High-Throughput Preparation and Properties Investigation of BNT Based Lead-Free Piezoelectric Ceramics

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Abstract: A high-throughput (HT) bulk ceramic preparation process was applied to synthesize multi-compositional lead-free piezoelectric ceramics. The lead-free piezoelectric ceramic sample library with a chemical composition of 87Bi\textsubscript{0.5}Na\textsubscript{0.5}TiO\textsubscript{3}-6BaTiO\textsubscript{3}-7K\textsubscript{0.5}Na\textsubscript{0.5}NbO\textsubscript{3} (87BNT-6BT-7KNN) were prepared to confirm the validity of the HT preparation process. The XRD pattern and surface SEM images showed great consistency of the phase and morphology of the 16 samples in the library. The mean value of dielectric constant and piezoelectric coefficient were $\varepsilon_r = 1848$ and $d_{33} = 14\text{pC/N}$. Ferroelectric and strain properties also demonstrated a high consistency of $P_s$, $P_r$, $E_c$ and $d_{33}^*$ with the mean values of 25.9 $\mu\text{C/cm}^2$, 3.6 $\mu\text{C/cm}^2$, 0.64 kV/mm and 290 pm/V, respectively. The corresponding Coefficient of Variance (CV) values of all these parameters are quite low, which indicate that the HT method reported in this work is feasible in the discovering of new lead-free piezoelectric materials.

1. Introduction

The 1970s witnessed the beginning of high-throughput (HT) experiments when Hanaket \textit{et al.} put forward the concept of “multi-samples” in the research of superconducting materials [1]. Since then much attention has been paid to develop the HT method and great progress has been made in HT technology for material libraries synthesis and screening in the past decades [2-10]. Hubble \textit{et al.} developed a HT fabrication and testing methodology using an automated liquid handling workstation for the in-situ functionalization of Au NP films [11]. Stegk \textit{et al.} adopted a HT approach to investigate the phase boundaries of $(K_{x}Na_{1-x})_{1.3}Li_{x}(Nb_{1-}\gamma Ta_{\gamma})O_{3}$ system, the analysis of which was performed by a HT-compatible technique called automated powder X-ray diffraction[12]. Hasegawa \textit{et al.} prepared Al\textsubscript{2}O\textsubscript{3}-Y\textsubscript{2}O\textsubscript{3}-HfO\textsubscript{2} material library using a combinatorial film sample library preparation system based on pulsed laser deposition and achieved a dielectric mapping by a scanning microwave microscope and the crystal structure by a combinatorial X-ray diffractometer[13]. Chang \textit{et al.} developed a HT parallel preparation method to investigate the micro-wave dielectric material system of Li - Nb - Ti-O and revealed the dependence of composition-structure-performance of the materials[14]. These examples showed that HT methods have been successfully and effectively applied in the research of functional materials, which aroused great interest in the lead-free piezoelectric filed.
The excellent piezoelectric and ferroelectric properties as well as the abundant morphology phase boundary (MPB) make the $\text{Bi}_0.5\text{Na}_0.5\text{TiO}_3$-$\text{BaTiO}_3$-$\text{K}_0.5\text{Na}_0.5\text{NbO}_3$ system promising for the future applications on sensors and actuators via further doping or composite engineering [15-23]. However, the long research periods of traditional ceramics process, which usually includes a sequential process of raw material weighing, ball mixing, calcination, shaping and sintering, were unfavorable for accelerating the development of optimized material composition. In this work, we explored a HT approach for the preparation of lead-free piezoceramics. Due to its sensitivity on the uniformity of compositions, the $\text{87BNT-6BT-7KNN}$ material was selected as model system to verify the feasibility of the HT method.

2. Experimental procedure

The samples were prepared by using the $\text{BaTiO}_3$ (BT), $\text{Bi}_0.5\text{Na}_0.5\text{TiO}_3$ (BNT) and $\text{K}_0.5\text{Na}_0.5\text{NbO}_3$ (KNN) powders as the precursor materials. The BT powders are commercial product with a purity of 99.9% and an average particle size of 200 nm. The BNT and KNN powders were pre-synthesized using a conventional solid-state reaction method. The raw powders were $\text{Na}_2\text{CO}_3$ (99.0%), $\text{K}_2\text{CO}_3$ (99.0%), $\text{TiO}_2$ (99.0%), $\text{Bi}_2\text{O}_3$ (99.999%) and $\text{Nb}_2\text{O}_5$ (99.5%). For BNT and KNN powders, the raw materials were dried thoroughly and then weighed with stoichiometric amounts and ball-milled for 6 h in ethanol. The slurries were dried and then calcined at 750°C for 2 h (for BNT) and 850°C for 5 h (for KNN), respectively. The BNT and KNN powders were ready for use after ball-milled for 6 h.

A library of 16 samples with the same composition of $\text{87BNT-6BT-7KNN}$ were prepared parallely using BT, BNT and KNN as precursor powders, which went through automatically weighing, parallel mixing, batch shaping and sintering process (Figure 1). The automatic weighing was realized via material weighing instrument (SAP-1, Malcom, Japan) which equipped with 4 powder dosing units and an analytical balance accompanied a controlling software for sample weighing. Then, the batches of precursor materials in the numeric labeled jars were mixed in ethanol using zirconia balls as milling media for 1 h in a vertical vibration ball mill system (Xianou-96, China), which allows a library containing 16 batches of 20 ml PE jar to be mixed in parallel. After drying and sieving, the mixed powders were put into numbered assembling molds with cylindrical cavity and pressed using a cold isostatic press machine into disks. Finally, the disks were sintered at 1120°C for 3 h in a Muffle furnace.

