Piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$ - $BaTiO_3$ lead-free ceramics prepared by spark plasma sintering

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$(K,Na)NbO_3$ (KNN)-based lead-free piezoceramics have been the spotlight in search for practically viable candidates to replace the hazardous but dominating lead-containing counterparts. In this work, $BaTiO_3$ (BT) modified KNN ceramics were fabricated by spark plasma sintering (SPS) and the influence of BT content as well as sintering temperature on the phase structure, microstructure, and electrical properties were investigated. It was found that the $0.96(Na_{0.5}K_{0.5})NbO_3$ - $0.04BaTiO_3$ (BT4) ceramics sintered at 1000°C have the optimal performance. Additionally, in-depth analysis of the electrical hysteresis revealed that the internal bias field originating from accumulation of space charges at grain boundaries is responsible for the asymmetry in the hysteresis loops.

Keywords: $(K,Na)NbO_3$; $BaTiO_3$; piezoelectric ceramics; spark plasma sintering.

1. Introduction

High-end piezoelectric materials, which enable direct conversion between mechanical and electrical energy, are pivotal to wide-ranging smart devices, for example, sensors, actuators, transducers, etc. Typically, such functional materials are lead-based solid solutions with strongly enhanced piezoelectricity in the vicinity of a morphotropic phase boundary (MPB). However, as concerns on health and environmental issues are intensified, lead-based piezoelectric materials are subjected to global restrictions, due to the richness and toxicity of lead in the compositions. To resolve the problem, researches on high-performance lead-free alternatives have been carried out intensively.

$(K,Na)NbO_3$, a lead-free piezoelectric solid solution between $KNbO_3$ and $NaNbO_3$, particularly since the breakthrough made by Saito *et al.*¹ has been considered as one of the most promising candidates to substitute lead-containing systems.^{2–4} Up to present, a lot of research papers on KNN-based lead-free piezoelectric ceramics have been published, including the piezoelectric properties,^{5–7} the energy-storage properties,⁸ etc. In order to further improve the piezoelectric properties of KNN, engineering of the polymorphic phase transition (PPT) between tetragonal and orthorhombic phases, i.e., shifting downward the PPT point T_{O-T} to ambient temperature through chemical modifications,⁹ has been employed, represented by the formation of pseudobinary solid solutions between KNN and one additional component,

e.g., $KNN-LiTaO_3$,^{10–14} $KNN-LiSbO_3$,^{15–17} $KNN-BiFeO_3$,¹⁸ and so on.

Despite the promising piezoelectric response, KNN-based piezoceramics is well known for suffering poor sinterability, such as narrow sintering temperature range and severe volatilization of alkaline elements.^{19,20} To address these issues, pressure-assisted sintering processes, such as spark plasma sintering (SPS) and hot-pressing, were used in the sintering of KNN-based ceramics.^{21–23} SPS has the advantages of short soaking time and lower sintering temperature, yielding higher mechanical properties and restraining the volatilization of alkaline elements in KNN-based ceramics, compared with the conventional sintering approaches. Park *et al.* have found that the abnormal grain growth in KNN ceramics is related to the volatilization of Na_2O ,²⁴ which limits the applications of KNN-based ceramics sintered by conventional process. It is worth noticing that SPS is favorable to improve piezoelectric properties of KNN with relatively simple compositions, such as pure KNN²⁵ and $(Na_{0.535}K_{0.485})_{0.95}Li_{0.05}(Nb_{0.8}Ta_{0.2})O_3(KNNLT)$,²⁶ but it has no significant positive effect on more complex compositions, e.g., $0.95(Na_{0.49}K_{0.49}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ - $0.05CaZrO_3$ (CZ5),²⁷ is possibly attributed to the severe compositional segregation. As is shown, a simple composition is preferred for SPS-sintered KNN-based ceramics.

In this study, the $(1-x)(Na_{0.5}K_{0.5})NbO_3$ - $xBaTiO_3$ - $(KNN-BT)$ ceramics are successfully sintered by SPS and the

piezoelectric properties are investigated. The influence of BT content on the crystal structure and piezoelectric properties was studied, revealing that KNN-BT ceramics sintered by SPS show the best performance when BT content is 4 mol%. As KNN-based lead-free piezoelectric ceramics are sensitive to the sintering temperature, variation of the phase structure and piezoelectric properties with different sintering temperatures were also discussed. It was found that 1000°C is the best sintering temperature for KNN-BT ceramics. Diffuse peaks were observed in the temperature-dependent permittivity curves, when BT content increases or sintering temperature decreases. Asymmetry in the hysteresis loops was found in some samples with specific sintering conditions, which is caused by the internal bias field. The present study indicates that SPS is an effective method to obtain highly dense KNN-based ceramics with enhanced piezoelectric response. Meanwhile, with the increase of inhomogeneity, the best sintering conditions such as BaTiO₃ content and sintering temperature show the deviation with the conditions of normal sintering.²⁴

