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Chapter 4

CURRENT PROGRESS IN SYNTHESIS AND PROPERTIES OF DOPED BISMUTH TITANATE FOR ADVANCED ELECTRONIC APPLICATIONS

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ABSTRACT

Lead-free bismuth-layered compounds have been widely studied as alternative materials for advanced electronics applications such as ferroelectric random access memories (FRAM), piezoelectric applications, electro-optic devices, micro-sensors, micro-electro-mechanical systems, actuators, transducers and capacitors. Lead-free bismuth-based materials have been chosen to overcome the toxicity issue produced from lead-based compounds. Various methods have been used to produce bismuth-layered compounds such as solid state reaction, hydrothermal, sol gel and soft combustion techniques. All of these techniques have advantages and disadvantages. In early stage, $Bi_4Ti_3O_{12}$ (BIT) has been widely studied. However, serious issues of low remanent polarization, high leakage current, low fatigue resistance and high processing temperature are obstacles to practical applications. Therefore, various dopants have been used to modify the properties. This review describes the progress in the synthesis of BIT using various methods. The effects of dopants on properties of BIT are also explained. Selected applications of the compounds are also discussed.

Keywords: Synthesis; Doping; A-site; B-site; Ferroelectric; Application; Properties.

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1. INTRODUCTION

Bismuth-oxide layered perovskite ferroelectric was discovered by Bengt Aurivillius in the late 1949 [1]. In many cases, all compounds which are derived from the general formula $(Bi_2O_2)^{2+}$ $(A_{x-1}B_xO_{3x+1})^{2-}$ are also known as Aurivillius compounds. Newnham et al. [2] claimed that more than 50 ferroelectrics belong to bismuth-based layered compounds and these could exist from one-layer structures to five-layer structures. Among these, bismuth titanate, ($Bi_4Ti_3O_{12}$ or BIT) is one of the interesting subjects for further discussion. As of today, BIT is described in several terms such as bismuth layered structure ferroelectric, bismuth-based ferroelectric compounds, perovskite-based layered structure or layered bismuth oxide [3, 4]. BIT is derived with respective element and value; $(Bi_2O_2)^{2+}$ $(A_{x-1}B_xO_{3x+1})^{2-}$ where A = Bi, B = Ti and $x = 3$ to become $(Bi_2O_2)^{2+}$ $(Bi_2Ti_3O_{10})^{2-}$, which also corresponds the basic structure of BIT [5-9]. The layered structure of BIT is characterized by the perovskite-like $(Bi_2Ti_3O_{10})^{2-}$ layers sandwiched between $(Bi_2O_2)^{2+}$ layers along its crystallographic c-axis. BIT has a strong anisotropic property with the lattice constant, *c*-axis larger than *a*- and *b*-axes. Based on this, the lattice parameters of BIT can be written a = 5.450 Å, b = 5.4059 Å and c = 32.832 Å, and $\beta = 90.01\ ^{o}$.

There is some misunderstanding in the crystal structure of BIT. In previous reports, BIT has a monoclinic system, *Pc*, but in practice the structure is often regarded as orthorhombic as the β-angle is very close to 90^{o} [2, 10]. In contrast, Kim and Jeon [11] reported that the monoclinic system is more suitable than the orthorhombic structure at room temperature. In addition, BIT then turns into tetragonal above the Curie temperature [12]. To date, there are a lot of discussions on this particular compound which the improvement has been extensively carried out towards the development for ferroelectric and piezoelectric applications [13-17].

2. PROPERTIES OF BIT CERAMICS AND THIN FILMS

In general, BIT is known to have several outstanding electrical properties. The specific value for each property is different from one to another due to the differences in processing method, materials sources, and environment. However, most researchers agreed that BIT has high remanent polarization (P_r), low coercive field (E_c), high dielectric constant (ε_r), low dielectric loss (tan δ), high Curie temperature (T_c), high breakdown strength, stable piezoelectric response, etc. With this regard, BIT has been used as essential ceramics and films for ferroelectric random access memory (FRAM) and high-precision piezoelectric applications, micro-electromechanical system (MEMS), tunable high-frequency devices, and integrated photonics, optical displays and pyroelectric devices [4, 18-21]. In addition, the use of such technologies is safe since BIT is a lead-free material.

BIT has been widely prepared either in bulk ceramics or thin films using various methods. Bulk BIT has been produced using conventional ball milling, mechanical activation, sol-gel, hydrothermal, molten salt synthesis, chemical synthesis, precipitation, citrate, urea, self-propagation high temperature synthesis, metalorganic decomposition, microemulsion methods etc. [6, 7, 9, 12, 14, 15, 18-20, 22-65]. On the other hand, BIT thin film has been deposited using chemical vapor deposition (CVD), metal-organic chemical vapor deposition

(MOCVD), chemical solution deposition (CSD), rf magnetron sputtering, spin-coating technique, sol-gel, polymeric precursor method etc. [13, 66-89].

The conventional ball milling or mixed oxide route often results in high agglomeration and compositional inhomogeneity of powders because of high calcination temperature and repeated grinding. Consequently, the sinterability of BIT derived from the conventional solid-state reaction is poor [19, 29]. As an alternative, several methods from mechanosynthesis and wet-chemical synthesis have been used to solve the conventional issues.

The mechanical activation method is superior compared to the conventional solid-state reaction for several reasons. This technique uses low-cost and widely available oxides as starting materials and skips the calcination step at an intermediate temperature, leading to a simplified process. Furthermore, the mechanically derived powders have higher sinterability than those powders synthesized by the conventional ball milling [22, 30-33, 38, 39]. In addition, the wet chemical synthesis is described into several ways such as sol-gel, hydrothermal, molten salt, chemical synthesis, precipitation, microemulsion methods and etc. These methods are beneficial to reduce the calcination temperature. In addition, these methods lead to improvement in the reactivity of the raw materials and homogeneity of the composition, leading to a decrease in the calcination temperature [23].

