BNBT: An Alternative to Lead Free Ceramics

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Abstract

Ferroelectric materials with Perovskite structure have widespread use in many electromechanical devices such as actuators, sensors, transducers and are candidates for memory devices and spintronics applications. Since a long time, the materials used for the fabrication of devices providing these applications contained lead such as Lead Titanate, Lead Magnesium Niobates and the most dominant one- Lead Zirconate Titanate (PZT). Despite the success in electrical devices there is a global concern for the development of environment–friendly lead-free materials considering the fatal effects which Pb causes to environment. A large body of work has been reported in the last 10 years on the development of lead-free piezoceramics. This review paper summarizes the properties and characteristics of one of the most studied lead free ceramic $Ba_x(Na_{1/2}Bi_{1/2})_{1-x}TiO_3$ (BNBT) which has recently been the starting point for the development of many other lead free piezoelectric materials.

Keywords: Perovskites, Ferroelectrics, Morphotropic Phase Boundary (MPB), Depolarization Temperature.

Introduction

Ferroelectric materials with ABO_3 type of structure have received considerable attention for the past several years owing to their promising applications in many electrical/electronic devices such as in capacitors, piezoelectric transducers, pyroelectric detectors/sensors, ultra sound applications, electrorestrictive actuators, SAW substrates, MEMS, catalyst electrodes in certain type of fuel cells and are candidates for memory devices and spintronics applications [1-13]. These materials have indeed high pyroelectric, electromechanical and promising electrical characteristics, which can be controlled either by doping or compositional change. Since a long time, the materials used for the fabrication of devices providing the above applications contained lead such as Lead Titanate, Lead Magnesium Niobates and the most dominant one- Lead Zirconate Titanate (PZT) [14]. Lead based ceramics have so long been of paramount importance due to absence of alternatives whose properties are comparative to those of lead-based counterparts, they can be sintered effortlessly by conventional pressureless sintering technique, due to their excellent properties and due to the fact that commercially available lead based piezoceramics address the challenges of high prices as all are based on relatively inexpensive raw materials.

Despite these benefits and the success in electrical devices there is a global concern and awareness for the development of environment–friendly lead-free materials considering the fatal effects which Pb cause to living organism and in general to environment. Legislation has been passed by European Union on the restriction of the use of certain hazardous substances in electrical and electronic equipment commonly referred to as the Restriction of Hazardous Substances Directive or RoHS and was adopted in February 2003 by the European Union. The RoHS directive took effect on 1 July 2006. This directive restricts the use of six hazardous materials in the manufacture of various types of electronic and electrical equipment.

- Lead (Pb)
- Mercury (Hg)
- Cadmium (Cd)
- Hexavalent Chromium (Cr^{6+})
- Polybrominated Biphenyls (PBB)
- Polybrominated Diphenyl Ether (PBDE)

In order to develop ceramics which are mirror images of PZT in terms of its properties but lead free, the physics behind the extraordinary behaviour of Pb containing compounds needs to be considered.

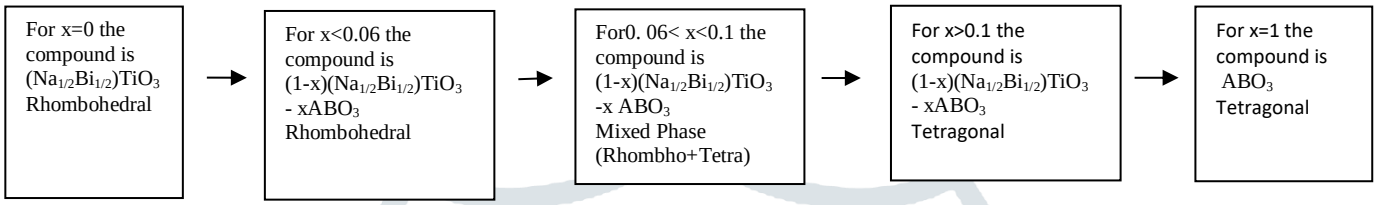
Lead ions have relatively high polarizability. This high polarizability is due to large effective crystal radius of the ion as well as comparably high effective number of electrons. Also, the special electronic configuration of Pb^{2+} ion contributes to its extraordinary properties. It contains two electrons in the outermost filled $6s^2$ subshell. These two electrons are coupled by their antiparallel spin in a filled subshell, do not participate in chemical bonding and form a dumbbell like extrusion of the electron density on one side of the ion, increasing the polarizability and thus allowing the distortion of the unit cell. Additionally, they lend themselves very easily to hybridization with the orbitals of other ions. This in turn enhances the distortion of unit cell. Distortion of the crystallographic unit cell in Perovskite structure makes them useful to piezoelectric application. Lead based compounds also exhibit a Morphotropic Phase Boundary (MPB) between rhombohedral and tetragonal phases and at MPB dielectric permittivity, piezoelectric coefficient and coupling factor have their maximum values[15].

