practical application of those materials is to obtain mechanically stable and dense ceramics [37].

Crystalline structure of Aurivillius type of compounds promotes a plate-like morphology, with platelets growing preferentially in the basal plane (*ab* plane). Typical microstructure of this kind of ceramics observed by SEM is given on Fig. 8. Properties of the polycrystalline materials are strongly affected by their microstructure, especially by the orientation of the plate-like grains and by the length to thickness ratio (aspect ratio) of the grains. In comparison with almost isotropic (cubic) structure of BT, PMN and PZT [38–40], intrinsic electrical properties of bismuth based compounds are anisotropic with the maximum value of conductivity and the major component



SEM MAG: 10.00 kx   DET: SE Detector
HV:  20.0 kV         DATE: 08/11/11   5 um
VAC: HiVac          Device: VEGA TS 5130MM   Digital Microscopy Imaging
Vega ©Tescan

**Figure 8. Typical microstructure of BBT ceramics with randomly oriented plate-like grains observed by SEM [23]**

of spontaneous polarization parallel to the $(Bi_2O_2)^{2+}$ layers [1].

By aforementioned conventional methods of synthesis, BBT ceramics with randomly oriented plate grains could be obtained. The materials with randomly oriented microstructure present several advantages over textured one. Firstly, the piezoelectric properties are homogeneous in any polarization direction; the second, the smaller cost because no sophisticated manufacturing methods are needed; the third no restrictions in the shape of the samples are imposed [3].

Because the crystal structure of BLSF is highly anisotropic, the properties of polycrystalline ceramics prepared by the conventional sintering method are lower than those of single crystal, and texturing is necessary for practical use. However, the properties of BLSF ceramics are worse than those of lead containing compositions due to an anisotropic nature of the crystal structure. Therefore, grain oriented BLSF ceramics seem to be a superior candidate for the lead-free piezoelectric materials. The degree of orientation of textured ceramics can be evaluated with various methods, but most frequently used is X-ray diffraction analysis method. Among them, the Lotgering factor (*LF*) proved to be of good use as a result of its easy calculation and the simplicity of the representation for the orientation degree. Lotgering factor (*LF*) can be obtained using the formula:

$$LF = \frac{p - p_0}{1 - p_0} \qquad (3)$$

where *p* denotes the ratio of the sum of the peak intensities corresponding to the preferred orientation axis to the sum of all diffraction peaks intensities in particle-oriented materials ($p = \Sigma I_{(00l)} / \Sigma I_{(hkl)}$) and $p_o$ is *p* of a material with a random particle distribution ($p_o = \Sigma I^o_{(00l)} / \Sigma I^o_{(hkl)}$). The *LF* varies between zero and unity; *LF* = 0 corresponds to random orientation, and *LF* = 1 to perfect orientation.

Several processing techniques can be used to obtain textured ceramics with a high degree of grain orientation. Texture engineering intends to enhance the performance of ceramics by controlling grain orientation. Texturing of polycrystalline materials is related to the mutual orientation of crystallographic planes or individual grains. Such materials exhibit a significant anisotropy of electrical conductivity along the *c* axis and in the *ab* plane. Common methods for obtaining textured ceramics are pressure-assisted sintering methods, so called *hot forging or hot pressing* and *casting method* (enabling preparation of ceramics with aligned grains).

Hot pressing and hot forging of Aurivillius compounds have been traditionally used to produce highly dense ceramics, where pressures and high temperatures are applied simultaneously [41,42]. Both processes occur within a die that gives shape to the final densified component.

However, more convenient preparation method of textured BLSF ceramics is the templated grain growth (TGG) method [43,44]. In this method, a mixture of large anisotropic (plate-like) template particles and small, equiaxed matrix particles is tape cast to form a green sheet, in which the plate-like particles are aligned with their plate faces parallel to the sheet surface [45]. The template content is kept below 10 vol.% to minimize the adverse effects of constrained sintering that larger template contents would incur. The template particles are oriented prior to sintering, typically by shear forming processes during forming. The resulting compact is sintered to densify the matrix, creating a favourable growth environment for the template particles. Additional heat treatment allows the templates to grow by consuming the randomly oriented matrix. The resulting microstructure has strong crystallographic texture (Fig. 9a) [46]. Figure 9b shows XRD of BBT patterns as an example of random and textured ceramics [44]. The

process of texturing, shown schematically in Fig. 9c, is simple for a wide range of systems [45].