2. Experimental Methods

Reagent-grade K₂CO₃, Na₂CO₃, Nb₂O₅ and BaTiO₃ were used in this study. Raw materials were weighed stoichiometrically and ball milled for 12 h in ethanol using ZrO₂ balls. After drying and sieving, the mixed powders were calcinated at 900°C for 5 h and ball milled again to enhance the compositional homogeneity. The synthesized powders were loaded into a graphite die of 12 mm inner diameter and sintered into ceramics by an SPS apparatus (Dr. Sinter 1020 SPS, Sumitomo Coal Mining Co. Ltd., Kawasaki, Japan) at 50 MPa and different sintering temperatures for 3 min with a heating rate of 100°C/min. After cooling down, the ceramics were polished and annealed in air at 900°C for 8 h to eliminate oxygen vacancies formed during the SPS process.

The Archimedes method was used to measure the densities of the sintered samples. Their crystal structure was determined by X-ray diffraction (XRD, Rigaku, D/Max250, Tokyo, Japan). The microstructure was observed by scanning electron microscope (SEM, JSM-6460LV, JEOL, Tokyo, Japan). For macroscopic electrical characterizations, the samples were painted with silver paste on both surfaces, then fired at 550°C for 1 h to form electrodes. Polarization $P-E$ hysteresis loops, bipolar strain curves and field-dependent piezoelectric coefficient $d_{33}-E$ curves and permittivity $\varepsilon-E$ curves were recorded on a ferroelectric work station (aix-ACCT TF Analyzer 1000, Germany). The small-signal d_{33} and ε_{33} were measured by applying a triangular signal of 3 kV/mm and the frequency of 1 Hz combined with an AC voltage of 25 V and the frequency of 250 Hz. The temperature dependence of permittivity were determined with an impedance analyzer (TH2827, Changzhou Tonghui Electronic Co, China). The samples were polarized under an electric field of

3 kV/mm at 100°C for 30 min, and then the piezoelectric coefficient d_{33} was characterized by a quasi-static piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China).

3. Results and Discussion

3.1. The effect of BaTiO₃ content

Figure 1 shows the XRD patterns of the $(1-x)$ KNN- x BT (abbreviated as BT_y, $y = 100x$) ceramics sintered by SPS with $x = 0, 0.03, 0.04, 0.05, 0.06$ (BT0, BT3, BT4, BT5, BT6). All the samples possess a single-phase perovskite structure, but the peak intensity varies depending on the x value. For $x \leq 0.04$, the relative intensity rate of (200) to (020) is about 2:1, which is the characteristic of an orthorhombic symmetry. With further increasing BT content, the two separated peaks begin to merge into one single peak, which indicates the evolution of phase structure from orthorhombic to pseudocubic. For KNN-BT ceramics prepared by conventional method, however, tetragonal and orthorhombic phases coexist when $0.04 \leq x \leq 0.06$; when x exceeds 0.06, the tetragonal phase becomes dominant.²⁸ This phenomenon may be caused by small-sized grains of BT6 as shown later and was once found in another research.²⁹

Figure 2 displays the SEM images of the fracture surface of the SPS-sintered KNN-BT ceramics with different BT contents. Homogeneous grain size distribution is observed in all compositions. According to the report by Park *et al.*,²⁴ KNN-based ceramics sintered by conventional sintering exhibit an abnormal grain growth behavior, which is related to the large amount of liquid phase engendered during the conventional sintering process. In contrast, the reduced soaking time and sintering temperature during SPS process can dramatically suppress the abnormal grain growth.

Figure 3 presents the temperature dependence of the relative dielectric constant of the KNN-BT ceramics sintered by SPS at 1000°C with different BT contents. The corresponding data of KNN ceramics prepared by conventional sintering at 1070°C was included for comparison. As shown in the

Fig. 1. XRD patterns of ceramics with $x = 0$ (BT0), $x = 0.03$ (BT3), $x = 0.04$ (BT4), $x = 0.05$ (BT5) and $x = 0.06$ (BT6).

Fig. 2. SEM images of fracture surface of ceramics with different BT contents: (a) BT0, (b) BT3, (c) BT4, (d) BT5 and (e) BT6.

figure, both the Curie temperature (T_C) and the orthogonal-tetragonal PPT point (T_{O-T}) decrease with raising BT content when x is below 0.04. However, for the $x > 0.04$ samples, the shape of the permittivity peak becomes remarkably broadened, indicating that the BT content reached the solid solubility. Meanwhile, the pure KNN sintered by SPS shows a higher relative dielectric constant in the whole temperature range than that sintered by the conventional method.

