Doping modification in lead-free piezoelectric ceramics

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Abstract. Piezoelectric ceramics are functional information ceramic materials that can convert mechanical and electrical energy into each other. They are widely used in high-tech fields, such as the electronics industry, machinery, and aerospace. Currently, $Pb(ZrTi)O_3$ (PZT) piezoelectric materials are most commonly used, but the main component, PbO, is toxic and volatile during production and manufacturing, thus causing certain damage to human health and the environment. Therefore, research on green and environmentally friendly lead-free piezoelectric materials has been attracting much attention. This paper will therefore present two lead-free piezoelectric ceramics that have the potential to replace PZT-based lead-containing piezoelectric materials: Potassium Sodium Niobate (KNN)-based piezoelectric ceramics and Bismuth Sodium Titanate (BNT)-based lead-free piezoelectric ceramics. The piezoelectric constants of lead-free piezoelectric ceramics represented by systems such as KNN and BNT are now comparable to those of lead-containing piezoelectric ceramics and are gradually replacing traditional lead-based piezoelectric ceramics in fields such as ultrasonic atomization and hydroacoustic energy transfer.

Keywords: Piezoelectric ceramics; KNN piezoelectric ceramics; BNT piezoelectric ceramics; Doping modification.

1. Introduction

The piezoelectric effect refers to the internal polarization of some dielectric when it is deformed by an external force in a certain direction. At the same time on its two opposite surfaces appear positive and negative charges. If the external force is removed, the material returns to its uncharged state, the principle of the piezoelectric effect is shown in Figure 1. The generation of positive and negative charges is actually the non-coincidence of positive and negative centers in the crystal. Piezoelectric materials have extensive use in life, such as transducers [1], actuators [2], sensors, frequency discriminators, piezoelectric oscillators, transformers, filters, etc. For example, the igniter in the lighter is made of piezoelectric ceramics. When the piezoelectric ceramic is added to the pressure will undergo mechanical deformation, and its poles will produce voltage; The instantaneous impact produces several thousand volts of high voltage, and this voltage can penetrate the air to the negative electrode discharge to form an electric arc to ignite the gas emitted by the lighter.

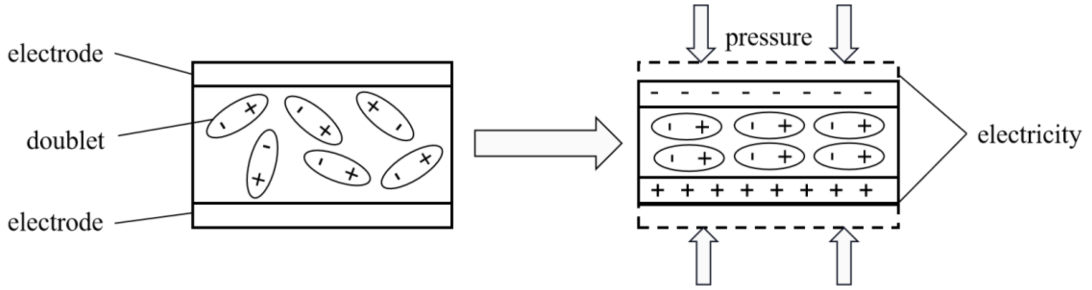

Figure 1. Schematic diagram of piezoelectric effect

Traditional piezoelectric materials can be divided into two categories: inorganic piezoelectric materials and organic piezoelectric materials. Inorganic piezoelectric materials are further divided into piezoelectric crystals and piezoelectric ceramics. Piezoelectric crystals are generally referred to as piezoelectric single crystals, which have no center of symmetry in their structure are therefore have piezoelectric properties. Piezoelectric single crystals are widely used in various fields of the electronic information industry. Single crystal piezoelectric materials represented by quartz have high stability and mechanical quality factor but weak piezoelectricity, low dielectric constant, and size limitation due to cut type. Piezoelectric polymers, also known as organic piezoelectric materials, are flexible, with low density, low impedance, and high electrical voltage constants, Polyvinylidene fluoride (PVDF) is the most typical organic piezoelectric material. However, the low upper-temperature limit for the use of these materials limits the application in high temperature environments. Ceramic piezoelectric materials are obtained by mixing various oxides and sintering them at high temperatures. They have piezoelectric effect and can convert mechanical and electrical energy to each other. They are widely used in the field of precision electronic instruments because of their high sensitivity, resistance to acids and bases, medium dielectric coefficient and high electromechanical coupling coefficient, and easy to be made into arbitrary shapes.

Traditional piezoelectric ceramics, such as PZT-based piezoelectric ceramics, are solid solutions formed by the pre-sintered synthesis of PbO_4, TiO_2, and ZrO_2 followed by high temperature sintering. The high lead content of PZT not only produces substances such as volatile lead oxide that are harmful to humans and the environment in its preparation [3], but also causes serious environmental problems [4].The Curie temperature is mostly below 400 °C, which greatly limits its application in high-temperature fields. Therefore, this paper introduce 2 lead-free piezoelectric ceramics and their modifications that make them promising alternatives to existing piezoelectric ceramics.