Paper of Kimura and co-authors [47] deals with the effect of the templated and matrix particle sizes on the microstructure development of textured BBT. They prepared two kinds of equiaxed matrix particles and two kinds of plate-like template particles with different sizes. Powder mixture which contained 20 vol.% of template and 80 vol.% of matrix particles was mixed with a solvent (60 vol.% toluene – 40 vol.% ethanol), a binder (poly-vinyl butyral) and a plasticizer (di-n-butyl phthalater), and tape cast to form a sheet in which plate-like particles were aligned. The sheets were cut and laminated to form a green compact. The binders were burn out and then the compacts were sintered under various conditions. During sintering, the shape of matrix particles changed from equiaxed to plate-like at first stage. The presence of aligned template particles determined the orientation of plate faces of matrix particles by form-



a)



b)



c)
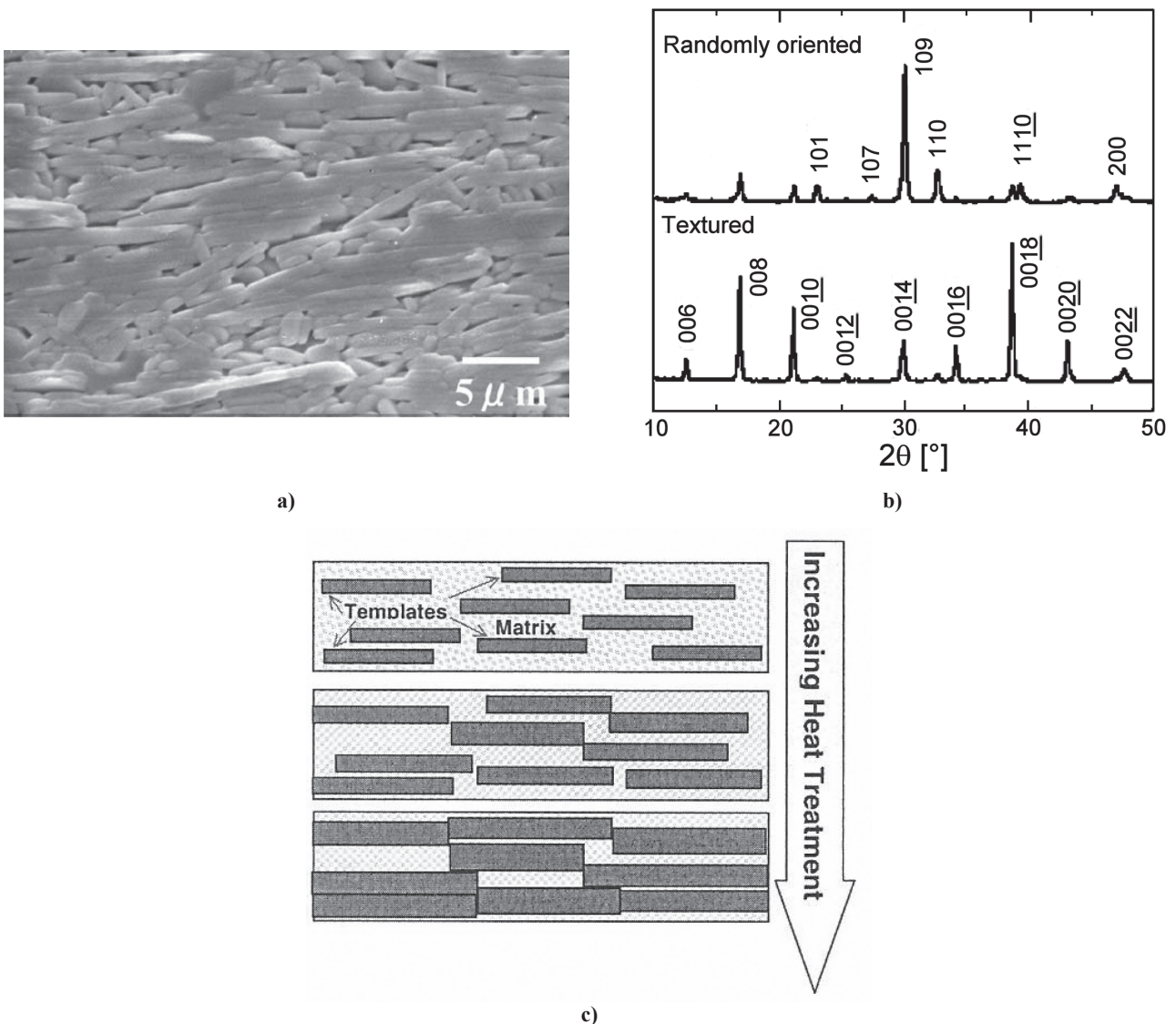
**Figure 9. Schematic presentation of: a) SEM image of textured ceramics with plate-like grains (the surface was thermally etched), b) XRD of random and textured BBT compounds, c) TGG method [44–46]**