Deposition process of thin film is generally divided into two major process; physical vapor deposition (PVD) and chemical vapor deposition methods (CVD). CVD is favourable owing to its capability to produce a high quality thin film compared to PVD. Commonly used techniques for depositing ferroelectric thin films including metal organic chemical vapor deposition (MOCVD), sputtering, and sol-gel methods. Each technique has merits and drawbacks. For instance MOCVD can be used for large-scale production, but elevated growing temperature is required for cracking the metal-organic (MO) source. Sol-gel method is the simplest method to produce thin films. Sol-gel process involves hydrolysis and polycondensation of relevant molecular precursors. Sol-gel method also offers several advantages including pre- and post-deposition at low temperature, easier compositional control and better uniformity of the films, economical compared to CVD and PVD techniques [81].

Regardless of the method by which they are formed, the process must be economical and the resulted doped BIT must exhibit the following characteristics: (a) high degree of crystallinity and purity, (b) narrow particles size distribution, (c) controlled composition stoichiometries, (d) good electrical properties, (e) excellent adhesion and (f) good deposition coverage. Table 1 shows the comparison of processing parameters from BIT ceramics which were prepared by various methods.

Subbarao [6, 9] prepared the BIT ceramics using the solid state reaction and sintered from 1000 to 1250°C to achieve the theoretical density of about 80%. Macedo et al. [40, 91, 92] reported that the laser sintered BIT ceramics reach 98 to 99% density at significantly lower temperature than that registered for typical conventional process. In their works, the samples were heated up to 350°C at a heating rate of about 50°C min^{-1} with maximum power, $P_{\max}$ 10 to 30 W. Watcharapasorn et al. [48] sintered the BIT samples at 1150°C at various sintering times; 4, 10, 24 and 48 h. It was found that the relative density (91 – 94 %) did not vary much with sintering time. According to Kong et al. [38] the reduction in density is believed to be a result of the formation of the plate-like grains. Additionally, high density is needed to produce a better remanent polarization, P_r with low coercive field, E_c. Macedo et al. [40, 92] claimed that P_r was significantly increased with increasing density, reaching $P_r = 6.5$

μC/cm^2. Moreover, the variation in microstructure and grain size is an important factor to determine other electrical properties such as dielectric constant, dissipation factor, piezoelectric coupling coefficient, pyroelectric coefficient, electrical conductivity and so forth.

Table 1. Comparison of processing parameters from BIT ceramics prepared by various methods

Methods	Calcination, °C	Sintering, °C	Density, %	Remanent polarization, Pr (μC/cm2)	Coercive field, Ec (kV/cm)	References
Conventional	750-800	1000 - 1250	80 - 99	5 – 6.5	3 – 23.5	[6, 9, 40, 48, 90-92]
Mech. Act	*1-20 h	750 - 1100	98	0.23	1.8	[22, 31-34, 38, 39, 50, 53, 63]
Sol-gel	300-750	950 - 1150	-	-	-	[23, 41, 57]
Hydrothermal	150-240	800 - 1000	90 - 95	-	-	[24, 26, 29, 37, 44, 49, 93]
Molten salt	600-1100	-	-	-	-	[25, 27]
Chemical syn.	400-900	850 - 1100	93 - 96	-	-	[12, 36, 54]
Precipitation	500-900	900 - 1000	-	-	-	[14, 35, 52]
Microemulsion	800	-	-	-	-	[28]
Combustion	650 – 1000	1050	98	-	-	[51, 61]

*milling duration.

Kong et al. [38] obtained the large P_r (24 μC/cm^2) and low E_c (11 kV/cm) for BIT ceramics with better density of 98% after low temperature sintering at 850°C for the powder derived from mechanical activation technique. Stojanovic et al. [43, 53] reported that the BIT powder can be directly synthesized using high impact milling for about 3 to 12 hours and then sintered at 1000°C for 2 h. Lazarevic et al. [30-34] also reported that similar observation was found in their study on mechanically activated BIT powder. Han et al. [39] stated the formation of BIT phase is highly dependent on the processing parameters particularly the impact energy or milling intensity. Zdujic et al. [63] reported that a mixture of α-Bi_2O_3 transformed to $Bi_2O_2CO_3$ at a milling intensity of ~ 0.49 W/g, which in turn was converted directly into a nanocrystalline BIT phase when the intensity was increased to ~ 2.68 W/g.

For the wet chemical synthesis, a number of authors discussed the properties of BIT synthesized powders. Du et al. [23, 57] used the sol-gel route to synthesize the nanoplate-like BIT powders. They found that BIT began to crystallize before 450°C according to thermal analysis and X-ray diffraction (XRD) patterns. Shi et al. [24] reported that BIT fine powders can be synthesized by hydrothermal method at 240°C. They also added that the formation of BIT is dependent on the content of mineralizer KOH, the molar ratio of Bi/Ti, reaction time and temperature. Pookmanee et al. [37] stated that the single phase and the particles size of hydrothermally derived BIT fine powders increased with increasing reaction time, as shown in Fig. 1. Yang et al. [29] reported that the crystallinity and the particle size of BIT powders increased with rising reaction temperature and time. Kan et al. [27] studied the molten salt synthesis method to produce BIT platelets in NaCl-KCl and Na_2SO_4-K_2SO_4 fluxes. They found that the calcination temperature of BIT was influenced by homogeneity of the starting materials. Additionally, the crystallization behavior and particles morphology of BIT showed a strong dependence on the types of the salt flux used.