2. Potassium Sodium Niobate (KNN)-based lead-free piezoelectric ceramics

Potassium Sodium Niobate ($K_{0.5}Na_{0.5}NbO_3$, KNN)-based piezoelectric ceramics are binary systems with a perovskite structure formed by solid solution of the ferroelectric $KNbO_3$ and the antiferroelectric $NaNbO_3$, where the ratio of the two components is close to 1:1 [5]. KNN-based ceramics with high Curie temperature ($T_C \approx 420$ °C) [6] and high radial electromechanical coupling coefficient ($k_r \approx 0.48$) are the most promising environmentally friendly materials to replace conventional lead-based piezoelectric ceramics. As shown in Figure 2, KNN has three temperature values used for phase structure transition: $T_{R\text{-}O}$, $T_{O\text{-}T}$, and Curie temperature T_C. with temperature change, KNN ceramics undergo a tripartite phase (R)-orthogonal phase (O) transition at -100 °C, an orthogonal phase - tetragonal phase (T) transition at 200 °C and a tetragonal phase - cubic phase (C) transition at 420 °C [1].

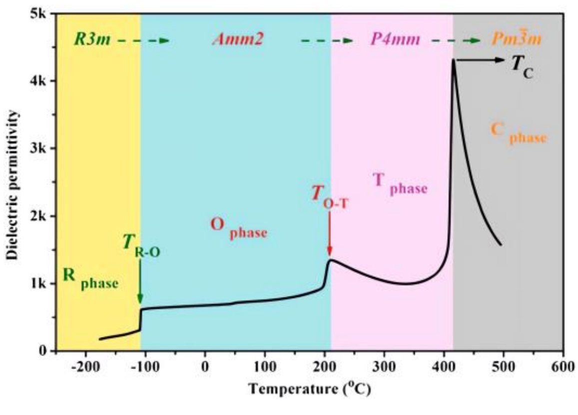

Figure 2. Phase boundary of KNN piezoelectric ceramics [7]

KNN-based piezoelectric ceramics have two problems in terms of applications. Firstly, their piezoelectric coefficient ($d_{33} \approx$ 80-160 pC/N) is relatively low, which limits the further application of this type of ceramics. The second is the poor doping densities of the ceramics obtained during the preparation due to the easy volatilization of potassium and sodium, which in turn leads to poor electrical properties of the ceramic materials [8]. In practical applications, the phase transition temperature of KNN-based lead-free piezoelectric ceramics can be shifted to near room temperature by ion doping or substitution, the addition of a second component or multi-component compounds, to build a new phase boundary at room temperature. In the new phase boundary region, there are more possible polarization states due to the coexistence of multiple phases, and the anisotropy between the different phases is reduced, which makes the electric domains more easily deflected, thus improving the performance of KNN-based lead-free piezoelectric ceramics. As shown in Figure 3, the latest KNN-based ceramic part of the piezoelectric performance even exceeds that of PZT-based piezoelectric materials, with good prospects for development.

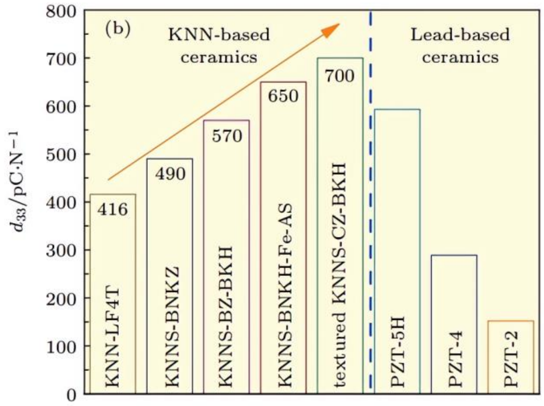

Figure 3. d_{33} of KNN-based lead-free piezoelectric ceramics compared to lead-based ceramics

The crystal structure of calcium titanate ($CaTiO_3$) is known as the perovskite structure, the general chemical expression for perovskite is ABO_3 and its structure is schematically shown in Figure 4. In KNN, Nb^{5+} occupies the B-site, K^+, and Na^+ occupy the A-site, and Nb^{5+} forms [NbO_6] octahedra with O^{2-}. Both the A and B-site can be partially replaced by other metal ions of similar radii while keeping their crystal structures essentially unchanged. At present, doping of A and B site ions is the simplest and most efficient way to improve the piezoelectric properties of KNN-based ceramics, which are mainly divided into A-site doping, B-site doping and A and B-site co-doping.