ing "face-to-face contact" between template and matrix particles. The formation of "face-to-face contact" extended to the matrix; the contact was formed between matrix particles. Thus, the textured region was developed in the matrix phase at this stage. When the template size was small, the matrix particle size determined the extent of the "face-to face contact" formation. Prolonged heating at high temperature did not increase the degree of texture development to a considerable extent, but caused the growth of matrix grains in contact with large template grains, resulting in an increase in microstructural homogeneity. In the final stage, the grain size was determined by the size of template particles. The use of the $Bi_2O_3$ liquid phase did not alter the mechanisms of microstructure development; it only promoted the shape change of matrix particles.

A more sophisticated method for obtaining of crystal-oriented BBT ceramics, like the use of magnetic field, has been also reported [48]. In this study, BBT ferroelectric ceramics is fabricated by the two-step method involving particle alignment in the magnetic field and a subsequent reaction sintering. In the first step, a mixed slurry containing BiT and $BaTiO_3$ (BT) powders was set in the magnetic field (plastic container was placed horizontally in a superconducting magnet). The container was continually exposed to a magnetic field (10 T) for 1 day at room temperature until the slurry was completely dried. The powder compact had *a*- and *b*-axis-oriented BiT particles and randomly oriented BT particles. It was shown that $BaBi_4Ti_4O_{15}$ ceramic with *a*- and *b*-axis orientation can be obtained via the reaction sintering of BiT and BT:

$$Bi_4Ti_3O_{12} + BaTiO_3 = BaBi_4Ti_4O_{15} \qquad (4)$$
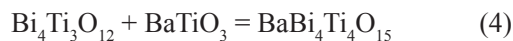
after sintering above 1120 °C.

## V. Ferroelectric, electric and piezoelectric properties of $BaBi_4Ti_4O_{15}$

As we already mentioned, BBT is good candidate for replacing lead based materials for many electrical applications as lead is going to be banned across Europe in all industrial applications in the nearest future. A great challenge exists on how to replace PZT with less toxic, more environmentally friendly materials, and the same time keeping the performance comparable with PZT. Generally, main problem in application of bismuth based ceramics for many devices is their high electrical conductivity in the *ab* plane, which makes the poling of the ceramics difficult. This conductivity is an electronic p-type, where oxygen vacancies are main conduction species in bismuth layered compounds [1,49]. Conductivity of the grains is the highest in the plane of the layers while the piezoelectric properties are high along the polarization direction and small or zero in the direction perpendicular to the plane of the layers [36].

$BaBi_4Ti_4O_{15}$ ceramics at room temperature exhibit ferroelectric properties. The existence of spontaneous polarization leads to the formation of hysteresis loop in alternating fields of high intensity. The polarization versus electric field (*P-E*) of BBT ceramics obtained by the standard solid-state reaction method with the 8 MV/m applied electric field at room temperature was shown in Fig. 10. It can be seen that the capacitor exhibits a ferroelectric hysteresis with a remanent polarization of 5.4 $\mu C/cm^2$ and a coercive field of 4.03 MV/m [26].

