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PROGRESSES AND FURTHER CONSIDERATIONS ON THE RESEARCH OF PEROVSKITE LEAD-FREE PIEZOELECTRIC CERAMICS

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The research on lead-free piezoelectric ceramics has been one of the important fields worldwide for years for the sustainable development of the world. In recent years, the author and his group concentrated their work on perovskite lead-free piezoelectric ceramics, especially on $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT)- and $K_{1/2}Na_{1/2}NbO_3$ (KNN)-based ceramics. In this paper, the researches of the composition design on BNT- and KNN-based lead-free piezoelectric ceramics, the effects of doping on the properties of these ceramics, the study of the temperature stability of these ceramics, and the fabrication technique used in the author's group for these ceramics are reviewed, and the further considerations and some prospects to be resolved in coming years from the viewpoint of the device applications of these ceramics are suggested.

Keywords: Lead-free piezoelectric ceramics; $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT); $K_{1/2}Na_{1/2}NbO_3$ (KNN); perovskite structure.

1. Introduction

$Pb(Ti, Zr)O_3$ (PZT) and PZT-based multi-component piezoelectric ceramics have been widely used in various devices for more than half century because of their superior properties. However the toxicity of lead oxide and its high vapor pressure during material processing may bring serious problems. The demand of the sustainable development of the world and of the environmental and safety concerns has induced a new surge in developing lead-free piezoelectric ceramics with their properties comparable to the PZT-based ones.

Lead-free piezoelectric ceramics can roughly be divided into three kinds[1]: perovskite, tungsten bronze, and bismuth layered structure ceramics. Bismuth layered structure ceramics, such as $Bi_4Ti_3O_{12}$, with their low dielectric constant, high T_c, and high anisotropy in the longitudinal and transverse coupling coefficients are susceptible for high T_c sensors, resonators and filters applications. Tungsten bronze materials, such as $Sr_xBa_{1-x}Nb_2O_6$, are useful for electro-optic and photorefractive applications. Lead-free piezoelectric ceramics with perovskite structure, such as bismuth sodium titanate $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT)- and $K_{1/2}Na_{1/2}NbO_3$ (KNN)-based ceramics, have shown high electromechanical properties, and some of the ceramics also show high Curie temperature T_c. It is believed that these ceramics are good

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candidates for actuator and high power applications, and also for invasive ultrasonic applications. In recent years, especially after the publication of the grain-oriented KNN-based ceramics,[2] the researches on lead-free piezoelectric ceramics have got much progress, and the people believe that new piezoelectric ceramics should be "lead-free at last".[3]

Since the late 1990s, the author has paid much attention to the research on lead-free piezoelectric ceramics. For example, at the 9th International Meeting on Ferroelectricity (August 24–29, 1997, Seoul, Korea), the author pointed out that "ferroelectric materials should comprise non-hazardous substances with a small environmental load, and the manufacturing processes for these materials should also be with a small environmental load", and "the research on lead-free piezoelectric ceramics is a typical example".[4] The author's group has concentrated the research work on perovskite lead-free piezoelectric ceramics, especially on the BNT- and KNN-based ceramics, in recent years. In present paper, the main results obtained in the author's group are reviewed, and the further considerations and some prospects to be resolved in coming years from the viewpoint of the device applications of these ceramics are suggested.

2. Composition Design of BNT- and KNN-Based Ceramics

2.1. *Design for new BNT-based ceramics*[1,5,6]

$(Bi_{0.5}Na_{0.5})TiO_3$(BNT) ceramics are considered to be excellent candidates for lead-free piezoelectric ceramics because of its relatively high remnant polarization ($38\,\mu C/cm^2$). However, BNT ceramics without substitutive ions and/or additives are very difficult to pole because of their relatively large coercive field ($E_c = 73\,kV/cm$) and high electrical conductivity, and the piezoelectric properties of these ceramics are not good enough for most practical uses.