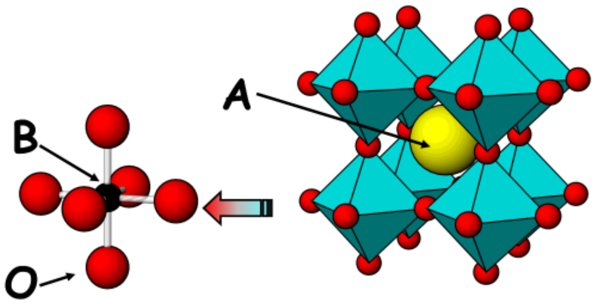

Figure 4. Schematic diagram of perovskite structure

2.1. A-site doping

A-site doping means that the A-site potassium and sodium ions of KNN are partially replaced by ions of similar valence and radius size to their ions. Lithium is one of the most commonly used dopants to achieve and maintain high Curie temperatures because it lowers the T_{O-T} close to room temperature while increasing the T_C. Zhao et al [9] found that the content and ionic shift of the tetragonal phase in the coexisting phase at room temperature increased with the increase of Li^+ content. It is the Li^+ that decreases the T_O while increasing the T_C. Li^+ becomes one of the essential elements to be added in the construction of polycrystalline phase boundaries. Wong et al [10] prepared KNN-based piezoelectric materials with high T_C = 483 °C and d_{33} > 200 pC/N using Lithium as dopant. For the material $0.995(K_{0.5}Na_{0.5})_{1-x}Li_xNbO_3$ - $0.005BiAlO_3$, the results of the electrical properties are inconsistent when x is different. The electrical property coefficient reaches its maximum only when the material is at the orthogonal-quadratic phase boundary. Other commonly used A-site ion dopants are Ag^+, and Yang et al [11] used Ag^+ to achieve a high Curie temperature and obtained T_C = 250 °C for doped KNN-based high-voltage electrical performance piezoelectric materials.

2.2. B-site doping

The commonly used B-site doping ions are Sb^{5+}, Ta^{5+}, Zr^{4+}, Hf^{4+}, etc. Wang et al [12] studied $(K_{0.5}Na_{0.5})_{0.97}Bi_{0.01}(Nb_{1-x}Zr_x)O_3$ and concluded that the phase structure is related to the zirconium content, and the ceramics undergo a phase transition from pseudo-cubic to orthorhombic phase as the zirconium content increases. The optimal piezoelectric properties of the material are obtained when x = 0.02, when d_{33} = 161 pC/N, $T_{O\text{-}T}$ = 130 °C. However, the addition of antimony, tantalum, and hafnium decreases the $T_{O\text{-}T}$ and $T_{R\text{-}O}$ also decreases the T_C of the piezoelectric material, which reduces the operating range of the piezoelectric material. Therefore, it is necessary to combine the advantages of A-site doping and B-site doping, i.e., A and B-site co-doping, to obtain better piezoelectric properties.

2.3. A and B-site co-doping

A and B-site co-doping is the substitution of A and B-site by corresponding single ions or multiple ions, which combines the advantages of A-site doping and B-site doping to achieve the overall improvement of electrical properties of piezoelectric ceramic materials. Duong et al [13] compared in detail the crystal structure phase transition of Ba^{2+} doping and Ba^{2+}, Zr^{4+} co-doping by introducing $BaZrO_3$ in pure KNN and found that single Ba^{2+} doping does not cause crystal structure phase transition, while Ba^{2+}, Zr^{4+} co-doping causes phase transition from orthotropic phase to pseudo-quadratic phase. The piezoelectric properties such as piezoelectric constants and electromechanical coupling coefficients of the ceramics are optimized when the doping amount of $BaZrO_3$ is 0.06 mol. Currently, KNN-based ceramics doped with three or more elements exhibit better piezoelectric properties. On the one hand, multi-element doping leads to greater lattice distortion in ceramics, and lattice distortion and multiphase coexistence are the intrinsic contributions to improving the piezoelectric properties of the material. On the other hand, the formation of new phase boundaries (NPB) with multiphase coexistence increases the polarization direction of ceramics, and with low polarization anisotropy, the ceramic domains are more easily polarized and flipped, which is beneficial to the macroscopic piezoelectric properties.

In addition to ionic doping, another commonly used dopant is perovskite dopant. Where A can be lithium, calcium, strontium, barium, and bismuth; B can be tantalum, zirconium, and iron, such as $LiSbO_3$, $Bi_{0.5}Na_{0.5}TiO_3$, $BaZrO_3$, etc. Sun et al [14] found that the domain size of $(K_{0.48}Na_{0.52})(Nb_{0.955}Sb_{0.045})O_3$-$0.01SrZrO_3$ ceramic system before doping with $(Bi_{0.5}Ag_{0.5})ZrO_3$ was 0.2-1 μm, and in the ceramic system after doping with $(Bi_{0.5}Ag_{0.5})ZrO_3$ In the doped $(Bi_{0.5}Ag_{0.5})$ ZrO_3 ceramic system, the domain sizes of 30-65 nm, 65-160 nm stripes and, 30-45 nm nanodomains were also observed. The ceramic system is doped with d_{33} ≈ 487 pC/N. More properties of KNN-based ceramics modified with ABO_3 group elements are shown in Table 1. Adding new group element compounds can play a more significant role than A and B site doping, which not only facilitates the construction of polycrystalline phase boundaries but also the generation of ferroelectric nanodomains.