Generally, ferroelectric materials can be classified into three groups based on their dielectric, polarization and phase transition behaviour: normal ferroelectrics, ferroelectric with diffuse phase transition and relaxor ferroelectrics. Ferroelectric materials with diffuse phase transition (DPT) characteristics and/or relaxor properties have been extensively studied in the last few decades mainly due to their very interesting and still not completely explained physical properties [50–52]. $BaBi_4Ti_4O_{15}$ belongs to group of relaxor materials. A generic feature of relaxors is a broad maximum in temperature dependence of the dielectric permittivity, whose position, $T_m$, is shifted to lower temperatures as the frequency of the probing field decreases. Different models are proposed to explain the relaxor ferroelectric behaviour and it is generally difficult to model and understand these dynamic relaxations in solid state materials [53]. In the BLSF family, most of the members exhibit normal ferroelectric behaviour while only a few compounds, such as $BaBi_2Nb_2O_9$, $BaBi_2Ta_2O_9$, $BaBi_4Ti_4O_{15}$ etc, compounds display relaxor behaviour [27,54–56].

Typical dielectric response of *BBT ceramics* is shown in Fig 11. [57]. The dielectric constant (ε) and loss tangent (tanδ) as a function of temperature are determined during cooling in frequency interval between 1.21 kHz and 1 MHz. As the frequency increased, the dielectric maximum shifted to higher temperature (from 660 K to 678 K) and the dielectric constant became smaller (from 2458 to 1951). The degree of relaxation behaviour, obtained by $\Delta T_{relaxor} = T_{m(1\,MHz)} - T_{m(1,2\,kHz)}$ is found to be 18
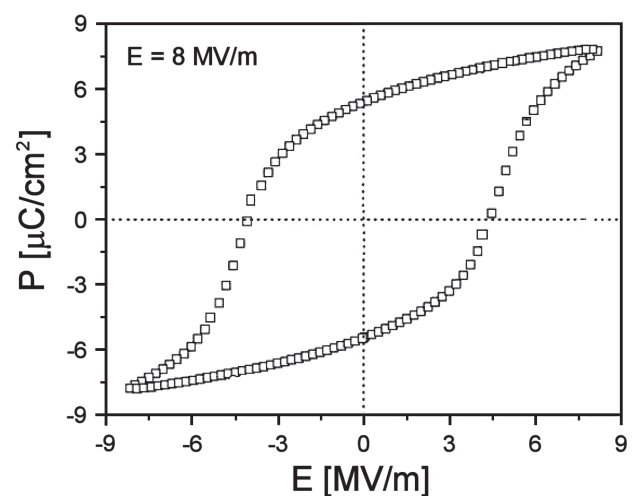


**Figure 10. The polarization versus electric field (*P-E*) of BBT specimen [26]**

K. The shift of $T_m$ with frequency is comparable with $\Delta T_{relaxor}$ of perovskite relaxor where the degree of relaxation is ~20 K and ~14 K in PMN and PLZT(8/65/35) ceramics [58,59]. Similar to materials with the perovskite structure, the relaxor behaviour in the BLSF compounds is attributed to a structural disorder. The loss tangent of BBT ceramics is very low at room temperature (about 0.03) and almost constant from room temperature to 200 °C and thereafter increases with temperature. Table 1 resumes some of the properties of BBT compounds in different forms.

Irie *et al.* [60] evaluated the ferroelectric properties of *BBT single crystals* on the basis of the saturated hysteresis loop, in which the remanent polarization and the coercive field are in the saturated state, applying $E_m = 5.6$ MV/m. The results are presented in Table 1. BBT single crystal was grown from the melt of stoichiometric mixture of $Bi_2O_3$, $BaCO_3$ and $TiO_2$ by slow cooling with a vertical temperature gradient of 2–3 °C/min. The saturated remanent polarization was enhanced in comparison with ceramics samples. The absence of remanent polarization in crystals along the *c*-axis was confirmed. The authors were also investigating the temperature dependence of the relative dielectric permittivity of BBT single crystals at $f = 1$ MHz in the temperature range of 25 °C to 800 °C (Table 1). They found that $\varepsilon_{a,b}/\varepsilon_c = 9$ at room temperature and $\varepsilon_{a,b}/\varepsilon_c = 53$ at Curie temperature. This indicates a large anisotropy of the electrical properties of $(Bi_2O_2)^{2+}$ layer that acts as paraelectric layer in Aurivillius type of structure.