It is notable that the diffuseness of the peak of relative permittivity is related to the BaTiO_3 content. Analogous phenomenon was reported in KNN-LT-BS piezoceramic, which is attributed to the core-shell structure formed from compositional inhomogeneity.³⁰ In the core-shell structure, the grains are composed of core and shell parts with different contents of elements. In the samples with low doping level, the core-shell structure is inconspicuous because of the

Fig. 3. Temperature dependence of the relative dielectric constant for samples with various BT contents.

restricted chemical inhomogeneity, and will only result in the formation of a slightly broad peak. However, in the samples with doping compound content up to solubility, the inhomogeneity is more severe, causing obvious core-shell structure. In these samples, multi-peaks could be observed in the permittivity curves. In certain situations, the peaks couple with each other, resulting in a very diffuse peak as those in curves of BT5 and BT6 in Fig. 3.

Figure 4 shows the polarization P – E hysteresis loops, bipolar strain curves, field-dependent piezoelectric coefficient d_{33} – E curves and permittivity ε – E curves of SPS-sintered KNN-BT ceramics. All samples were measured under an electric field around 3 kV/mm. The P – E hysteresis loops and bipolar strain curves of KNN-BT ceramics were depicted in Figs. 4(a) and 4(b), respectively, from which it can be

concluded that the BT3 and BT4 ceramics exhibit superior performance to BT5 and BT6 counterparts. The measurements of d_{33} – E for all components, as shown in Fig. 4(c), reveal that the BT4 sample shows the highest piezoresponse, consistent with the above results. Generally, the piezoelectric response is composed of intrinsic and extrinsic contributions. The former refers to linear piezoelectric effect derived from lattice displacement, while the latter is related to the dynamics of domain wall motions, which is strongly influenced by the amplitude of input stimuli. In the case of d_{33} – E curves of lead-free piezoceramics, the d_{33} value reaches the peak around zero field, then it decreases linearly with increasing the magnitude of electric field, which can be ascribed to the restrained domain wall movement upon application of external electric field. In the present research, however, the piezoelectric coefficient barely decreases when the electric field is applied and increases. It is believed that it originates from the defects inherent in the ceramics, which were introduced during the SPS process. Defects will impede the movement of domain walls, resulting in limited extrinsic contribution to macroscopic piezoresponse; while the intrinsic counterpart will not be influenced by the defects. Consequently, reduced piezoelectric coefficient at zero electric field and electric-field-insensitive piezoresponse can be expected.

Figure 5 shows the piezoelectric coefficient d_{33} as a function of BT content. It can be seen that the piezoelectric coefficient reaches an optimal value as high as 124 pC/N at the BT concentration of 0.04, which is about two-fold of the response from pure KNN; while the piezoelectric constant of BT5 and BT6 is pretty low. While barium titanate is another popular piezoelectric material,^{31,32} the piezoelectricity of KNN-BT ceramics does not follow a linear relationship with increasing BT content.

Fig. 4. (a) P – E hysteresis loops (b) bipolar strain curves (c) d_{33} – E curves and (d) ε – E curves of BT x ceramics.

Fig. 5. Piezoelectric coefficient d_{33} of samples with different BT content.

Fig. 6. XRD patterns of BT4 ceramics with different sintering temperatures.

3.2. The effect of sintering temperature

Due to the problem of a narrow sintering temperature, the properties of KNN-based ceramics show obvious variation even when sintering temperature changes slightly.¹² Therefore, the sintering temperature should be considered as an

important factor on the properties of KNN-BT ceramics. With best comprehensive properties, BT4 ceramics were chosen as an example in this part. Temperatures were set to be 900°C, 950°C, 1000°C and 1050°C and then the properties of the ceramics were evaluated.

Figure 6 shows the XRD patterns of the BT4 samples sintered by SPS at different temperatures ranging from 900°C to 1050°C. It is observed that a pseudocubic phase exists for BT4 ceramics sintered at 900°C, which is attributed to a comparatively low sintering temperature, while the orthorhombic symmetry appears at higher temperatures. Figure 7 shows the SEM images of fracture surface of all samples. With increasing sintering temperature, the number of pores inside the sintered bulks gradually decreases. The samples sintered over 1000°C possess the highest density with few pores as well as inconspicuous blocky grains, and are expected to exhibit enhanced mechanical properties.

Figure 8 shows the temperature dependence of permittivity curves from the BT4 ceramics sintered by SPS at different temperatures. The sample sintered at 1000°C demonstrates a comparatively sharp peak around the Curie temperature as well as an obvious orthorhombic-tetragonal PPT hump. For other samples, the permittivity curves tend to be flat, resembling characteristics of diffused phase transitions. It is noted that a small fluctuation appears in all curves above the Curie temperature, while it is the most obvious for the sample sintered at 900°C. This phenomenon may indicate that certain inhomogeneous micro-structure appears in the BT4 sample regardless of the sintering temperature.