In order to enhance the properties of BNT-based ceramics and meet the requirements for practical uses, the author's group did much work on BNT-based ceramics based on the design of the multiple complex in the A-site within perovskite ABO_3 compounds, resulting in that a group of new members of BNT-based ceramics, such as $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$,

$[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$,
$[Bi_{1-y}(Na_{1-x}Li_x)]_{0.5}Ba_yTiO_3$,
$[Bi_{1-y-z}(Na_{1-x-y-z}Li_x)]_{0.5}Ba_ySr_zTiO_3$,
$[Bi_{1-y-z}(Na_{1-x-y-z}K_x)]_{0.5}Ba_ySr_zTiO_3$
$[Bi_{1-y}(Na_{1-x-y}Li_x)]_{0.5}Sr_yTiO_3$
$(Bi_{0.5}Na_{0.5})_{1-x-y-z}Ba_xSr_yCa_zTiO_3$,

$[(Bi_{1-x-y}L_x)Na_{1-y}]_{0.5}Ba_yTiO_3$, were proposed and patented, and the piezoelectric and ferroelectric properties were investigated. These new ceramics possess a single-phase perovskite structure, and the substitute ions diffuse into the BNT lattices to form solid solutions. The bulk density of the ceramics is higher than 97% of the theoretical density. Table 1 exhibits the piezoelectric and ferroelectric properties of new BNT-based ceramics developed in the authors' group. From Table 1 it can be obtained that among the new BNT-based ceramics, $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$(BNKLT-$x/y$) ceramics possess essential and also excellent electrical properties. Compared with pure BNT ceramics, BNKLT-x/y ceramics possess simultaneously a very large P_r and a relatively low E_c, which leads to significant enhancement of piezoelectric properties of the ceramics.

From the viewpoint of device applications, the depolarization temperature T_d is an important factor for BNT-based ceramics. Generally, for some classical BNT-based ceramics, the obvious enhancement

Table 1. Piezoelectric and ferroelectric properties of new BNT-based ceramics developed in the author's group.[1]

New BNT-based systems	d_{33} (pC/N)	k_p	k_t	P_r ($\mu C/cm^2$)	E_c (kV/mm)
$Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$	230	0.41	0.505	40.4	2.5–4.0
$[Bi_{1-z}(Na_{1-y-z}Li_y)]_{0.5}Ba_zTiO_3$	208	0.37	—	38.5	3.29
$[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$	202	0.37	—	38.5	2.8–5.16
$[Bi_{1-z-u}(Na_{1-y-z-u}Li_y)]_{0.5}Ba_zSr_uTiO_3$	202	0.34	—	40.4	2.47–4.98
$[Bi_{1-z-u}(Na_{1-x-z-u}K_x)]_{0.5}Ba_zSr_uTiO_3$	191	0.36	—	34.4	2.58

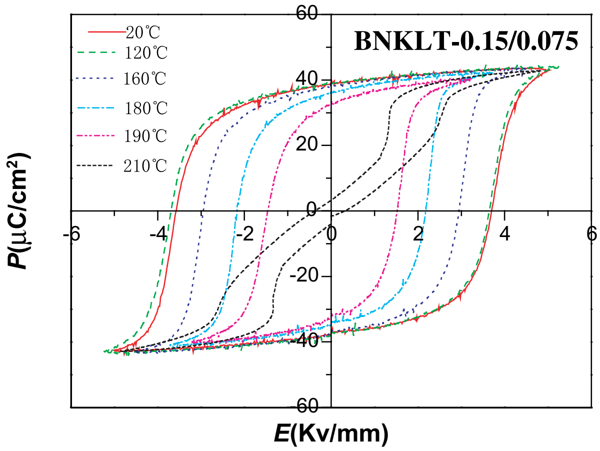


Fig. 1. (Color online) P–E hysteresis loops of BNKLT-0.15/0.075 ceramics at different temperature.[6]

of piezoelectric properties is accompanied simultaneously by the significant reduction of T_d. However, BNKLT-x/y ceramics provide simultaneously good piezoelectric properties, strong ferroelectricity, and higher T_d. Figure 1 shows the P–E hysteresis loops of BNKLT-0.15/0.075 ceramics at different temperature.[6] From Fig. 1 it can be found that BNKLT-0.15/0.075 ceramics provide simultaneously good piezoelectric properties ($d_{33} = 146$ pC/N, $k_p = 0.36$), strong ferroelectricity ($P_r = 38.9\,\mu$C/cm^2, $E_c = 3.7$ kV/mm), and higher T_d (about 200°C). The BNKLT-x/y ceramics have been used for making ceramic middle frequency filters and buzzers. The techniques used and the performances obtained for the devices made from BNT-based ceramics are almost the same as those made from PZT-based ceramics.