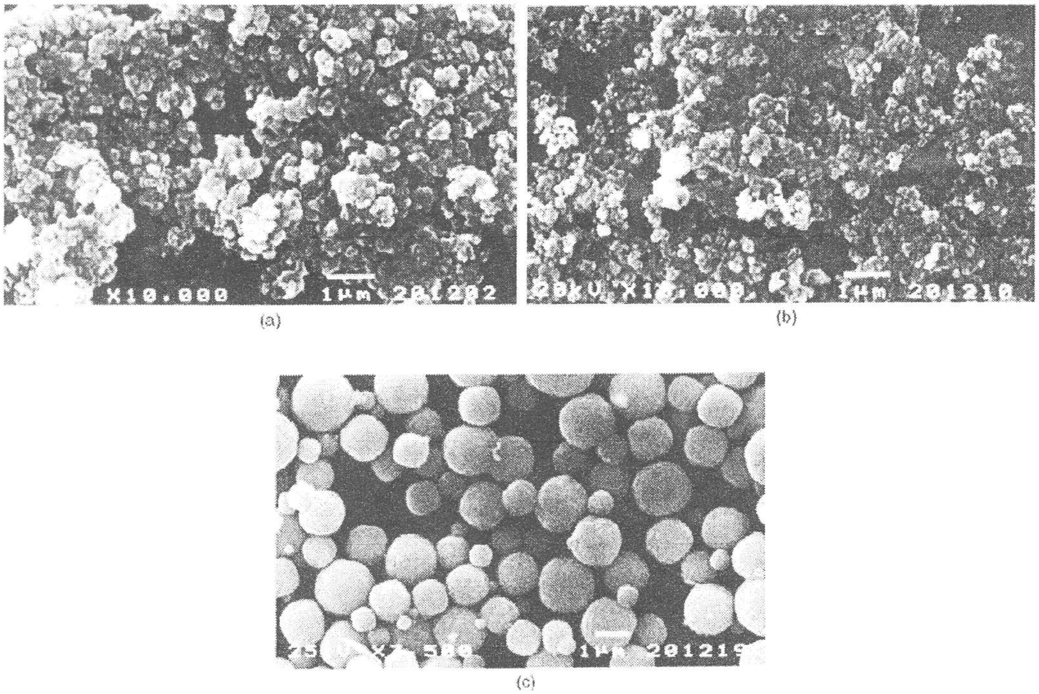

Figure 1. SEM micrographs of BIT powders synthesized by the hydrothermal process at 150°C at different reaction times of (a) 5 h, (b) 10 h, and (c) 15 h [37].

Pookmanee et al. [12] successfully prepared the BIT micro-particles powder using a chemical co-precipitation route with subsequent calcinations process at 500 to 700°C. They found that the average grain size increased with increasing calcination temperature. Pookmanee et al. [36] claimed that BIT single phase was only obtained at 900°C with oxalic acid added. Zhi-hui et al. [54] reported that dispersion of BIT nanopowders was improved by azeotropic co-precipitation method. Xie et al. [28] compared the particulate properties of BIT derived from co-precipitation method and microemulsion method. They found that the microemulsion method exhibits a narrow size distribution with average particle size of about 35 nm, while co-precipitation method exhibits a wide size distribution with large particle size. Macedo et al. [48, 58] reported that self-propagation high-temperature synthesis (SHS) is beneficial to reduce the processing time in short period. Additionally, the properties of BIT derived from SHS are comparable to that observed for the conventional solid-state reaction.

The physical and ferroelectric properties of BIT thin films are listed in Table 2. A variety of deposition techniques, including sol-gel, metal organic deposition (MOD), rf sputtering, chemical solution deposition (CSD) and polymeric have been used to synthesize BIT films. In general, the deposition technique affects the properties of BIT thin films. As shown in Table 2, the annealing temperature to form crystalline film was in the range of 500 to 700°C, which is lower than the sintering temperature of BIT ceramic. It is essential to obtain the lowest possible processing temperature to comply with silicon technology and to retain the resistance of films. Another important parameter is film thickness whereby it is influenced by several factors such as spin coating parameters, the properties of precursor solution, the deposition temperature and so forth.

Table 2. Physical and ferroelectric properties of BIT thin films

Deposition technique	Substrate	Annealing, °C	Thickness, nm	Remanent polarization, P_r ($\mu C/cm^2$)	Coercive field, E_c (kV/cm)	References
Sol-gel	Pt/Si	600	400	5	45	[81]
	$Si/SiO_2/Ti/Pt$	700	400	11	160	[82]
	$Pt/Ti/SiO_2/Si$	700	150 - 1000	8 – 13.5	60 - 129	[78, 79]
	Si, Pt/Si	600	400	-	-	[83]
	$Pt/TiO_x/SiO_2/S$	-	300 - 400	-	-	[94]
	Si	600	200	-	-	[76]
MOD	Pt	450	130	15.6	-	[13]
Sputtering	ITO/glass	610 - 700	300 - 700	3.7 - 9.2	50 - 82	[70, 80]
	Si	500	-	2.4	2.3	[69, 74]
CSD	$LaNiO_3/Si$	690	600	7.1	11.27	[88]
Polymeric	$LaNiO_3/SiO_2/Si$	700	300	10	2.3 V	[71]
	$RuO_2/SiO_2/Si$	700	300	15	1.6 V	[71]
	$Pt/Ti/SiO_2/Si$	700	300 - 407	8.5 – 23.7	3.1 V	[68, 71]
	$Pt/Ti/SiO_2/Si$	700	290 (staticair) 240 (oxygen)	15 9	60 40	[75]

Simões et al. [71] investigated the properties of BIT thin films which were deposited on different substrates. They found that substrate with bottom electrodes from $LaNiO_3/SiO_2/Si$ and $RuO_2/SiO_2/Si$ exhibit better ferroelectric properties, high remanent polarization, low drive voltage and good fatigue endurance. For the films deposited on $Pt/SiO_2/Si$ substrates the remanent polarization was low due to stronger contribution of the grain orientation in the *c*-axis direction.