Table 1. Performance parameters of KNN ceramics modified with ABO_3 group elements

Chemical Formula	d_{33} (pC/N)	k_p	ε_r	T_C(°C)
KNNL–xBZ (x=0.08)	317	0.429	2600	—
KNNT-xBNKLZ (x=0.045)	290	0.42	1750	322
KNN-LS-xCT (x=0.01)	210	0.49	1170	330
KNN-KCT-BM-xLS (x=0.045)	208	0.405	1178	335

2.4. Application of KNN-based piezoelectric ceramics

Ultrasound imaging transducer is a powerful tool for the non-invasive detection of living organisms, among which high-frequency ultrasound transducer has excellent resolution and is important for clinical diagnosis in the field of biomedical imaging, the piezoelectric material is the core component of the ultrasound transducer, but the choice of piezoelectric material in ultrasound transducer has long been lead-based piezoelectric material with excellent piezoelectric response and stability. Xing et al [15] prepared $(0.965\text{-}x)(K_{0.48}Na_{0.52})NbO_3\text{-}xBiAlO_3\text{-}0.035(Bi_{0.5}Na_{0.5})ZrO_3$ piezoelectric ceramics using a conventional solid-phase technique and obtained the best overall performance at x=0.003 (KNN-3) (T_C ~ 336 °C, d_{33} ~ 306 pC/N, k_p = 0.48). On this basis, KNN-3 was made to design and fabricate a high-frequency ultrasonic imaging transducer as shown in Figure 5(a). The transducer has a high center frequency (~ 24.5 MHz) and a wide 6 dB bandwidth (~ 97 %) as shown in Figure 5(b) and 5(c), and the transducer has a low insertion loss (17 dB) as shown in Figure 5(d). The good imaging characteristics of the lead-free transducer were demonstrated by ex vivo imaging of biological tissue structures.

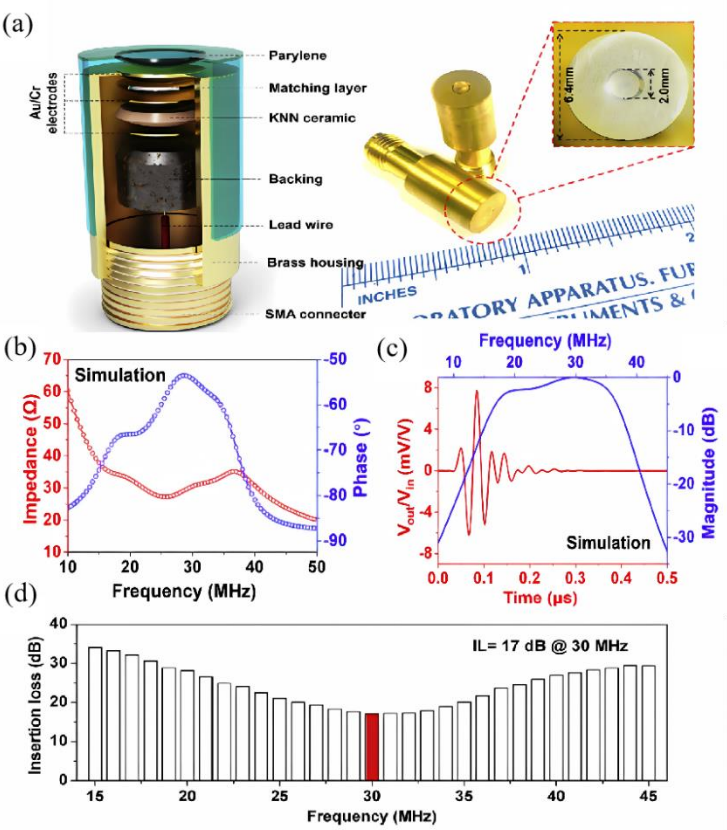

Figure 5. (a) Schematic diagram of the internal structure of the KNN-3 ceramic transducer (left) and photo of the finished sample (right); (b) (c) PiezoCAD simulated impedance results and pulse-echo response spectrum of the KNN-3 ceramic transducer; (d) Measured insertion loss of the KNN-3 ceramic transducer [15]

In addition, KNN-based lead-free piezoelectric ceramics have great potential in other areas of precision mechanical instrumentation. Weng et al [16] designed a $(Na_{0.53}5K_{0.48})NbO_3+0.05LiNbO_3$ (NKL0.05N) ceramic and the sound surface wave sensor fabricated using NKL0.05N exhibited high phase velocity (3210 m/s) and high electromechanical coupling coefficient (about 6.7 %), which is higher than that of most PZT ceramics (1 % to 4 %). This device can be applied to electromechanical sensors and various acoustic surface wave sensors. A burst sensor is a piezoelectric sensor that converts vibration energy into electrical energy and is usually installed in the engine of a car. This sensor is used to detect the possibility of engine detonation so that the ignition timing can be adjusted in advance by the electronic control system to avoid detonation.