Kobayashi and co-authors [61,62] were investigating dielectric and ferroelectric properties of superlattice-structured $Bi_4Ti_3O_{12}$–$BaBi_4Ti_4O_{15}$ ($n$ = 3–4) single crystals and ceramics and compared it with those of $Bi_4Ti_3O_{12}$ and $BaBi_4Ti_4O_{15}$. It has been widely known that BiT has the largest $P_s$ among the BLSFs ($P_s$ = 46 $\mu C/cm^2$) [63], and that the $P_s$ of BBT (~ 15 $\mu C/cm^2$) is much smaller. If the intrinsic ferroelectric distortions in BiT and BBT were maintained in the superlattice structure, the $P_s$ of BiT–BBT would be the average of those for BiT and BBT. However, the $P_s$ observed for the BiT–BBT crystals is much larger than the average $P_s$. The enhanced $P_s$ of the BiT–BBT crystals implies that the lattice strain induced by the alternate stacking of $n$ = 3 and $n$ = 4 layers with different cell size promotes ferroelectric distortion. The $P_s$ of the BiT–BBT crystals along the $a(b)$-axis was 52 $\mu C/cm^2$, which is larger than those of BiT and BBT crystals. It is suggested that the Bi substitution at the Ba site and the local symmetry breaking of the $(Bi_2O_2)^{2+}$ layers are partially responsible for the larger $P_s$ of BiT–BBT.

As it was already mentioned, *textured BBT ceramics* have been fabricated by TGG method up to now, but dielectric and ferroelectric properties of obtained ceramics have not been reported jet. However, Swartz and co-authors [64] have shown that in textured bismuth titanate ceramics with 98% of grain orientation, the conductivity in *ab* plane is one order of magnitude higher than in the *c*-axis direction (in the temperature range 500–700 °C). This anisotropy in conductivity is slight-

**Table 1. Dielectric parameters for BBT ceramics, single crystal and thin films [26,57,60,65–67]**

| Sample | Orientation | $\varepsilon_{RT}$ (at 1 kHz) | $\varepsilon_m$ | $T_m$ [°C] | $P_r$ [$\mu C/cm^2$] | $E_c$ [MV/m] | $E_m$ [MV/m] |
|---|---|---|---|---|---|---|---|
| BBT-SS ceramics | random | 205 | 2429 | 415 | 5.4 | 4.03 | 8 |
| BBT single crystal | *ab*-axis | ~1000 | 8000 | 410 | 14.8 | 3.2 | 5.6 |
| | *c*-axis | 110 | 150 | 410 | - | - | - |
| BBT thin films | *a*-axis | 380 | - | - | 2 | 6 | - |