2.2. *Design for new KNN-based ceramics*

The researches on the composition design of KNN-based lead-free piezoelectric ceramics in the author's group were mainly focused on four aspects, which are the effects of K/Na ratio on KNN-based ceramics, the effect of Ag ion substitution on KNN-based ceramics, the effect of $LiSbO_3$ on KNN-based ceramics, and the effect of adding other perovskite components to KNN-based ceramics (also see Ref. 1). Here the author would like to mention the research work on the effects of K/Na ratio on KNN-based ceramics.

It is well accepted that the electrical properties of KNN-based ceramics depend not only on the composition but also on the temperature, and the coexistence of orthorhombic and tetragonal phases is responsible for the improvement of piezoelectric properties of the ceramics. The researches published show that not the morphotropic phase boundary (MPB), but the polymorphic phase transition (PPT) at room temperature plays an important role on KNN-based materials.[7–9] Therefore, it is necessary to shift the PPT of the KNN-based ceramics to near room temperature in order to obtain good electrical properties.

The effects of K/Na ratio on the phase structure and electrical properties of $(K_xNa_{0.96-x}Li_{0.04}) \times (Nb_{0.91}Ta_{0.05}Sb_{0.04})O_3$ (K_xNLNTS, $x = 0.32-0.56$) ceramics were studied.[10] The polymorphic orthorhombic-tetragonal (O–T) phase transition temperature was modified by changing the K/Na ratio in the K_xNLNTS ceramics, and the ceramics with a desired PPT near room temperature were obtained. Figure 2 shows the piezoelectric and dielectric properties of K_xNLNTS ceramics as a function of x, and Fig. 3 gives the temperature dependence of the dielectric constant at 10 kHz (a), and the Curie temperature (T_c) and the polymorphic orthorhombic–tetragonal (O–T) phase transition temperature ($T_{o\text{-}t}$) (b) for K_xNLNTS ceramics as a function of x. From the results it was found that the PPT temperature plays an important role on the electrical properties of K_xNLNTS ceramics. The ceramics with $x = 0.38$ exhibit enhanced electrical properties ($d_{33} \sim 306$ pC/N; $k_p \sim 48\%$; $k_t \sim 49\%$; $T_c \sim 337$°C; $\varepsilon_r \sim 1327$; $\tan\delta \sim 2.5\%$; $P_r \sim 34.9\,\mu$C/cm^2; $E_c \sim 11.3$ kV/cm) for a PPT near room temperature. Similar results were also obtained for related KNN-based ceramics.[11,12]

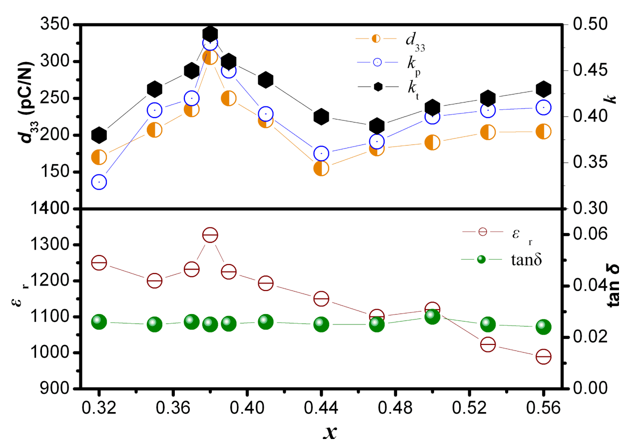
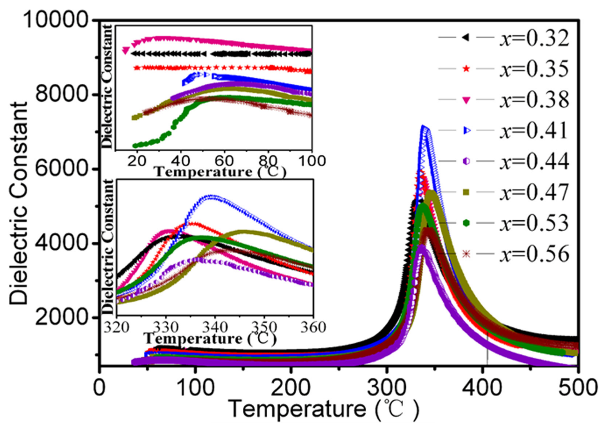
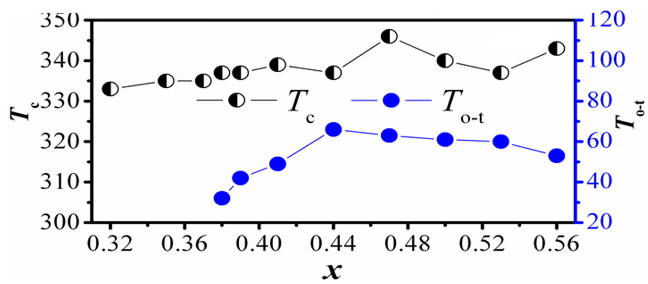