Additionally, the grain orientation of films was influenced by annealing temperature [68]. The grain orientation of sol-gel derived films is highly dependent on precursor type, solution synthesis method, film composition, annealing temperature, heat treatment, films thickness and substrates [94].

Kong et al. [78] pointed out that ferroelectric properties are affected by several factors such as grain orientation, properties of the substrate and film thickness. Xu et al. [79] reported that the increase in excess Bi concentration showed a significance increase on the 00*l* and 020/200 crystalline orientation and grain growth. However, the comparison values of P_r, E_c and fatigue behavior with different Bi concentration were not reported.

Simões et al. [75] reported that the BIT thin films annealed at different atmosphere also can influence the ferroelectric properties of films. They found that the films annealed in static air were better than the films annealed in oxygen atmosphere.

3. PROPERTIES OF DOPED BIT

There are several reasons why BIT requires further improvement especially for ferroelectric properties. Based on previous reports, BIT has critical drawbacks on its ferroelectric properties such as high leakage current and domain pinning which leads to small remanent polarization and low fatigue endurance [95-98]. All of these limitations are closely related to the vacancies left by Bi^{3+} ions in their structures due to volatilization effect. These can be improved effectively by doping with impurities. The so-called ion doping technique is believed to be an effective method to improve the ferroelectric properties of BIT [99]. Through this way, BIT doped materials have better chemical stability of the adjacent oxide ions and reduces the concentration of oxygen vacancies [100]. As mentioned earlier, BIT with general formula of $(Bi_2O_2)^{2+}(A_{x-1}B_xO_{3x+1})^{2-}$, where A = Bi; B = Ti, x is the number of BO_6 octahedra in the pseudo-perovskite block ($x = 3$). The ion doping can be performed at A-site, B-site and A- and B-sites.

3.1. Ion Doping on A-Site

In $Bi_4Ti_3O_{12}$ or BIT, the Bi^{3+} ions can be partially substituted by other elements to enhance the ferroelectric properties. In this regard, the lanthanide elements such as lanthanum (La^{3+}), cerium (Ce^{3+}), praseodymium (Pr^{3+}), neodymium (Nd^{3+}), samarium (Sm^{3+}) and gadolinium (Gd^{3+}) ions have been used as the doping elements in BIT materials. Lanthanide doped BIT has been prepared using the conventional solid-state reaction [90, 101-107], sol-gel method [98, 108-117], hydrolysis method [118, 119], polymeric precursor method [120, 121], chemical solution deposition (CSD) [122-125], metal organic solution decomposition (MOD) [95, 126-130], pulsed laser deposition (PLD) [131], and metalorganic chemical vapor deposition (MOCVD) [132].

The ferroelectric properties of doped BIT ceramics at A-site prepared by the conventional solid-state reaction are listed in Table 3. The effects of La dopants on the ferroelectric properties of BIT was studied by Noguchi et al. [100]. La doping was found to be an effective way to reduce the oxygen vacancies and electron holes. Additionally, the remanent polarization of ceramics can be improved with high-pressure oxygen annealing. Chon et al. [133] investigated the effect of La content in BIT on the grain orientation and ferroelectric properties. It was found that the films with La = 0.85 exhibits large remanent polarization with strong grain orientation in c-axis. The fatigue endurance was also improved with La doping.

Kim et al. [90] studied the effect of Nd doping on the crystal structure, dielectric, ferroelectric and other electrical properties. They found that the Nd doping exhibits small grain size, high dielectric constant, low dissipation factor, large remanent polarization, P_r and low conductivity. Mao et al. [104] claimed that maximum remanent polarization, P_r was reached with a certain Nd doping. However, the increase in Nd content in BIT showed the increase in coercive field, E_c and decrease in Curie temperature, T_c as well as decrease in dissipation factor. The improved properties are associated to the decrease of the oxygen vacancy concentration and the increase of mobility of domain wall. Chen et al. [103] studied the effect of Sm doping on the ferroelectric properties and microstructures of BIT. The maximum remanent polarization, P_r of about 16 μC/cm^2 and minimum coercive field, E_c of about 70 kV/cm was obtained for Sm = 0.8. Additionally, the Curie temperature, T_c was also low with Sm doping.

Table 3. Electrical properties of doped on A-site BIT ceramics using the conventional solid state reaction

Compound	Sintering temperature, °C	Dielectric constant, ε_r	Remanent polarization, P_r (μC/cm^2)	Coercive field, E_c (kV/cm)	Fatigue cycle	References
$Bi_{4-x}La_xTi_3O_{12}$	800 - 1310	101-391	5 – 36	30 - 50	6.5 x 10^{10}	[100, 133-137]
$Bi_{4-x}Nd_xTi_3O_{12}$	950 – 1200	140 - 180	5.5 – 29	24 - 45	-	[90, 96, 104, 138, 139]
$Bi_{4-x}Sm_xTi_3O_{12}$	1100	270	16	70	-	[103]

Table 4 shows the electrical properties of various doping on A-site in BIT thin films. In comparison to Table 3, the annealing temperatures of thin films are much lower than the sintering temperature of ceramics. In comparison to Table 2, the ferroelectric properties of doped BIT thin films are much better than that of BIT thin films. According to significant findings by Park et al. [156], the La doping in BIT thin films exhibits better fatigue endurance than lead zirconate titanate, PZT and lower deposition temperature than strontium bismuth tantalite, SBT.