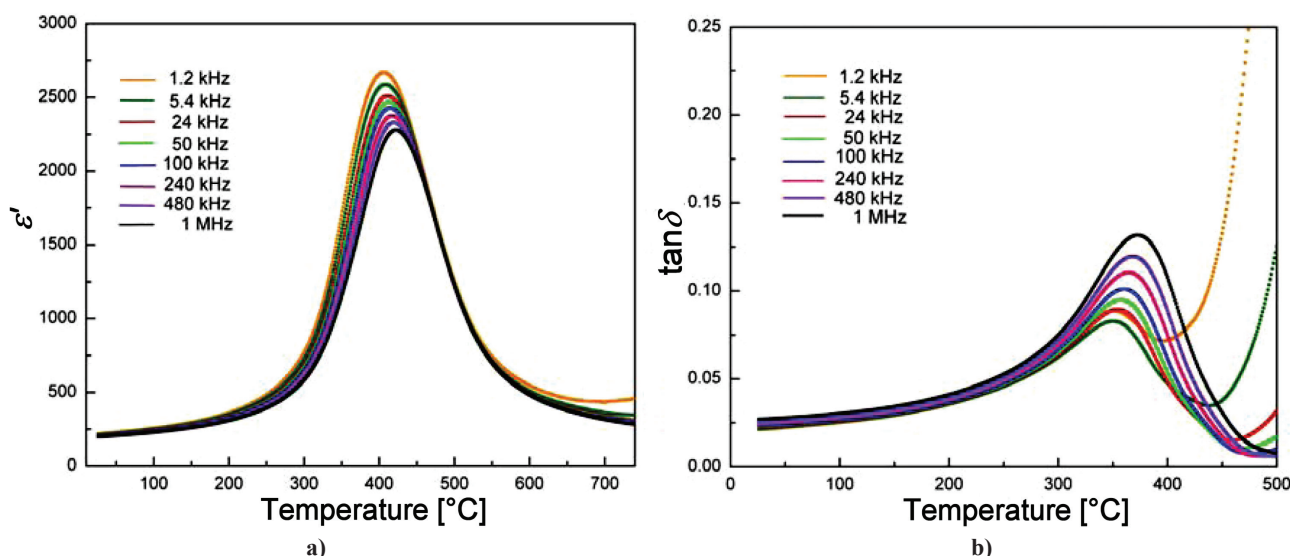a)                                                                                b)

**Figure 11. Dielectric constant (a) and dielectric loss (b) as function of temperature for BBT ceramics at different frequencies [57]**
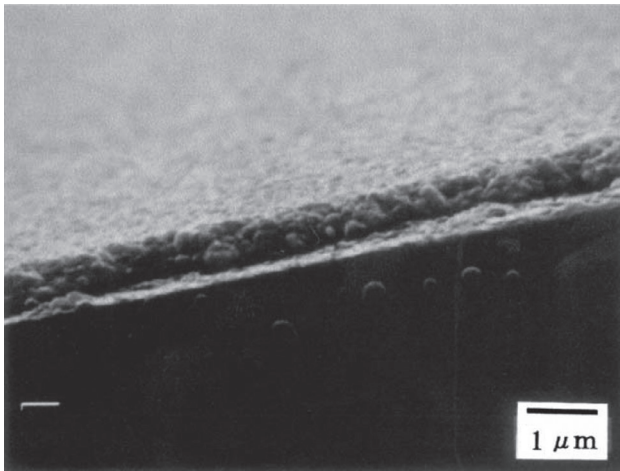
**Figure 12. SEM picture of the cross-section of the BaBi$_4$Ti$_4$O$_{15}$ film deposited on Pt/Ti/SiO$_2$/Si substrate via non-repetitive, single step deposition [67]**
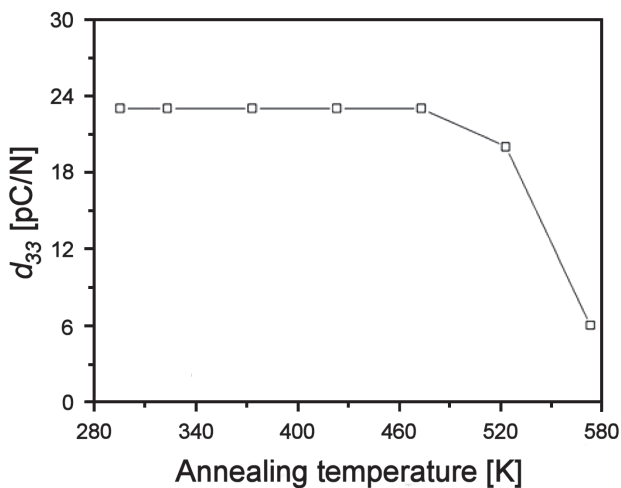


**Figure 13. The annealing temperature dependence of piezoelectric coefficient ($d_{33}$) for BBT specimen [26]**

ly less present in single BLSF crystals than in textured ceramics [65]. Undesirable feature of textured ceramics is that the polarization and electrical conductivity reach maximum values in the same, *ab* direction.