Fig. 2. (Color online) Piezoelectric and dielectric properties for K_xNLNTS ceramics as a function of x.[10]



(a)



(b)

Fig. 3. (Color online) Temperature dependence of the dielectric constant at 10 kHz (a) and T_c and $T_{o\text{-}t}$ (b) for K_xNLNTS ceramics as a function of x.[10]

3. Effects of Doping on the Properties of BNT- and KNN-Based Ceramics

3.1. *Effect of doping on the properties of BNT-based ceramics*

The effects of some additives, such as CeO_2, La_2O_3, Sm_2O_3, $MnCO_3$, MnO_2, Co_2O_3, on the electrical properties of the $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ (BNKLT-x/y) ceramics was investigated. Table 2 shows the electrical properties of the BNKLT-0.175/0.10 ceramics by doping of certain amount of the oxides.[1] It was obtained that for a small amount of doping both the La_2O_3 and Sm_2O_3 only act as "donor" for BNKLT ceramics, and the doping of MnO_2 and Co_2O_3 shows the "acceptor" effect. More details of the doping effect, such as the effects on the electrical properties, relaxor-like ferroelectric behavior, and the transition temperature from ferroelectric to antiferroelectric phases can be found in Refs. 1, 13 and 14.

3.2. *Effects of doping on the properties of KNN-based ceramics*

The effect of $CaTiO_3$-doping on the properties of KNN-based ceramics, $CaTiO_3$-modified $(K_{0.5}Na_{0.5})(Nb_{0.96}Sb_{0.04})O_3$ [$(1-x)$NKNS$-x$CT] ceramics, were investigated, the phase structure and piezoelectric properties of the ceramics were studied, and the effect of the poling temperature on the piezoelectric properties of the ceramics was also investigated.[15] The results show that $CaTiO_3$-modified $(K_{0.50}Na_{0.50})(Nb_{0.96}Sb_{0.04})O_3$ ceramics form stable solution with orthorhombic structure, and the Curie temperature and the polymorphic phase transition of the ceramics decreased with the increase of x. Figure 4 shows the piezoelectric and mechanical quality factor (a) and dielectric properties (b) of the $(1-x)$KNNS$-x$CT ceramics as a function of x, which indicates that when $x = 0.01$, the piezoelectric properties of d_{33} and k_p of the $(1-x)$KNNS$-x$CT ceramics reach to maximum. Moreover, the polarization temperature (T_p) will affect the piezoelectric properties of the ceramics.

The effect of doping of the oxides such as Co_2O_3, Pr_2O_3 and Yb_2O_3 on the properties of KNN-based ceramics was also investigated. For example, the effects of the doping of Co_2O_3 (0.03–0.4 mol%) on the phase structure and piezoelectric properties of lead-free piezoelectric ceramics $(K_{0.474}Na_{0.474}Li_{0.052})(Nb_{0.948}Sb_{0.052})O_3-x\%Co_2O_3$ [KLNLS$-x$%Co_2O_3] were systematically studied.[16] The results show that the phase structure of the

Table 2. Electrical properties of BNKLT-0.175/0.10 ceramics doped with different oxides.[1]