If we wish to replace Pb^{2+} ions while retaining the good ferro and piezo properties, we should think about ions that have high polarizability *i.e.* a large crystal radius and a high effective number of electrons and possess a lone pair of electrons in the outer shell. Very few elements viz Sb^{3+}, Te^{4+}, Tl^{+} and Bi^{3+} fulfil the requirements partially or completely. But some have polarizability significantly smaller than Pb^{2+} (Sb^{3+}, Te^{4+}). Some are very expensive and even more toxic than Pb^{2+} (Tl^{+}). Bi has high polarizability greater than 5 (in units of $Å^3$), it is non-toxic and has no harmful effect. Thus, Bi based compounds seem to be the most likely replacement to the lead based piezoceramics.

The search for alternative piezoelectric/pyroelectric materials is now being focal theme of the present-day research. Exhaustive literature survey suggests that lead-free Sodium Bismuth Titanate -($Na_{1/2}Bi_{1/2}$)TiO_3 (NBT) ceramic discovered by Smolenskii et. al. in 1960 is a promising material for ferroelectric, piezoelectric and pyroelectric applications with high curie temperature.[16]

Further, recent reports showed relaxor behaviour of NBT [17], which indicated new variety of applications and potentiality of this compound. Besides, NBT possess highly tolerant structures, which allow their electrical properties to be controlled by suitable modifications either at A- or B-sites.[18]

To improve the properties of NBT several solid solutions of NBT with $SrTiO_3$[19], $CaTiO_3$[20], $La_2(TiO_3)_2$[21],$PbTiO_3$ [22] ,$BaTiO_3$[23] have been studied. Basically the search is focused on those systems in which a Morphotropic Phase boundary(MPB) occur or systems in which a multiphase occurs in which one extreme of the phase is Tetragonal and other extreme is Rhombohedral. NBT is Rhombohedral at room temperature and the dopants mentioned above are tetragonal. The general formula for the solid solution of NBT with other tetragonal titanates may be written as **(1-x)**($Na_{1/2}Bi_{1/2}$)TiO_3 **- x** ABO_3.



Among these BNT based systems Barium modified NBT i.e. $Ba_x(Na_{1/2}Bi_{1/2})_{1-x}TiO_3$ (BNBT) is more attracting. Other complex systems based on NBT have also been explored, but BNBT has recently been the starting point for the development of many other lead free piezoelectric materials.

The composition $Ba_x(Na_{1/2}Bi_{1/2})_{1-x}TiO_3$ has been tried for different values of x by many researchers and by different methods like Takenaka et al.[21], Gomah-Pettry et. al.[24]. They have studied the structural, dielectric properties and the phase transition for different compositions of $BaTiO_3$ (BT).

Phase transition in BNBT

In normal ferroelectrics there is only one critical temperature known as Curie temperature (T_c) where transition takes place between ferroelectric phase and paraelectric phase. Whereas there is another class of ferroelectrics which exhibit two dielectric anomalies at T_d and T_m. T_d is the depolarization temperature which corresponds to the transition from a ferroelectric state to anti-ferroelectric state, while T_m is the temperature at which the dielectric constant (ε_r) of the sample reaches a maximum value and corresponds to a transition from an anti-ferroelectric state to a paraelectric state.