3. Bismuth Titanate Sodium (BNT)-based lead-free piezoelectric ceramics

Bismuth Titanate Sodium [$(Bi_{0.5}Na_{0.5})TiO_3$, BNT] is an A-site composite perovskite structure relaxation type ferroelectric. Its A-site is occupied by Bi^{3+} and Na^{+} ions, while the oxygen anion forms an octahedron and the center of the octahedron is occupied by Ti^{4+} cations. The BNT-based ceramic material has a high residual polarization (P_R = 38 μC/cm^2) and a high Curie temperature (T_C = 320 °C). Relaxation state BNT-based ceramics have excellent properties such as large electrically induced strain and high mechanical quality factor, especially its unique advantages in high power devices. However, the poor electrical conductivity of pure BNT and the high coercivity field (E_C = 73 kV/cm) [4]lead to difficulties in its polarization. Due to the polarization problem, BNT has a low piezoelectric coefficient (d_{33} = 73-95 pC/N). Earlier researchers improved the piezoelectric constants by ion substitution at A or B-site, but the enhancement was limited.

The construction of a morphotropic phase boundary (MPB) is effective in enhancing the piezoelectric properties of the material. In addition to the quasi-homotypic phase boundary MPB (I), which contains both ferroelectric R and T phases, BNT-based ceramics also have a quasi-homotypic phase boundary MPB(II), which has a polar ferroelectric phase and a nonpolar relaxation phase. This is due to the simultaneous occupation of the A-site of the BNT lattice by two heterovalent cations, Bismuth and Sodium, resulting in the chemical disorder of the A-site and the evolution of the ferroelectric domains into polar nano-micro-regions PNRs, which exhibit a nonpolar relaxation phase. After applying a unidirectional electric field to the sample and holding it for a period of time, the sample is polarized and the originally disordered polar nano-micro-regions turn to the same direction as the polarization direction under the action of the electric field and a long-range ordered ferroelectric phase is formed. When the external temperature increases, the electric domains lose their directionality and the ordered polar nano-micro-region transforms into a disordered state again, as shown in Figure 6, where depolarization occurs. The depolarization temperature of the BNT system is the characteristic temperature of the transition from the ferroelectric to the relaxed state, which directly determines the maximum operating temperature of the BNT-based ceramics. At MPB (I), the piezoelectric properties of BNT-based ceramics d33 are effectively improved, while at MPB (II), the field strain properties of the ceramics are significantly higher[17]. Lowering the MPB (II) phase boundary temperature T_d to room temperature or raising T_d above the service temperature is an effective way to optimize the strain performance, mainly by constructing chalcogenide multicomponent solid solution, ion doping and adjusting the non-chemical stoichiometry ratio.

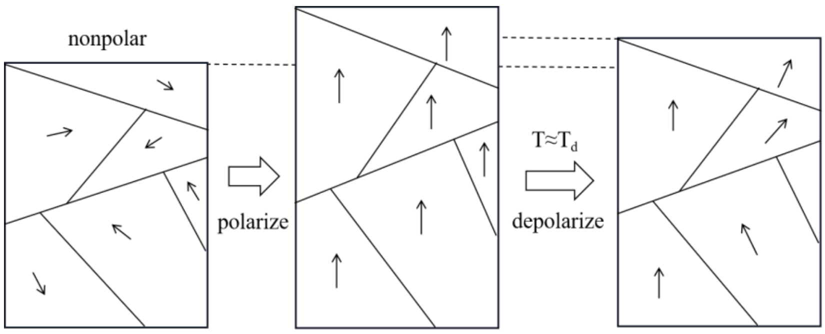

Figure 6. Polarization and depolarization diagram

3.1. Metal oxide dopant modification

ZnO is a polar semiconductor and possesses its piezoelectric properties, which can provide a compensating charge, and building a composite material with BNT-based ceramics can improve the T_d. Zhang et al [18] found that ZnO was able to inhibit the depolarization behavior of BNT due to the distribution of ZnO compound at the grain boundaries of the material, which provided charge to compensate for the depolarization of partially polarized electric field by using the nature of ZnO polar semiconductor, thus increasing the depolarization temperature and even making the depolarization phenomenon disappear. Zhang et al [19] suggested that the depolarization behavior in composites is not simply a transfer of T_d to higher temperatures, but a gradual diffusion to a wider temperature region. In addition, the residual stress exerts a pegging effect on the nanodomains around the ZnO particles, and the micron domains formed in the grains are bound by the charges generated by the spontaneous polarization of ZnO. Of course, other non-semiconductor metal oxides can also increase T_d. Wu et al [20] found that composite Al_2O_3 could increase the T_d of BNT-BKT ceramics from 116 ℃ to 227 ℃, and the samples could still maintain a stable piezoelectric coefficient (d_{33} > 60 pC/N) at high temperature (210 ℃).