Amount	$\varepsilon_{33}^T/\varepsilon_0$	$\tan\delta$	d_{33} (pC/N)	k_p (%)	Q_m	P_r (μC/cm^2)	E_c (kV/mm)
0%	882	0.038	198	37.2	94	38.6	3.60
0.1 wt% CeO_2	915	0.026	220	38.8	104	37.0	2.90
0.5 mol% La_2O_3	1248	0.041	178	34.5	81	31.3	3.42
0.3 wt% Sm_2O_3	1265	0.054	212	35.4	78	33.5	3.12
0.05 wt% $MnCO_3$	931	0.033	209	39.0	102	39.5	3.40
0.1 wt% MnO_2	1053	0.033	192	33.5	102	36.0	3.59
0.05 wt% Co_2O_3	956	0.036	195	35.9	125	36.2	3.65

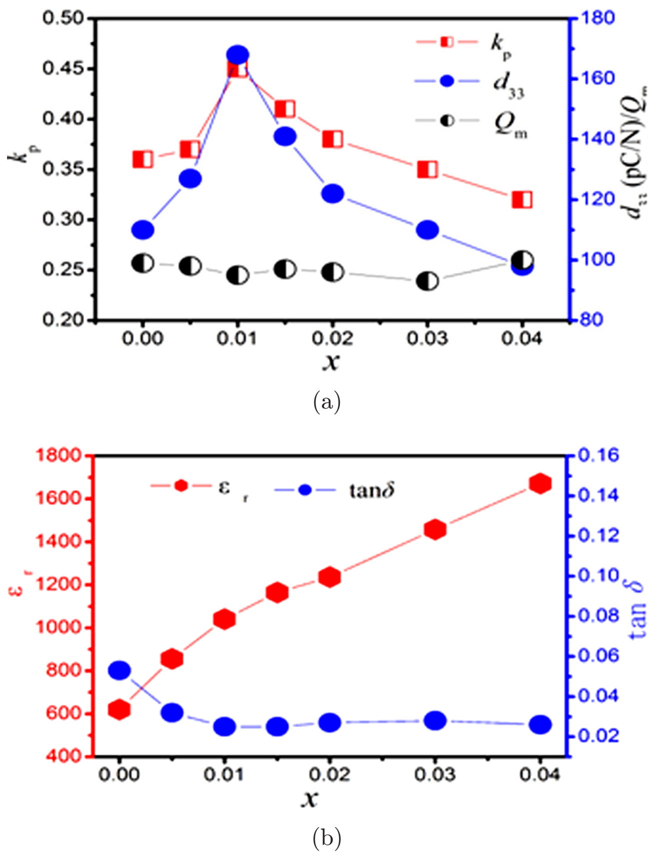


Fig. 4. (Color online) (a) Piezoelectric, mechanical quality factor and (b) dielectric properties of the $(1-x)$KNNS$-x$CT ceramics as a function of x.[15]

KNLNS$-x$%Co_2O_3 ceramics at room temperature is tetragonal one, and only a small amount of the additives of Co_2O_3 can diffuse into KNLNS lattices to form a stable solid solution. The density ρ of the ceramics increases gradually with the Co_2O_3 addition. KNLNS$-$0.03 mol%Co_2O_3 lead-free ceramics exhibit optimum properties ($d_{33} = 269$ pC/N, $k_p = 0.42$, $\varepsilon_r = 1371$, tan $\delta = 0.03$ and $T_c = 349$°C).

4. Temperature Stability of BNT- and KNN-Based Ceramics

It is known that the electrical properties of the BNT-based ceramics will change markedly above the depolarization temperature (T_d). Thus, it is very important to study the T_d of BNT-based ceramics from the viewpoint of application. The piezoelectric properties and their temperature dependence of $Bi_{0.5}(Na_{1-x}Ag_x)_{0.5}]_{1-y}Ba_yTiO_3$ (BNBT$y-x$Ag) ceramics were investigated, and the features of the T_d of the ceramics were discussed. The temperature dependence of dielectric and ferroelectric properties of the BNBTy–xAg ceramics were also measured. The detailed research results on the temperature stability of BNT-based ceramics can be found in Refs. 1, 17 and 18.