The phase transition temperatures of the composition BNBT were studied by using electrical measurements such as dielectric and piezoelectric properties by many researchers like Takenaka et al. [21], Yuji Hiruma [25], Suchanicz et al. [26]. As mentioned earlier in normal ferroelectrics depolarization temperature (T_d) and maximum temperature (T_m) of ε_r-T curves coincide with each other, which is termed as Curie temperature (T_c), where transition takes place between ferroelectric phase and paraelectric phase. However, it is not the case for BNBT ceramics, it exhibit two dielectric anomalies at T_d and T_m. The phase transition temperatures as a function of *x* in $Ba_x(Na_{1/2}Bi_{1/2})_{1-x}TiO_3$ are summarized as below

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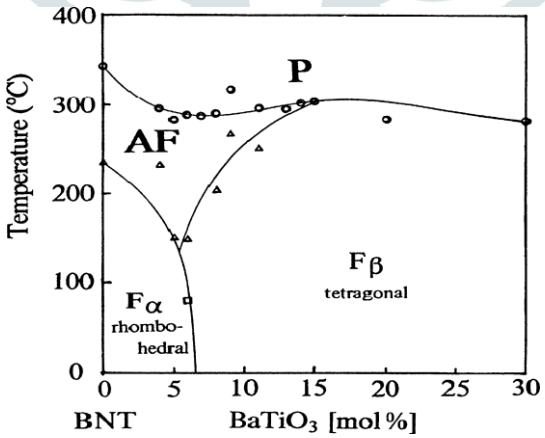

Fig. 1 Phase diagram for Barium doped NBT as a function of concentration of Ba and temperature. [F: Ferroelectric, AF: Anti-ferroelectric; P: Paraelectric]

Takenaka et. al. reported that the system exhibits a rhombohedral tetragonal morphotropic phase boundary (MPB) at $0.06 \leq x \leq 0.08$ with outstanding piezoelectric and electromagnetic properties. For the compositions $Ba_x(Na_{1/2}Bi_{1/2})_{1-x}TiO_3$ with x = 0.06, at the ferroelectric antiferroelectric transition temperature (T_d) the dielectric constant (ε_r) increases sharply. They reported that the frequency dispersion in ε_r and tanδ is minimum at temperatures below T_d but suddenly becomes significant above T_d. The minimum frequency dispersion below T_d and the sharp anomaly at T_d characterize the long-range ferroelectric order. The strong frequency dispersion in ε_r and tanδ above T_d suggests that the phase that was previously believed as antiferroelectric in this temperature range has relaxor characteristics.

Shan-Tao Zhang et al. [27] confirmed the existence of diffuse phase transition. They found that the phase transition, from ferroelectric to antiferroelectric or from antiferroelectric to paraelectric phase, occur in a wide temperature range.

C. Ma et al. [28]studied the phase diagram for unpoled ceramics in $Ba_x(Na_{1/2}Bi_{1/2})_{1-x}TiO_3$ system using transmission electron microscopy (TEM).The ferroelectric region below x = 0.06 has R3c symmetry and the ferroelectric phase above x = 0.10 has P4mm symmetry. An additional phase region exhibiting P4bm symmetry was revealed between the Rhombohedral Ferroelectric R3c phase and the tetragonal ferroelectric P4mm phase at room temperatures. The region with $0.06 \leq x \leq 0.10$ having P4mm symmetry shows relaxor antiferroelectric behaviour. The existence of antiferroelectric behaviour with the increasing addition of $BaTiO_3$ in $Na_{1/2}Bi_{1/2}TiO_3$ was attributed to macro – micro domain switching.

John E. Daniels et al. [29]proposed a field induced phase transformation of the solid solution of $(1-x)Bi_{0.5}Na_{0.5}TiO_3–xBaTiO_3$ at compositions near x = 0.06–0.07.They suggested that the room temperature structure of the sample at zero field is cubic or pseudocubic which was reported to be rhombohedral in literature. On application of an electric field to the sample, grains of pseudocubic symmetry transform to tetragonal symmetry. The macroscopically measured electric-field-induced strain at 3 kV/mm was found to be 0.73 x 10^{-3}, while a strain in excess of $2x10^{-3}$ was reached at field strength of 8 KV/mm. The strain observed in $(Na_{1/2}Bi_{1/2})_{0.93}$ $Ba_{0.07}TiO_3$ arises from an electric-field-induced phase transformation from a pseudocubic to a tetragonal structure. X-ray measurements reveal that the field-induced phase transformation in the sample is irreversible.