Bae et al. [98] found that La doping in BIT (La content = 0.75) thin films deposited on Pt/Ti/SiO_2/Si substrate using sol-gel spin coating had grain orientation in *c*-axis that was strongly dependent on the annealing temperature, as shown in Figure 2. The films thickness of La doping was about 400nm at annealing temperature of 650°C. Additionally, the remanent polarization, P_r, coercive field, E_c and fatigue endurance of La-doped BIT films were about 35 μC/cm^2, 66 kV/cm and 4.5 x 10^{10} read/write cycles.

Simões et al. [121] studied the La doping in BIT with various La content (0, 0.25, 0.5, 0.75) in BIT thin films deposited on Pt/Ti/SiO_2/Si substrates using a polymeric precursor solution and spin coating method. They observed the change in grain morphology with La doping. The remanent polarization of La doping was better than that of pure BIT. Simões et al. [140] also found that the La doping improved the leakage current densities. The dielectric and ferroelectric properties of the La-doped BIT thin films were reported strongly affected by pH of the solution [141]. The La doped BIT obtained from acid solution and basic solution showed elongated grains around 200 nm in size and spherical grains around 100 nm in size, respectively.

Kao et al. [142] compared the properties of La-doped BIT thin films which were annealed using the conventional thermal annealing (CTA) and rapid thermal annealing (RTA). It was found that the crystallinity, structure, ferroelectric and leakage current properties of films were strongly dependent on the heating rate of the annealing process. The RTA process showed excellent ferroelectric properties with small leakage current density compared to the CTA process, as shown in Figure 3.

Table 4. Electrical properties of various doping on A-site BIT thin films

Compound	Film thickness (nm)	Annealing temperature, °C	Dielectric constant, ε_r	Remanent polarization, P_r ($\mu C/cm^2$)	Coercive field, E_c (kV/cm)	Fatigue cycle	Refs
$Bi_{4-x}La_xTi_3O_{12}$	320	700	148	20.3	0.99V	-	[140]
	208 - 216	700	83-158	20.6-21.5	0.66-1.09V	-	[121]
	275-418	700	-	15-20.2	1.35-1.69V	-	[141]
	400	650	-	35	66	4.5 X 10^{10}	[98]
	50-500	700	230-280	18-25	52-63	10^8	[142]
	200	750	-	3-9	3.5-4V	10^9	[143]
$Bi_{4-x}Nd_xTi_3O_{12}$	280 – 300	650	395	10 – 50	60 – 100	4.5 x 10^{10}	[144]
	300	650	-	35	-	-	[95]
	20	680	-	19	-	-	[124]
	120	750	-	22	80	10^{11}	[145
	500	700	-	60	150	-	[116]
	600	750	343, a-axis 331, random 218, c-axis	19.5 10 6.5	108 95 108	- - -	[115] [115] [115]
	500	600	-	32	73	10^{10}	[146]
	295	-	177	8.8	86	1.44 x 10^{10}	[131]
$Bi_{4-x}Sm_xTi_3O_{12}$	500	700	-	-	-	-	[127
	280	680	387	29.5	110	4.5 x 10^{10}	[147]
	500	700	-	-	-	-	[128]
	370	750	202	15.7	-	-	[125]
$Bi_{4-x}Pr_xTi_3O_{12}$	500-680	650-700	-	31	102	1.5 x 10^{10}	[148], [149], [150]
$Bi_{4-x}Y_xTi_3O_{12}$	700	800	-	29	58	10^8	[153]
	300-400	700	-	10	-	10^{10}	[154]
	450	700 750	-	16 7.5	140 -	- 10^{10}	[153]
$Bi_{4-x}Ce_xTi_3O_{12}$	220	700	-	9.9	179	7 x 10^9	[154]
$Bi_{4-x}Gd_xTi_3O_{12}$	360	700	468	37.5	136	4.5 x 10^{10}	[155]

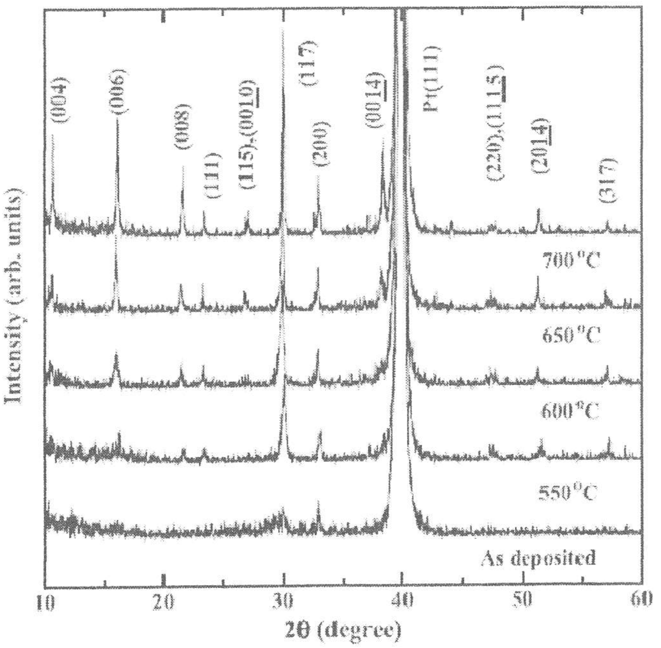

Figure 2. X-ray diffraction patterns of the BLT thin films annealed at different temperatures ranging from 550 to 700°C for 30 min in oxygen [98].