3.2. Multi-group meta-modification

BNT has poor ferroelectric properties, while barium titanate ($BaTiO_3$, BT) has a high piezoelectric constant and dielectric constant. In order to take advantage of the performance of both, some scholars compounded BNT with BT to form a binary solid solution to obtain better ferroelectric properties. Devi et al [21] prepared BT doped BNT piezoelectric materials. BT doping reduced the coercivity field and they obtained d_{33} = 90 pC/N piezoelectric materials with T_C = 295 ℃. In addition, BNT-based and KNN-based ferroelectric ceramics are the most promising perovskite structural ceramics, and better ferroelectric properties are obtained by combining BNT and KNN to build MPB. Singh [22] et al. prepared (1-x)$Bi_{0.5}Na_{0.5}TiO_3$-x$K_{0.47}Na_{0.47}Li_{0.06}Nb_{0.47}Sb_{0.06}Ta_{0.2}O_3$ (BNT-KNNLTS) and found that the coexistence of ferroelectric and antiferroelectric phases at x = 0.08 , the electric field-induced bipolar strain reaches a maximum of 0.40 %. Better properties may be obtained if the composites are further ion doped. Other common multivariate systems include BNT-BKT, BNT-BZT, BNT-NN, etc. More perovskite, oxide and other types of doped BNT-based piezoelectric materials and their properties are shown in Table 2.

Table 2. Perovskite, oxide and other types of doped BNT-based piezoelectric materials

Chemical Formula	T_C (℃)	T_d (℃)	E_C (kV/cm)	d_{33} (pC/N)
0.8$Na_{0.5}Bi_{0.5}TiO_3$ + 0.2$BaTiO_3$	295	—	3.56	90
0.7Bi0.5Na0.5TiO_3-0.2Bi0.5K0.5TiO_3-0.1$BaZr_{0.05}Ti_{0.95}O_3$	320	—	19.1	240
0.94$Bi_{0.5}Na_{0.5}TiO_3$-0.06$BaTiO_3$	290	72	—	155
0.98(0.83$Bi_{0.5}Na_{0.5}TiO_3$-0.17$Bi_{0.5}K_{0.5}TiO_3$)-0.02$NaNbO_3$	—	—	38	214
0.93$Bi_{0.5}Na_{0.5}TiO_3$-0.06$BaTiO_3$-0.01 $K_{0.5}Na_{0.5}NbO_3$-0.01CuO	288	—	—	28
0.83$Na_{0.5}Bi_{0.5}TiO_3$-0.17$Bi_{0.5}K_{0.5}TiO_3$ + 5 mol BT	—	17	6.6	12
0.83$Na_{0.5}Bi_{0.5}TiO_3$-0.17$Bi_{0.5}K_{0.5}TiO_3$ + 5 mol NN	—	—	4.8	136

3.3. Quenching

Heat treatment processes are also an important means to increase the depolarization temperature of BNT-based ceramic materials. Nagata et al [23] first proposed that the T_d of BNT-based ceramics could be improved by quenching, and the T_d of BNT-based ceramics was increased by nearly 50 ℃ after quenching at 1100 ℃, and the ferroelectric and piezoelectric properties of the ceramics were not reduced. It is believed that quenching causes an increase in oxygen vacancies in ceramic samples, and the excess oxygen vacancies peg the electric domains and inhibit the steering of the domains at high temperatures, thus increasing T_d. The quenching medium and annealing atmosphere needs to be selected during quenching, and the cooling rate of the quenched ceramic needs to be controlled as well as the residual stresses present in the quenched ceramic need to be accurately tested to prevent microcracking and cracking of the ceramic.

Lead-free ceramic capacitors play an important role in electrical energy storage devices due to their ultra-fast charge and discharge rates and high-power density. and has fast prediction speed and convenient operation. Yang et al [24] prepared by solid-phase reaction method (1-x)[0.8$Bi_{0.5}Na_{0.5}TiO_3$-0.2$Ba(Zr_{0.3}Ti_{0.7})O_3$]-x$Sr_{0.7}La_{0.2}TiO_3$((1-x)(BNT-BZT)-xSLT) ceramics. excellent integrated energy storage performance was obtained. As shown in Figure 7, when x = 0.3, a high recoverable energy density (W_{rec} ~ 2.6 J/cm^3) and a high efficiency (η ~ 92.2 %) can be obtained simultaneously at 210 kV/cm. Meanwhile, the corresponding ceramics exhibit excellent temperature (20-140 ℃), frequency (1-200 Hz), and period stability (10^6 st). It is shown that the 0.7(BNT-BZT)-0.3SLT ceramics with well-integrated energy storage properties can be candidates for advanced pulsed power devices.5

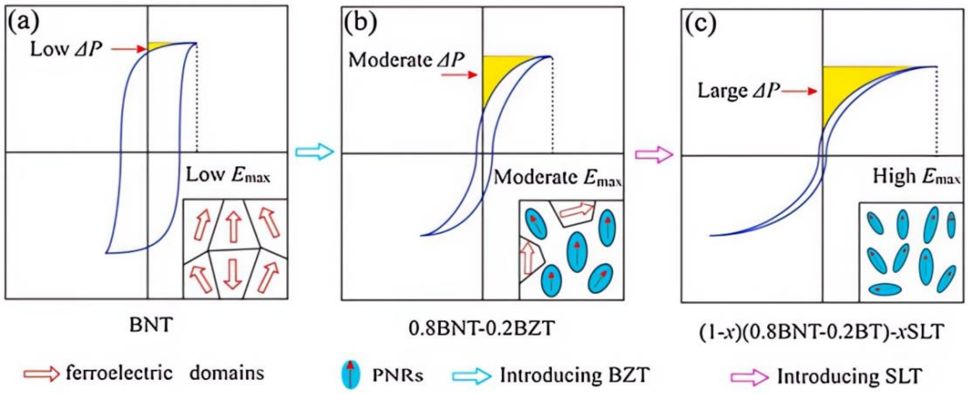

Figure 7. Schematic design strategy for relaxation ferroelectric ceramics with both high W_{rec} and high η [25]