In *hot forged ceramics*, in which there is preferential grain growth along the axis of compaction, the dielectric permittivity shows anisotropic properties and depends on the direction of pressing. The measured values of dielectric permittivity at room temperatures, parallel and perpendicular to the direction of hot forging are $\varepsilon(\parallel) = 200$, $\varepsilon(\perp) = 110$ [41].

Several authors investigated the properties of *BaBi$_4$Ti$_4$O$_{15}$ thin film* [65–67]. Satyalakshim [65] reported on the orientation-dependent ferroelectric properties of strongly oriented BBT thin films on conduction epitaxial LaNiO$_3$ electrodes grown by pulsed laser deposition. Saturated ferroelectric hysteresis loop with $P_r$ of 2 μC/cm$^2$ and $E_C$ of 6.0 MV/m has been obtained for the regions with *a*-oriented crystallites, whereas per-

fect *c*-axis oriented regions exhibit linear *P-E* curves. They concluded that macroscopic ferroelectric properties of these layer-structured oxide thin films strongly depend on the crystalline orientation of the films. Ferroelectric domain structure of epitaxial BaBi$_4$Ti$_4$O$_{15}$ thin films with different orientations has been imaged for the first time at nanometer scale by Harnagea and co-authors [66]. Ferroelectric domains, as small as 150 nm in lateral size, were switched within single crystallites. They confirmed absence of ferroelectricity along the *c*-axis (no piezoelectric activity) evidencing the fact that in BBT the spontaneous polarization is confirmed in the *ab* crystallographic plane.

Dielectric constant and loss tangent of BBT thin films was investigate by Kozuka and co-authors [67] showing higher values of dielectric constant at 1 kHz ($\varepsilon = 380$) at room temperature compared to conventionally sintered polycrystalline ceramics [27,34,58]. SEM picture of cross-section of obtained BBT film was shown in Fig. 12 [67].

Very little is known about the piezoelectric properties of BBT ferroelectric ceramics. As it has been already mentioned, the bismuth-based layered compounds present a relatively high electrical conductivity in the *ab* plane, which makes the poling of the ceramics difficult and therefore the existence of piezoelectric response. Improving the piezoelectric response of Aurivillius compounds implies the design of poling strategies that take into account the strength of the electrical field, the temperature and poling time. The annealing temperature dependence of the piezoelectric coefficient ($d_{33}$) of BBT specimen was shown in Fig. 13. Fang and co-authors [26] reported that the maximum value of $d_{33}$ was found to be 23 pC/N, which is higher than the reported $d_{33}$ values of other bismuth layer-structured ferroelectric ceramic systems (~ 5–19 pC/N) [3]. Reports on piezoelectric properties of BBT single crystal and thin films are still deficient.

## VI. Conclusions

The Aurivillius oxides family has attracted great interest in resent years due to their prospects as high temperature piezoelectric materials. BaBi$_4$Ti$_4$O$_{15}$ is a member of this large Aurivillius family of compounds with general formula (Me$_2$O$_2$)(A$_{n-1}$B$_n$O$_{3n+1}$). The room temperature crystal structure of BBT is orthorhombic (space group *A21am*) and transforms to a tetragonal structure at high Curie temperature of 417 °C. The most frequently used synthesis method for powder preparation are solid state reaction, mechanochemical method and wet chemical methods such as sol-gel, polymeric precursor method and coprecipitation method. Crystalline structure of BaBi$_4$Ti$_4$O$_{15}$ promotes a plate-like morphology, with platelets growing preferentially in the *ab* plane. Main problem in application of this compound for many devices is its high electrical conductivity,

which makes the poling of the ceramics difficult. Because of highly anisotropic crystal structure, the properties of polycrystalline ceramics prepared by the conventional sintering method are worse than those of single crystal, and texturing is necessary for practical use. In this paper we reviewed the dielectric and ferroelectric properties of polycrystalline and textured ceramics, thin films and single crystal of BBT compounds.

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