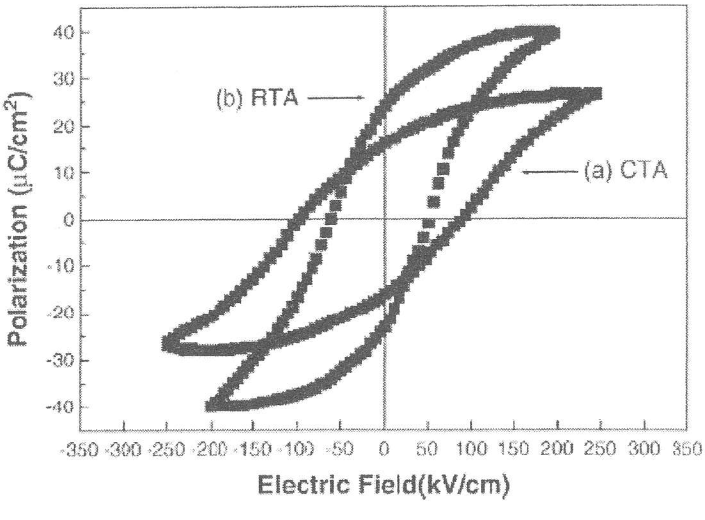

Figure 3. Hysteresis loops of BLT thin films annealed by CTA (a), and RTA methods (b) [142].

The effect of excess Bi_2O_3 content (0%, 2%, 5%, 8%, 10% and 15%) on microstructure and ferroelectric properties of BLT ceramics and thin films was studied by Yunyi et al.[143]. The optimum Bi excess for ceramics and thin films was achieved at 5% and 10% Bi_2O_3, respectively. These optimum values showed the maximum remanent polarization and dielectric constant.

Nd doped BIT has been widely studied by many authors. Xie et al. [145] found that the Nd-doped BIT films exhibits large remanent polarization and small coercive field at high annealing temperature of 750°C. The fatigue endurance of Nd doping showed little changes in polarization up to 10^{11} switching cycles, which were compatible for ferroelectric random access memory, FRAM application. Giridharan and Supriya [95] studied various crystallization parameter for the fabrication of Nd-doped BIT thin films on Pt/Ti/SiO_2/Si using metal organic solution decomposition method (MOCVD) in order to obtain highly *c*-axis oriented and randomly oriented thin films. They found that highly *c*-axis oriented films showed a large remanent polarization. Additionally, the remanent polarization also increases with film thickness.

Lu et al. [115] prepared the polycrystalline Nd-doped BIT thin films of *a*-axis preferential orientation and high *c*-axis orientation on Pt/Ti/SiO_2/Si substrates through a sol-gel method. They found that the ferroelectric and dielectric properties were strongly dependent on the film orientation. Chen et al. [124] studied the difference in crystallization layers of Nd-doped BIT thin films deposited on Pt electrodes using chemical solution deposition (CSD). They found that films prepared by the layer-by-layer crystallization were dominated by *a*-axis-oriented grains and showed high remanent polarization. In contrast, Zhang et al. [131] reported that highly *c*-axis of Nd-doped BIT thin films could enhance the remanent polarization and reduce the coercive field with better fatigue behavior. Chon et al. [144] also found that the maximum remanent polarization was obtained with *c*-axis orientation instead of the a-axis orientation.

Zhong and Shiosaki [157] reported that higher annealing temperature could enhance the intensities of (00*l*) reflections. Similar investigation was also found in other study in which a drastic change of crystallization behavior of films from non-*c*-axis to *c*-axis oriented resulting from high annealing temperature [123]. Both studies suggested that the *c*-axis orientation is significantly governed by the anisotropic growth of BIT grains. In addition, the interfacial energy of *c*-axis is low thus the nucleation of *c*-axis oriented grains would be dominant at high annealing temperature.

Hu et al. [125] studied Sm-doped BIT thin films deposited on Pt/TiO_x/SiO_2/Si substrates using chemical solution deposition (CSD) and pulsed laser deposition (PLD) at various annealing temperatures and 700°C, respectively. They found that crystallinity, dielectric, ferroelectric and leakage current properties were strongly dependent on the annealing temperature. The remanent polarization, coercive field and leakage current were found better in PLD-grown films. However, both films obtained from CSD and PLD showed fatigue-free behavior up to 10^9 read/write switching cycles.

Liu et al. [127-130] studied different parameters of Sm-doping in BIT thin films. The prepared films were deposited on *n*-type Si (100) substrates using metalorganic decomposition (MOCVD) with subsequent annealing at 700°C. They concluded that the crystallinity of the films increased with increasing annealing temperature. Additionally, the structural distortion could change with Sm content, which could be explained in terms of ionic radius and atomic mass of Sm ions. However, the measurement on ferroelectric properties was not reported. Chon et al. [147] studied the fatigue-free and highly *c*-axis oriented Sm-doped BIT thin films deposited on Pt/TiO_2/SiO_2/Si substrates using metalorganic sol decomposition method. They claimed that the prepared films showed the improved values of the remanent polarization and the nonvolatile charge compared to La-doped BIT films. This was due to the larger distortion was obtained in Sm-doped BIT than La-doped BIT. Hu et al. [125] stated that the degree of enhancement of remanent polarization, P_r in BIT dependent on the extent distortion in the oxygen octahedral within the perovskite block, which was also governed by the difference between ionic size of Bi^{3+} and the doping lanthanide ion.

The improvement in ferroelectric properties could also be performed by other lanthanide elements such as Pr, Y, Ce and Gd as shown in Table 4. In Pr doping, the increase in remanent polarization was found due to randomly oriented films [148, 149]. In Y and Ce doping, the improved ferroelectric properties were attributed to the enhanced degree of (117) orientation [151, 154, 158]. In Gd doping, the increase in annealing temperature from 400 to 700°C showed a highly *c*-axis-oriented preferential growth with a minor fraction of (117) orientation. Thus, the observed *c*-axis-oriented preferential growth of films exhibits the remanent polarization, P_r of about 37.5μC/cm^2, which was significantly higher than that for the highly *c*-axis-oriented La-doped BIT [157].