Structural and Dielectric Properties of BNBT

Gunnar Picht et al**. [30]** performed a systematic XRD investigation of poled and unpoled lead-free $(1-x)$ $Bi_{0.5}Na_{0.5}TiO_3–x$ $BaTiO_3$ ($0 \leq x \leq 0.2$) ceramics to determine its structural properties. Their experiment also confirmed a morphotropic phase boundary at $0.06 \leq x \leq 0.08$. For both poled and unpoled samples with increase in Ba content the rhombohedral cell expands and ultimately transforms into tetragonal system. They found a significant difference in unit cell parameters between poled and unpoled samples. Differences in the unit cell parameters between poled and unpoled samples suggest a significant stretching of unit cells along the poling field direction. Temperature-dependent XRD studies of selected compositions confirm a transition to the cubic high-temperature phase. This phase transition temperature is in agreement with the depolarization temperature. However, at temperatures above the appearance of the cubic phase a significant fraction of the tetragonal phase coexists within the cubic phase field.

Cheng Ma et al. also [28]reported that the morphotropic phase boundary in ferroelectric materials along with the associated strong piezoelectricity, can be created, destroyed, or even replaced by another morphotropic phase boundary through phase transitions during electrical poling.

Jean-Richard Gomah-Pettry et al. [24] investigated the effect of Barium doping on $(Na_{1/2}Bi_{1/2})TiO_3$(NBT).The Barium content was varied from 7 to 100 mol %. They found that varying Ba content influences both the temperatures, the temperature (T_d) at which the rhombohedral -tetragonal phase transition occurs and the temperature (T_m) at which the tetragonal – cubic phase transition occurs. The temperature of the maximum permittivity (T_m) and that of the hump (T_d) shifts towards the low temperature side with increasing Ba %. Both in the high frequency and low frequency range T_m drops from 325^0C to 100^0C as $BaTiO_3$(BT) % increases from 0 to 100%, though the trajectory of variation being different. Hump is observed in the permittivity temp curve only for % of BT that is near the MPB and T_d is found to decrease from nearly 225^0C to 170^0C when Ba content increases from 0 to the values near MPB. They also concluded that permittivity shows a strong frequency dependent dispersion, i.e. as the measurement frequency increases the maximum value of permittivity decreases as well as it displaces towards the high temperature side and this behaviour is more pronounced for NBT-rich compositions than for the BT-rich ones. That is, the substitution of Ba^{2+} for $(Bi_{0.5}Na_{0.5})^{2+}$ in the A-site of BNT causes an obvious change in the lower phase transition at T_d, but cannot change the characteristic of the higher phase transition at T_m. For relaxor ferroelectrics, the diffuseness in the phase transition can be described by the equation $\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = c\left(T - T_m\right)^{\gamma}$ proposed by Uchino and Nomura where ε_m is the maximum value of the dielectric constant at T_m, C and γ are assumed to be constant, with γ having value between 1 and 2. The limiting values $\gamma = 1$ and $\gamma = 2$ are the characteristics of a normal ferroelectric and an ideal relaxor ferroelectric, respectively..

Bao-Jin Chu et al. [31]studied the piezoelectric properties of $(1-x)Na_{1/2}Bi_{1/2}TiO_3–xBaTiO_3$ ceramics near the morphotropic phase boundary (MPB) and found that piezoelectric properties reach their extreme values near the MPB (about x = 0.06).They also studied the influences of nonstoichiometry and doping on the structures and piezoelectric properties of $(Na_{1/2}Bi_{1/2})_{0.92}Ba_{0.08}TiO_3$ ceramics. Specimens of nonstoichiometry (NBBT81 and NBBT82 ceramics) and doping in B-site (NBBT83 and NBBT84 ceramics) were prepared and studied. Nonstoichiometry and doping in B-site do not change the tetragonal symmetry of NBBT8 ceramics. Compared with pure NBBT8, the piezoelectric properties of NBBT81, NBBT82 and NBBT83 were enhanced. Their d_{33} values increase from 112 to 140, 125 & 149 pC/N respectively. But piezoelectric constant increases at the cost of lowering of depolarization temperature.