The influence of sintering temperature on the $P-E$ hysteresis loops, bipolar strain curves, $d_{33}-E$ curves and $\varepsilon-E$ curves of the BT4 ceramics was presented in Fig. 9. According to the $P-E$ hysteresis loops [Fig. 9(a)] and bipolar strain curves [Fig. 9(b)], the BT4 ceramics sintered at 1000°C show better performance than other samples. The $d_{33}-E$ and $\varepsilon-E$ curves reveal that the BT4 ceramics sintered at 1000°C have the best piezoelectric and dielectric

Fig. 7. SEM images of fracture surface of BT4 ceramics with different sintering temperatures: (a) 900°C, (b) 950°C, (c) 1000°C and (d) 1050°C.

Fig. 7. (Continued)

Fig. 8. Temperature dependence of the relative dielectric constant for BT4 samples with different sintering temperatures.

properties, in consistent with the above analyses. It is noted that the coercive field of all samples keeps constant of about 1 kV/mm regardless of sintering temperature.

It is interesting that all kinds of curves of the sample sintered at 1050°C show remarkable asymmetry, as shown in Fig. 9. It is believed that the phenomenon originates from the internal bias field, which is caused by the accumulation of space charges.^{33–36} The effective electric field at position r can be expressed as:

$$E(r) = E_0(r) + E_d(r) + E_a(r), \quad (1)$$

where E_0 is the extrinsic electric field applied to the dielectric medium, E_d is the depolarizing field caused by the bound charges and E_a is the intrinsic field.³⁷ In this case, E_a is the internal bias field. There are several explanations about the origin of the internal bias field. One is the defect dipole,

Fig. 9. (a) $P-E$ hysteresis loops (b) bipolar strain curves (c) $d_{33}-E$ curves and (d) $\epsilon-E$ curves of BT4 ceramics as a function of sintering temperature.

which acts as a normal dipole and requires an external field to be reversed.³⁸ Another one is that the internal bias field probably comes from deallocated space charges, which is dominant in the present study. The space charges are brought into the ceramics by defects or dopants. During poling process, the polarization vectors near the grain boundaries may mismatch, leading to a depolarizing field. The space charges then migrate and accumulate at the grain boundaries to counteract the depolarizing field, resulting in the internal bias field. The depolarizing field is reversed against the extrinsic field, while the internal bias field is homodromous to the extrinsic one. When an extrinsic electric field with the same direction to the internal bias field is applied, the ceramics experience an effective electric field as the superposition of these two kinds of electric fields. When an extrinsic electric field with opposite direction is applied, the effective electric field is the difference of them. Consequently, the values of the effective electric field along different directions are distinct. It can be easily inferred that the response in different directions will be different, resulting in asymmetry in the response curves.^{34,35}

The obvious internal bias field of samples sintered at 1050°C is related to the large amount of defects generated by the comparatively high sintering temperature as well as the feature of SPS. The SPS is a short-time, thermodynamically unbalanced process and leads to much more defects inside ceramics, compared with the conventional sintering process. Given a higher sintering temperature than the proper one, this effect is severely strengthened in several ways, such as the volatilization of alkaline elements, partial melting of the ceramics, etc. Thus, the ceramics sintered at a high temperature contain more available space charges, which will accumulate around grain boundaries, resulting in a strong internal bias field and contributing to the asymmetry in the response curves.

Figure 10 shows piezoelectric coefficient of the BT4 ceramics as a function of sintering temperature. The sample sintered at 900°C shows low piezoresponse, indicating that the sintering temperature is not enough. Nevertheless, all the other three components show a high piezoelectric coefficient

Fig. 10. Piezoelectric coefficient d_{33} of BT4 ceramics as a function of sintering temperature.

d_{33} over 100 pC/N. The highest piezoelectric coefficient appears at the sintering temperature of 1000°C. Note that the piezoelectric coefficient of the sample sintered at 950°C is almost as high as that of samples obtained at 1000°C, though it shows small responses in $d_{33} - E$ and $\varepsilon - E$ curves. This seemingly contradicting results still need further investigation.

4. Conclusions

The $(1-x)\text{KNN}-x\text{BT}$ lead-free piezoelectric ceramics have been prepared by the SPS method. The effects of BT content and sintering temperature on the phase structure, microstructure, and electrical properties were studied. It was found that the BT4 ceramics sintered at 1000°C show the best piezoelectric response, while the internal bias field induced by the accumulation of space charge at grain boundaries is responsible for the asymmetry in the electrical hysteresis curves. The present study indicates that SPS is an efficient method for densifying novel lead-free compounds and achieving enhanced piezoelectric output, especially for those with poor sinterability. Compared with conventional sintering, SPS will also change the best sintering condition a little.

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