3.2. Ion Doping on B-Site

In previous section, the trivalent cations were doped at A-site or Bi^{3+} in order to improve the ferroelectric properties of BIT materials. In this section, the ion doping on B-site or Ti^{4+} ions will be discussed. The donor cations from group V (Nb^{5+}, Sb^{5+}, Ta^{5+}) and group VI (e.g. W^{6+}) were used as doping elements for Ti^{4+} at B-site [118]. This technique was preferred to enhance the ferroelectric properties and other electrical properties. Table 5 lists the electrical properties of various donor cations for ion doping on B-site.

Table 5. Electrical properties of ion doping on B-site

Donor cations	Annealing temperature, °C	Dielectric constant, ε_r	Remanent polarization, P_r (μC/cm^2	Coercive field, E_c (kV/cm)	Fatigue cycle	References
Zr	700 - 950	204 - 493	0.95 – 14.8	7.3 V	1×10^8 - 7.22×10^9	[159-161]
Mn	700	-	38	25	-	[162]
Nb	500 - 1050	110	3.5 - 14	2.5 V, 55	4.5×10^{10}	[163-165]
V	900-950	-	6	32.5	-	[166]
W	700	-	10 – 17.5	45 -160	4.5 - 8×10^{10}	[167-169]

Zhang et al. [159] studied the thin films of B-site substituted BIT by various content of Zr deposited on Pt/Ti/SiO_2/Si substrates by pulsed laser deposition (PLD). The remanent polarization was dependent on the Zr content and the vibration modes of the TiO_6 octahedral weaken greatly. The maximum remanent polarization, P_r was achieved at 14.8 μC/cm^2 with Zr = 0.2 mol%. Further increase in Zr content resulted in the decrease of remanent polarization. Furthermore, the 0.2 mol% of Zr doping could not improve the fatigue resistance of films.

Du et al. [160] also studied the ceramics of B-site doped BIT by Zr with various content prepared by solid state reaction method. They found that the decrease in remanent polarization of ceramics was due to the hybridization effect instead of the structural distortion. This finding was contradicted to other studies whereby the increase in remanent polarization was attributed to the increase in structural distortion [125]. Additionally, the Zr doping could not decrease oxygen vacancies in BIT ceramics indicating low fatigue resistance.

Kim et al. [165] reported that Nb doping could reduce the oxygen vacancies and enhance ferroelectric properties of BIT films. Additionally, the fatigue behavior of Nb doping could retain the polarization up to 4.5 x 10^{10} cycles. Noguchi et al. [162] found that Mn doping could suppress the leakage current and enhance the polarization properties. Tang et al. [166] studied the properties of BIT with V^{5+} ion doping. They found that the lattice vibration of BIT became weaker with V content. The Curie temperature showed a slight decrease with increasing V content. Furthermore, the sintering behavior was also improved with V doping. The remanent polarization and coercive field were better in V doped BIT compared to undoped BIT. Li et al. [170] studied the effect of different donor dopants with various valences. They found that the increase in remanent polarization was not really dependent on the ionic radius and concentration of oxygen vacancy. However, the decrease in oxygen vacancy and domain pinning effect were important parameters to control the fatigue behavior.

3.3. Ion Doping an A- and B-Sites

Recently, it was reported that ion doping on A- and B-sites in BIT showed a good ferroelectric properties [171-178]. In the case of both doping, the Nd and Mn were partially used in BIT to investigate their effect on microstructure, dielectric and ferroelectric properties of films [171, 176]. It was found that the grain of Nd/Mn doped BIT had different shape and the grain size becomes smaller compared to those of Nd doping, as presented in Fig. 4. The prepared films were dominated with (117) and (00*l*) preferred orientation in polycrystalline structures. The Mn content affected the electrical properties of films such as high remanent polarization, dielectric tunability and dielectric constant and low in coercive field, dissipation factor and leakage current density. Additionally, the Nd/Mn doping exhibited good fatigue properties up to 1.5 x 10^{10} switching cycles.

Zhong et al. [173] reported that Nd/Zr co-doping exhibited greater ferroelectric properties compared to Nd doping. In other reports, the La/Zr doping in BIT thin film could enhance the remanent polarization with better fatigue resistance [174, 179]. Compared to Zr doping, the fatigue endurance was improved with La/Zr doping at low concentration content. However, further increased in Zr content resulted in the decrease of remanent polarization with low fatigue resistant. Additionally, the oxygen vacancy was the predominant factor to determine the ferroelectric fatigue. Uchida et al. [175] compared the properties of BIT with Nd doping, La doping and Nd/V doping. They found that V^{5+} ion doping could enhance the remanent polarization.

The coercive field of Nd/V doping was comparable with those of Nd and La doping. Lee et al. [177] also investigated the dielectric and ferroelectric properties of La, Nd and V doping in BIT ceramics. They found that La, Nd, La/V and Nd/V doping could reduce the leakage current density in the high electric field region. Hu et al. [180] studied the effect of Nd/Nb doping on the electrical properties of the BIT ceramics. The remanent polarization, piezoelectric coefficient, and pyroelectric coefficient increased with Nb doping, while dielectric constant, coercive field and leakage current density decreased.