The overall achieved properties of $(1-x)Na_{1/2}Bi_{1/2}TiO_3–xBaTiO_3$ solid solutions (with x = 0.02, 0.04, 0.06, 0.08 and 0.10) are summarized in Table below.

Table 1. Typical properties of $Ba_x(Na_{1/2}Bi_{1/2})_{1-x}TiO_3$ for x=0.02, 0.04, 0.06, 0.08 and 0.10

Property		BNBT2	BNBT4	BNBT6	BNBT8	BNBT10
Coupling factor	k_t	0.46	0.45	0.4	0.42	0.41
	k_p	0.2	0.21	0.29	0.13	0.14
Piezoelectric constant	d_{33}	78	87	122	112	94
Dielectric constant	ε^T_{33}	402	445	601	841	764
Frequency constant(Hz m)	N_p	3190	3000	3000	2950	2980
	N_t	2680	2570	2522	2375	2418
Poisson ratio	σ	0.26	0.25	0.25	0.25	0.24
Dielectric loss	tanδ	0.0173	0.0207	0.0179	0.0204	0.0239
Maximum tem of ε(^{0}C)	T_m	265	230	225	250	180
Depolarization temperature (^{0}C)	T_d	180	165	100	140	170
Remnant polarization(μC/cm^2)	P_r	37	-	40	36	22.5
Coercive Field(V/mm)	E_c	4700	-	2880	3200	2880

Table 1. contd.

Property		BNBT7	BNBT81	BNBT82	BNBT84	BNBT86
Coupling factor	k_t	-	-	-	-	-
	k_p	0.212	-	-	-	-
Piezoelectric constant	d_{33}	178	140	125	149	108
Dielectric constant	ε^T_{33}	1219	870	740	1230	450
Frequency constant(Hz m)	N_p	-	-	-	-	-
	N_t	-	-	-	-	-
Poisson ratio	σ	-	-	-	-	-
Dielectric loss	tanδ	3.8	0.0281	0.0212	0.039	0.015
Maximum tem of ε(^{0}C)	T_m	-	210	215	250	About 245
Depolarization temperature(^{0}C)	T_d	-	125	135	70	155
Remnant polarization(μC/cm^2)	P_r	37.8	-	-	-	-
Coercive Field(V/mm)	E_c	31.1	-	-	-	-

Chenggang Xu et al. [32] studied the structural and electrical properties of (1- x) $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ ceramics. For the pure NBT ceramic the grains are in the range of 4 to 6 μm which reduces considerably with the introduction of $BaTiO_3$ and further decreases with increase in Ba content. For the (1 - x) BNT-BT ceramics, remanent polarization (P_r) increases with increasing x and then decreases, giving a maximum value of 38.8 μC/cm^2 at x = 0.06 whereas coercive field (E_c) decreases steeply and continuously from 5.69 kV/mm to 3.25 kV/mm as x increases from 0 to 0.12. Because of the MPB and strong ferroelectricity (i.e low E_c and high P_r), the piezoelectric properties are significantly enhanced. A low coercive field facilitates the poling process of the ceramics, and a large remanent polarization favours the piezoelectric properties; and at MPB the number of possible spontaneous polarization directions increases and hence the ceramics can be easily poled. Deformed or slim P-E loops were observed at high temperatures, implying that polar and non-polar regions may co-exist in the ceramics at temperatures above T_d. Electrical properties of (1-x)BNT-xBT Ceramics as observed by Chenggang Xu et al. is listed as below.

Table 2. Electrical properties of $Ba_x(Na_{1/2}Bi_{1/2})_{1-x}TiO_3$ for x=0,0.02, 0.04, 0.06, 0.08. 0.10 and 0.12

x	**0**	**0.02**	**0.04**	**0.06**	**0.08**	**0.10**	**0.12**
d_{33}(pC/N)	83	97	116	155	143	137	132
k_p(%)	15.9	21.8	28.9	36.7	23	17.5	18.2
ε_r	408	470	564	826	1099	1058	910
tanδ	2.65	2.7	2.75	2.5	3.1	3.3	2.9
P_r	37	38.1	37.8	38.8	38.7	29.4	29
E_c	5.69	5.65	4.84	3.41	2.92	3.29	3.23
T_d	168	186	167	105	129	164	194
T_m	360	309	289	288	290	272	285