Multi-Layer Actuator (MLA) is a direct conversion of electrical energy into mechanical strain or stress using the inverse piezoelectric effect of piezoelectric materials. Jeong et al [25] prepared CuAg/($Na_{0.37}Bi_{0.37}Sr_{0.26}$)$TiO_3$ (CuAg/ BNST), which exhibited similar bipolar strain and polarization behavior as MLA and compared to conventional AgPd/BNST devices. As shown in Figure 8, CuAg/BNST exhibits extremely low resistivity and dielectric loss of 0.041 and 0.052, respectively. CuAg/BNST as a diesel injection valve system can easily achieve precisely controlled pre-injection and post-injection before and after the main injection compared with the traditional high-speed solenoid valve, which can increase power by about 10% and reduce fuel consumption by about 20%, and help a lot to reduce engine noise and improve exhaust emission rate.

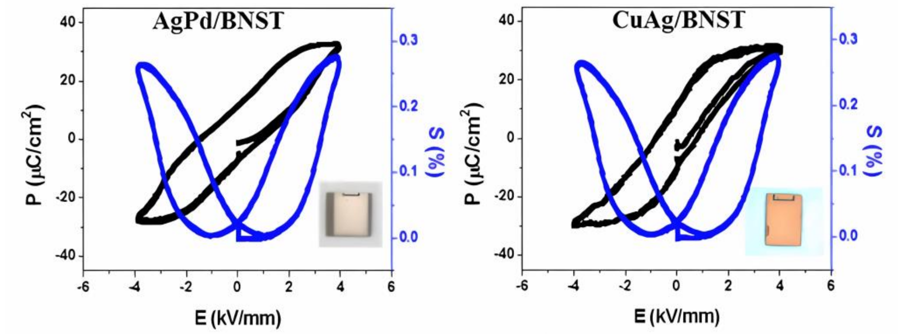

Figure 8. Variation of polarization and strain with electric field in AgPd/BNST and CuAg/BNST multilayer devices [26]

4. Summary

Piezoelectric materials are widely used in cutting-edge technologies such as automation, aerospace, and nanotechnology. Although traditional lead-based piezoelectric materials have excellent piezoelectric properties, they produce volatile PbO in the process of production and use, which can cause damage to human health and the environment. The research on new lead-free piezoelectric ceramics is an urgent need for the maturation of people's awareness of environmental protection and the implementation of the concept of sustainable development. Lead-free piezoelectric ceramic systems such as Bismuth Sodium Titanate (BNT), Potassium Bismuth Titanate (BKT), and Potassium Sodium Niobate (KNN) have been researched and discovered, they have high dielectric constant and Curie temperature, large electromechanical coupling coefficients, and mechanical qualities, as well as low losses when used. However, compared to lead-containing piezoelectric ceramics, sintering is difficult due to component volatilization, and most importantly, the low voltage electrical properties make it impossible for lead-free piezoelectric ceramics to replace lead-containing piezoelectric ceramics in production life on their own.

Therefore, KNN and BNT-based piezoelectric ceramics need to be further investigated. It is worth noting that BNT-based piezoceramics have a depolarization temperature which limits their applications, and the effect of depolarization temperature on the material needs to be reduced during modification. Lead-free piezoelectric ceramics can be improved by adding dopants, improving the preparation process, and achieving multi-phase coexistence to enhance the piezoelectric properties. Since both KNN and BNT have a perovskite structure, they are generally divided into A-site, B-site, and A and B-site co-doping during doping; When compounding, generally choose two or more lead-free ceramic systems for compounding, play the advantages of different components to complement each other's strengths. In addition, for lead-free piezoelectric ceramics, we need to investigate other properties such as mechanical properties, mechanical, and electrical fatigue behavior to further determine their possible application areas. In conclusion, KNN and BNT-based lead-free piezoelectric ceramics should be the focus of future research as a strong contender to replace lead-based piezoelectric ceramics.

References

[1] Shi, C., et al., Coexistence of excellent piezoelectric performance and high Curie temperature in KNN-based lead-free piezoelectric ceramics. Journal of Alloys and Compounds, 2020. 846.

[2] Jiang, M., et al., Ultrahigh piezoelectric coefficient of a lead-free K0.5Na0.5NbO3-based single crystal fabricated by a simple seed-free solid-state growth method. Journal of Materials Chemistry C, 2019. 7(47): p. 14845-14854.