The study on the temperature stability of electrical properties for KNN-based ceramics is also very important from the viewpoint of applications. For example, the temperature stability, the thermal-depoling behavior, and the age characteristics of 0.98 $[(K_{0.4725}Na_{0.4725}Li_{0.055})NbO_3]-0.02Ag(Ta_{1-x}Sb_x)O_3$ ceramics were investigated in the author's group. The experimental results show that Sb strongly affects the microstructure, electrical properties, thermal-depoling behavior, and temperature stability of the ceramics, and the ceramics with $x = 0.40$, which possesses the optimum piezoelectric properties, also possesses improved temperature stability.[19]

The investigation on the temperature stability of the dielectric, piezoelectric, and ferroelectric properties of the ceramics can be used to study the relationship between the PPT and electrical properties of the KNN-based ceramics. An example was given in Refs. 1 and 20. The results indicate that the temperature stability of the piezoelectric, dielectric, and ferroelectric properties is relatively poor near the PPT, and it is very necessary to shift the PPT away from the application temperature range in order to improve the temperature stability of the electrical properties of KNN-based ceramics.

In addition, the substitution or doping of KNN-based ceramics may also change the temperature stability of the materials. For example, the $CaTiO_3$-modified KNN ceramics possess good temperature stability and exhibit high piezoelectric properties when the ceramics were poled at optimum poling temperature.[15,21]

5. Fabrication Technique for BNT- and KNN-Based Ceramics

The fabrication techniques and their relations to the properties of the materials related are overall one of the main research topics for ceramics. From the applications point of view, especially from the viewpoint of the applications of the ceramics in industrial and commercial areas, the simpler, energy saving, environmentally conscious, and more convenient fabrication techniques are needed. The author's group paid much attention in the fabrication techniques for lead-free piezoelectric ceramics.

For all of the BNT- and KNN-based ceramics mentioned above, the fabrication techniques are compatible with those usually used for PZT-based ceramics.

The authors in Ref. 22 have synthesized the fine KNN powders at low temperature of 550°C through a modified solid-state reaction method, and the dense KNN ceramics with good piezoelectric properties were obtained by using the fine KNN powders. The author's group of present paper has developed and patented a fabrication method for the powders of multi-component alkaline metal niobate-based lead-free piezoelectric ceramics and the KNN-based lead-free ceramics were prepared by using this method.[23] The results show that the powder of the KNN-based ceramics with favorable piezoelectric properties can be synthesized at temperature as low as 450°C for 4−5 h, and the ceramics made by using the powders possess good piezoelectric properties as the ceramics fabricated through traditional techniques possess. An example by using this new technique for KNN-based ceramics was shown in Ref. 24, and it was demonstrated that this new technique can also be used for BNT-based ceramics as proved in author's group very recently.

6. Further Considerations and Some Prospects to be Resolved from the Viewpoint of the Applications

The research results on the dielectric, ferroelectric and piezoelectric properties of the perovskite BNT- and KNN-based ceramics published up to now demonstrate that the ceramics are superior candidates for lead-free piezoelectric materials, and these ceramics seem to be suitable for actuator and high-power applications that require a large piezoelectric constant, high Curie temperature, or high depolarization temperature.[1,25] However, compared the researches for lead-free piezoelectric ceramics with those for PZT-based ceramics, there is much more work to be done from the viewpoint of device applications of the ceramics.

6.1. *Studies on the related mechanisms needed*

Some basic studies on the related mechanisms of lead-free piezoelectric ceramics are really needed. Any of the basic problems, such as the origin of the piezoelectric effect of the ceramics; the mechanism of the loss of the ceramics at room temperature; the sintering mechanism and its relations with the density of the ceramics; the relations of the composition-preparation-structure-properties-performance of the ceramics; is needed for systematic study.

6.2. *Composition design of the ceramics*

The main objectives of the researches on the composition design of the lead-free piezoelectric ceramics are the understanding on the phase structure of the material system related and searching for special composition of the materials with excellent properties. For example, for KNN-related ceramics, the aim of the composition design of the ceramics is to understand the phase boundary, especially the polymorphic phase transition (PPT) of the ceramics; the role of the ion substitution and/or K/Na ratio for some special compositions of the ceramics; and the electrical and/or related properties of the ceramics with the compositions; etc. In which the key scientific question is the understanding the PPT of the system at or near room temperature, and the features of the phase transition of the ceramics.