Shan-Tao Zhang et al. [27]also collected information about strain of this lead free ceramics and the origin of the strain. They found that the composition exhibits giant bipolar and unipolar strains of 0.40 % and 0.42 %, respectively when the antiferroelectric order tends to appear and the temperature reaches 100 ^{0}C. This large strain is attributed to a field-induced antiferroelectric-ferroelectric (AFE-FE) transition. When the composition is further heated to 200^{0}C the strain begins to gradually decrease.

Modification in BNBT

Rare earth oxides are often used as additive in order to improve the properties of BNBT6 . The radius of rare earth ions are very close to the radius of Bi^{3+} (1.03 Å) and Na^{1+} (1.02 Å). Hence it is possible that the rare earth ions enter into the A-sites of BNBT6 perovskite and affect the properties of BNBT6 ceramics. Several kinds of rare earth oxides such as La_2O_3, Y_2O_3, Nd_2O_3 and CeO_2 have been attempted to improve the different properties of BNBT6 ceramics.

Hui-dong Li et al. [33]studied the microstructure, dielectric and piezoelectric properties of $(Bi_{1/2}Na_{1/2})TiO_3$–$6BaTiO_3$ doped with Nb^{5+}, Co^{3+} or La^{3+} . For all the samples namely, BNBT6-La, BNBT6-Nb, BNBT6-Co, BNBT6-La-Nb and BNBT6-La-Co Curie point shifted to higher temperatures indicating that the additives have influenced the crystal lattices. The doping of La^{3+} and Nb^{5+} enhances the value of d_{33}. All the modified BNBT6 samples were found to have dielectric constant higher than BNBT6 at room temperature. The permittivity temperature curves of all the modified compositions also exhibit strong dielectric dispersion with the increasing temperature, this may be because BNBT6 itself is a relaxation ferroelectric. For BNBT6 doped with La^{3+} or Nb^{5+}, the depolarization temperature is near about 100^{0}C which is very much same for that of pure BNBT6. But BNBT6 systems to which Co^{3+} was doped, no dielectric anomaly was observed before T_m due to the size of ionic radii. Co^{3+} has an ionic radius of 0.63Å , which is very close to that of Ti^{4+} (0.68 Å), due to this**,** Co^{3+} is most likely to go into B-site in perovskite system substituting Ti^{4+} **[17].**

Table 3. Effect of different additives on the properties of BNBT6

System	$\varepsilon^T_{33}/\varepsilon_0$ (1kHz, RT)	tanδ	k_p (%)	k_t (%)	d_{33} (pC/N)	S_{max}/E_{max} (pm/V)	P_r (μC/cm^2)	E_c (kV/mm)	T_d/T_2 (^{0}C)	T_c/T_m (^{0}C)	Mechanical Quality factor(Q_m)	References
BNT–xBT MPB X=6%–8%	601 - 826	**2.5**	21.2 - 36.7		122 - 176	700 (At 100^{0}C)	37.8-40	2.72-3.41	90-105	225-288		Chen et al[10] Shan-Tao Zhang et al[27]
BNT-6BT+7.5Li	990		36.8		208	-	39.2	3.27	85	260		Lin et al.
BNT-6BT+2KNN	-		-		30	567	16	1.3	-	260		Zhang et al[27]
BNBT6-La	1576	4.5	0.24	**0.38**	125	-	-	-	-	-	182	Hui-dong Li et al[33]
BNBT6-Nb	1614	4.6	0.2	**0.38**	118	-	-	-	-	-	199	
BNBT6-Co	1200	2.3	0.27	**0.46**	139	-	-	-	-	-	253	
BNBT6-La-Nb	1664	4.4	0.19	**0.38**	135	-	-	-	-	-	127	
BNBT6-La-Co	1284	2.1	0.25	**0.38**	127	-	-	-	-	-	263	

Table 3. contd.