[3] He, X., et al., High-Temperature Dielectric and Relaxation Behavior of Tantalum-Doped Sodium Bismuth Titanate-Barium Titanate Ceramics. Journal of Electronic Materials, 2020. 49(11): p. 6643-6655.

[4] Benyoussef, M., et al., Dielectric, ferroelectric, and energy storage properties in dysprosium doped sodium bismuth titanate ceramics. Ceramics International, 2018. 44(16): p. 19451-19460.

[5] Saito, Y. and H. Takao, High performance lead-free piezoelectric ceramics in the (K,Na)NbO3-LiTaO3 solid solution system. Ferroelectrics, 2006. 338: p. 1433-1448.

[6] Zhai, Y., et al., The photoluminescence and piezoelectric properties of Eu2O3 doped KNN-based ceramics. Journal of Alloys and Compounds, 2020. 829.

[7] Wu, J., Advances in Lead-Free Piezoelectric Materials. 2018: Advances in Lead-Free Piezoelectric Materials.

[8] Tao, H., et al., Relaxor behavior of potassium sodium niobate ceramics by domain evolution. Journal of the European Ceramic Society, 2021. 41(1): p. 335-343.

[9] Zhao, Y., et al., Domain switching mechanism of orthorhombic-tetragonal coexistence (Li, K, Na)NbO3 ceramics. Journal of Alloys and Compounds, 2018. 763: p. 695-700.

[10] Wong, J.Y.Y., N. Zhang, and Z.-g. Ye, High-temperature solution growth and vapour transport equilibration of (1−x)K1−yNaYNbO3–xLiNbO3 lead-free piezo-/ferroelectric single crystals. Journal of Crystal Growth, 2016. 452: p. 125-130.

[11] Yang, W., et al., Coexistence of excellent piezoelectric performance and thermal stability in KNN-based lead-free piezoelectric ceramics. Ceramics International, 2020. 46(2): p. 1390-1395.

[12] Wang, X., et al., Compositional dependence of phase structure and electrical properties in (K0.50Na0.50)(0.97)Bi-0.01(Nb1-xZrx)O-3 lead-free ceramics. Ceramics International, 2013. 39(7): p. 8021-8024.

[13] Duong, T.A., et al., Ferroelectric-to-relaxor crossover in KNN-based lead-free piezoceramics. Ceramics International, 2021. 47(4): p. 4925-4932.

[14] Sun, X.-x., et al., Understanding the piezoelectricity of high-performance potassium sodium niobate ceramics from diffused multi-phase coexistence and domain feature. Journal of Materials Chemistry A, 2019. 7(28): p. 16803-16811.

[15] Xing, J., et al., Potassium sodium niobate based lead-free ceramic for high-frequency ultrasound transducer applications. Journal of Materiomics, 2020. 6(3): p. 513-522.

[16] Weng, C.-M., et al., Effects of LiNbO3-doping on properties of (Na0.535K0.48)NbO3 piezoelectric ceramics with high electromechanical coupling coefficient for application in surface acoustic wave devices. Ceramics International, 2017. 43(14): p. 11324-11330.

[17] Zheng, T., et al., Recent development in lead-free perovskite piezoelectric bulk materials. Progress in Materials Science, 2018. 98: p. 552-624.

[18] Zhang, J., et al., Semiconductor/relaxor 0-3 type composites without thermal depolarization in Bi0.5Na0.5TiO3-based lead-free piezoceramics. Nature Communications, 2015. 6.

[19] Fan, Z., et al., Mechanisms of enhanced thermal stability of polarization in lead-free (Bi1/2Na1/2)(0.94)Ba0.06TiO3/ZnO ceramic composites. Physical Review Materials, 2019. 3(2).

[20] Yin, J., et al., Thermal depolarization regulation by oxides selection in lead-free BNT/oxides piezoelectric composites. Acta Materialia, 2018. 158: p. 269-277.

[21] Devi, C.S., et al., Influence of Ba2+ Ion Substitution on the Structural, Ferroelectric and Electrical Properties of Nano-Structured Na0.5Bi0.5TiO3 Lead Free Piezo Ceramics. Transactions of the Indian Ceramic Society, 2018. 77(1): p. 30-36.

[22] Singh, A. and R. Chatterjee, 0.40% Bipolar Strain in Lead Free BNT-KNN System Modified with Li, Ta and Sb. Journal of the American Ceramic Society, 2013. 96(2): p. 509-512.

[23] Muramatsu, H., H. Nagata, and T. Takenaka, Quenching effects for piezoelectric properties on lead-free (Bi1/2Na1/2)TiO3 ceramics. Japanese Journal of Applied Physics, 2016. 55(10).

[24] Yang, F., et al., Realizing high comprehensive energy storage performances of BNT-based ceramics for application in pulse power capacitors. Journal of the European Ceramic Society, 2021. 41(4): p. 2548-2558.

[25] Jeong, S.-J., et al., Properties of CuAg/(BiNaSr)TiO3 multilayer ceramic actuator. Ceramics International, 2018. 44: p. S112-S116.