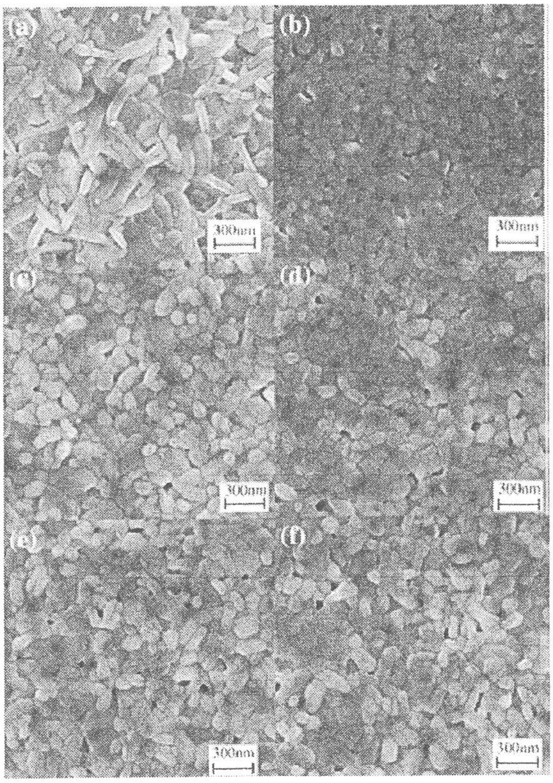

Figure 4. Surface morphologies of (a) BNT, (b) BNTM005, (c) BNTM01, (d) BNTM03, (e) BNTM05, and (f) BNTM1 thin films [176].

4. APPLICATION IN MEMORY DEVICES

Dielectric and ferroelectric based on simple perovskite structure and related Aurivillius-phase layered structure perovskite serves important functions for memory devices applications. Memory devices are generally used in various electronic applications such as cellular phones, note book, internet phone, PDA, MP3 music, and so forth. Among them are known as dynamic random access memory (DRAM), standard random access memory (SRAM), read only memory (ROM), erasable programmable read-only memory (EPROM), flash memory, ferroelectric random access memories (FRAM) etc [181].

Noh et al. [182] described the structure of FRAM was very similar to that of conventional dynamic random access memory (DRAM). They added that in FRAM, the dielectric material in the DRAM capacitor cells was replaced with ferroelectric thin films. In principle, FRAM was designed to store information using the ferroelectric effect in the absence of an applied electric field. Additionally, FRAM exhibited ideal memory properties such as non-volatility, fast access time, and low power consumption [181]. In order to fulfill these requirements, the ferroelectric properties of ceramics or thin films must meet certain criteria such as high remanent polarization, low coercive field and good fatigue resistant as well as low leakage current.

In end of 1999, Park et al. [156] successfully found that La-doped BIT thin films not only exhibited good ferroelectric properties but this films could be used to replace the lead-based thin films for similar applications. From 2000 to 2010, there were many studies on bismuth-layered compound and more than thousand of publications were established within that time. Table 6 shows the comparison of ferroelectric properties for specific compounds. Nowadays, most of the study are focusing on different preparation techniques or use other aid elements and compounds in order to enhance the remanent polarization with minimum losses of current and good fatigue endurance.

For example, Chen et al. [183] studied the effect of annealing atmospheres in different conditions including vacuum, ambient atmosphere and oxygen. They suddenly found that the remanent polarization, P_r of films annealed in oxygen atmosphere was higher than those annealed in ambient atmosphere and vacuum. The P_r for corresponding films annealed at oxygen atmosphere were about 29.5 μC/cm^2 with low coercive field of about 65 kV/cm and free-fatigue up to $\geq 10^{11}$ switching/cycles. Although the obtained values are still lower than other doping elements such as La, Nd, and Gd, the work must still be continued.

Table 6. Comparison ferroelectric properties with specific compound

Compound	Remanent polarization, P_r (μC/cm^2)	Coercive field, E_c (kV/cm)	Fatigue cycle	Leakage current density (A/cm^2)	References
$Bi_{3.25}La_{0.75}Ti_3O_{12}$	35	66	4.5 x 10^{10}	-	[98]
$Bi_{3.44}Nd_{0.56}Ti_3O_{12}$	60	150	-	10^{-7}	[116]
$Bi_{3.54}Nd_{0.46}Ti_3O_{12}$	32	73	10^{10}	-	[146]
$Bi_{3.15}Sm_{0.85}Ti_3O_{12}$	29.5	110	4.5 x 10_{10}	-	[147]
$Bi_{3.4}Pr_{0.6}Ti_3O_{12}$	31	102	1.5 x 10^{10}	2.1 x 10^{-6}	[148]
$Bi_{3.2}Y_{0.8}Ti_3O_{12}$	29	58	10^8	4.38 x 10^{-8}	[151]
$Bi_{3.25}Ce_{0.75}Ti_3O_{12}$	9.9	179	7 x 10^9	9 x 10^{-7}	[154]
$Bi_{3.15}Gd_{0.85}Ti_3O_{12}$	37.5	136	4.5 x 10^{10}	-	[155]
$Bi_4Ti_{2.97}Mn_{0.03}O_{12-\delta}$	38	25	-	~10^{-8}	[162]

CONCLUSION

In the early stage of work, BIT seems to be essential material in lead-free category for FRAM application. However, it suffers several issues such as small remanent polarization, non-fatigue-free behavior and high leakage current. The ionic doping is the best solution to improve these limitations.

There are many processes have been used in previous studies to prepare the BIT and doped-BIT. Both can be formed in different forms; ceramics and thin films. The increase in remanent polarization is strongly dependent on several parameters including processing method, structural distortion, grain orientation and grain size.

Free-fatigue behavior and low leakage current that belong to the doped-BIT can be explained in terms of chemical stability of oxygen ions in the perovskite block resulting from the doping effect.

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