6.3. *Effects of doping on the properties of the ceramics*

It is well known that the doping has great effect on the properties for PZT-based piezoelectric ceramics, and therefore doping is a very important and widely accepted technique to improve the properties of the specific ceramics. There are mainly three kinds of doping methods accepted: the acceptor doping resulting in the "hard" piezoelectric properties; the donor doping resulting in the "soft" piezoelectric properties; and the doping with the valence alternation resulting in the specific piezoelectric properties wanted. As compared with those used in study of PZT-based ceramics, different mechanisms for explaining different doping effects revealed in the investigation of lead-free piezoelectric ceramics should be proposed. Frankly speaking, comparing with the study of PZT-based ceramics people know only a little about the effects of doping on the properties of lead-free piezoelectric ceramics. In the author's opinion, the main focuses of the researches on doping effect for lead-free piezoelectric ceramics may be (1), to understand how various dopants or additives affect the properties of lead-free piezoelectric ceramics; (2), to understand whether there are the similar doping effects just as those for PZT-based ceramics, and what is the difference of the doping effect for both PZT-based and lead-free ceramics; (3), to understand the doping mechanisms for perovskite lead-free piezoelectric ceramics from microscopic scale and (4), to obtain typical optimized compositions of lead-free ceramics for specific devices or applications, just like the well-known typical PZT-based ceramics family (from PZT-4 to PZT-8).

6.4. *Temperature stability and aging characteristic of the ceramics*

Ideal temperature stability of the properties of the piezoelectric ceramics allows the applications of the ceramics to operate over wider temperature range, and the excellent aging characteristic properties allow the applications to operate over a long period. Therefore the researches on the temperature stability and the aging characteristic of piezoelectric ceramics are very important from the viewpoint of applications.

It is worth to be pointed out that the researches on the temperature stability and the aging characteristic properties of the lead-free ceramics need the researchers to pay more not only the carefulness but also the patience. The present author had done the researches on the aging characteristic properties of the lead-based ceramics through the continuous actual measurements of the properties of PZT-based ceramics for 15 years, and the results were very interesting and not quite as what expected.[27]

6.5. *Fabrication techniques and their relations to the ceramics*

The fabrication techniques and their relations to the properties of the materials related are overall the main topics for materials research, especially for ceramics. From the viewpoint of the applications of lead-free piezoelectric ceramics, the simpler, energy saving, and more convenient fabrication techniques are needed. Developing new processing techniques which are environmentally conscious and can make the materials possess optimum properties with low production cost are the objectives of the research for lead-free piezoelectric ceramics.

6.6. *Researches of the devices applications*

The researches on the properties of the perovskite lead-free piezoelectric ceramics published up to now demonstrate that the ceramics are suitable for different devices. However, compared with the researches on PZT-based ceramics, there is much more work to be done for the device applications. The general problems, such as the understanding of the loss mechanism of the ceramics and seeking of the technique to improve the mechanical quality factor of the materials; the seeking of various ceramics for different device applications with optimum properties; and the understanding of the properties of the ceramics under different conditions of pressure, frequency, and temperature; should be resolved. The optimized compositions of lead-free ceramics for specific applications, just like the well-known typical PZT series ceramics (from PZT-4 to PZT-8), should be developed. And, of course, the special designs and fabrications for the lead-free piezoelectric devices are very urgent.

7. Conclusion

The author and his group concentrated their work on perovskite $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT)- and $K_{1/2}Na_{1/2}NbO_3$ (KNN)-based ceramics in recent years. In this paper, the main results obtained, including the composition design of the ceramics, the effects of different oxides doping on the properties of the ceramics, the investigation of the temperature stability and aging characteristic of the ceramics, and the low-temperature synthesis technique for the powders of the ceramics, are reviewed. The further considerations and some prospects to be resolved in coming years, such as the study of related mechanisms, the composition design for the understanding of the phase structure of the materials and searching for special ceramics with excellent properties, the study of the doping for the ceramics, the researches on the temperature stability and the aging characteristic of the ceramics, the research of the simpler, energy saving, and more convenient fabrication techniques for the ceramics, and the special design and fabrications for related devices, are suggested.

Very recently, the authors in Ref. 28 invented a novel lead-free piezoelectric BZT−BCT (barium zirconate titanate−barium calcium titanate) ceramics, and achieved very excellent piezoelectric property.

All the published work on lead-free piezoelectric ceramics up to now shows that lead-free piezoelectric ceramics, especially the perovskite ones, will be put into practical applications in various devices in the very near future.

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