BNBT7	1291	3.8	21.2		178		37.8	31.1			91	Qing Xu et al.[36]
BNBT7-La	1331	4.5	20.7		188		45.2	26			87	
BNBT7-Pr	1462	4.2	20.6		184		34.3	31.4			77	
BNBT7-Eu	1222	4	20.4		120		30.3	45.9			102	
BNBT7-Gd	988	4.1	20.6		100		23.7	53.2			108	
BNBT6-Nd Nd_2O_3(0.4wt)	**1947**	0.057	0.31		175		38	3.8(aprox)			118	Peng Fu et al.[35]
BNBT7	**1291**	3.8	21.1	178		37.8	31.1				91	Qing Xu et al.[36] Citric method
BNBT-La	**1331**	4.5	20.7	188		45.2	26				87	
BNBT-Pr	**1462**	4.2	20.6	184		34.3	31.4				77	
BNBT-Eu	**1222**	4	20.4	120		30.3	45.9				102	
BNBT-Gd	**988**	4.1	20.6	100		23.7	53.2				108	

Y. Q. Yao et al. studied BNT–BT at the MPB with additional Zr but properties get worsened due to the formation of a cubic phase.

Haidong Wu et al. [34] prepared Y_2O_3-doped $Ba_{1-x}(Bi_{0.5}Na_{0.5})_xTiO_3$ ceramics by a conventional mixed oxide method. The relative permittivity and dielectric loss firstly increased and then decreased with the increase of NBT proportion. The relative permittivity reached the maximum value when the NBT content is 1 mol % and the dielectric loss had the minimum value when the NBT content is 0.25 mol %.

The effects of Nd_2O_3 on the microstructure, the dielectric, ferroelectric and piezoelectric properties of BNBT6 were investigated by Peng Fu et al.[35] They found that the Curie point does not change with the addition of Nd_2O_3. All (1-x)BNBT6−x Nd_2O_3 ceramics exhibited relaxor behaviour with diffuse phase transition. The average grain size of the ceramics doped with 0.2–0.6 wt.% Nd_2O_3 were slightly greater than pure BNBT6, but when doping percent was increased to 0.8 wt.% there was grain growth which leads to the decrease of crystalline grains and can be attributed to the excess Nd^{3+} concentration near grain boundaries. Peng Fu et al also found that compared with the pure BNBT6 ceramics, the remanant polarization P_r was found to increases with increasing x and then decreases, giving a maximum value of 38μC/cm^2 at x = 0.4. The coercive field E_c decreased gradually from 3.8 kV/mm to 2.30kV/mm with x increasing from 0.4 to 0.8 wt %. This result indicates that the BNBT6 ceramics doped with appropriate Nd_2O_3 exhibit a larger remanant polarization P_r and a lower coercive field E_c compared with the pure BNBT6 ceramics.

$(Na_{0.5}Bi_{0.5})_{0.93}Ba_{0.07}TiO_3$ ceramics added with 0.2 wt.% Ln_2O_3 (Ln = La, Pr, Eu, Gd) were prepared by a citrate method by Qing Xu et al. [36], and the structural and electrical properties of the ceramics were investigated with respect to the size of the lanthanide. All the specimens maintain a coexistence of rhombohedral and tetragonal phases in crystal structure. Compared with $(Na_{0.5}Bi_{0.5})_{0.93}Ba_{0.07}TiO_3$, the lanthanide addition resulted in an increased diffuseness in phase transition and a decrease in depolarization temperature (T_d). The variation in dielectric, piezoelectric and ferroelectric properties with the lanthanide addition presents evident of lanthanide size dependence. The addition of La_2O_3 or Pr_2O_3 tailored the electrical properties basically following a soft doping effect, with the specimens added with La_2O_3 and Pr_2O_3 attaining high piezoelectric constants (d_{33}) of 188 and 184 pC/N, respectively. By contrast, the Eu_2O_3 or Gd_2O_3 addition led to an abnormal change in the electrical properties, which was qualitatively interpreted by an internal stress effect.

Summary

Over the past few years there have been many developments in the field of lead-free piezoelectric materials. Several material systems have been explored, some of which show properties comparable to PZT. Bismuth based compounds have emerged as the most likely replacement to the lead based piezoceramics. Close look at atomic properties, crystal structure, and phase diagram in accordance with PZT, suggests further scope of improvement in the properties of Bi based compounds.

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