![Figure 1. High-throughput experiments schematic process.](image)

The 11th International Conference on High-Performance Ceramics

IOP Conf. Series: Materials Science and Engineering 678 (2019) 012140

IOP Publishing
doi:10.1088/1757-899X/678/1/012140
The bulk densities of the sintered ceramic samples were measured by the Archimedes method. The crystal structures of the ceramics were characterized using powder X-ray diffraction (XRD, D8 Advance, Bruker AXS GmbH, Germany). The surface microstructures of the samples were observed using scanning electron microscopy (SEM, XL30, Phillips, the Netherlands). To perform the electrical and electromechanical measurements, the sintered pellets were polished and painted with silver paste on both surfaces. Dielectric constant and loss at 1 kHz were measured using an impedance analyzer (DMS-1000, Partulab Co., Wuhan, China) at room temperature. The piezoelectric coefficient was measured using quasi-static piezoelectric $d_{33}$ meter (ZJ-6A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China) on the samples which were poled at room temperature and 4 kV/mm for 0.5 h. The polarization-electric field ($P-E$) hysteresis loops and the strain-electric field ($S-E$) curves were tested at 1 Hz using a FE analyzer connected with a laser interferometer (TF2000, aix-ACCT, Aachen, Germany).

![Figure 2. XRD patterns of the samples prepared by the parallel process (a); enlarge diffraction patterns in the $2\theta$ ranges of 45-48° (b); lattice constant and bulk density of the 16 samples in the library (c).](image)

3. Results and discussion

The uniformity and consistency of the samples are the most concerned issues of the HT process. The property sensitivity of the 87BNT-6BT-7KNN ceramics on composition gives us a reliable index to judge the validity of the parallel synthesis method. Figure 2a shows the XRD patterns of the 16
samples in the library. It can be seen that the XRD patterns of the 16 as-synthesized specimens are consistent with each other. A single perovskite phase was detected and no obvious traces of secondary phases were found, indicating that all the samples in the library were well mixed in the course of the parallel mixing process, and the BT, KNN and BNT were fully reacted during the sintering process. To give an insight into the structure, the enlarged diffraction pattern in the 2θ range of 45-48° is shown in Figure 2b. All of the samples exhibited a pseudo-cubic structure. No peak splitting was detected for the peaks of (200) at the corresponding angles, supporting the fact that there is no obvious long-range non-cubic distortion. Figure 2c is the lattice constant and bulk density of the 16 samples. All the samples have close lattice constants. The average values of a(b) and c are 5.52 Å and 3.90Å, respectively. The coefficient of variance (CV) was calculated according to equation (1):

\[
CV(x) = \frac{\sqrt{\sum_{i=1}^{16}(x_i - \bar{x})^2}}{\bar{x}} \times 100\%
\]

where ‘x’ presents the variable that was detected in the experiments, such as the lattice constant, density and etc. The calculated values of CV(a or b) and CV(c) were 0.058% and 0.038%, respectively. The small CV values demonstrate the test results are very close to their mean values. Meanwhile, the average bulk densities (ρ) of the samples are 5.37 g/cm³. It also shows quite small CV value (0.89%). These results indicate the good uniformity of samples synthesized by HT method.

![Figure 3. SEM images of 87BNT-6BT-7KNN ceramic sintered at 1120 °C.](image)

Figures 3a-f show the natural surface SEM images of 6 randomly selected ceramics. It can be seen that all the samples have the similar morphology feature where the square grains are always along with small particles. In order to get the quantitative description of the microstructure, the distribution of the grain size was counted. The distribution histograms were shown in the insets of images. The average grain sizes of the selected samples are 1.08 µm, 1.13 µm, 1.17 µm, 1.13 µm, 1.22 µm and 1.11 µm, respectively. A low average grain size CV value of 4.3% was obtained.

To further confirm the composition uniformity of the samples, the components of the samples were detected by EDS characterization. Figure 4a shows the SEM image of one selected 87BNT-6BT-
7KNN samples and the corresponding EDS surface scanning results of this area were shown in Figure 4b. As can be seen, its average contents are calculated to be 9.3\% (Bi), 9.8\% (Na), 19.0\% (Ti), 1.7\% (Ba), 0.8\% (K), 4.2\% (Nb), respectively, which agree with the nominal composition. Figures 4c-h show distribution maps of element Nb, Ti, K, Na, Bi and Ba. It can be seen that all components were homogenous and no obvious element segregation was observed, indicating that the prepared samples by using the HT method have very good composition uniformity.

Figure 4. SEM images of 87BNT-6BT-7KNN samples prepared through HT method (a); the corresponding EDS pattern (b) and the corresponding mappings of Nb, Ti, K, Na, Bi and Ba (c-h).

Figure 5. Dielectric constant, dielectric loss and piezoelectric coefficient $d_{33}$ values and corresponding mean values, CV values of 16 samples of 87BNT-6BT-7KNN ceramics.
As above mentioned, the electric performances of the 87BNT-6BT-7KNN ceramics are sensitive with the composition. Hence, the properties of the samples were further tested to judge the validity of HT method. The room temperature dielectric constant (ε_r) and dielectric loss (tan δ) of the samples were measured at 1 kHz and shown in Figure 5. The average dielectric constant is 1848 and the average dielectric loss is 0.0635. The CV values of average dielectric constant and average dielectric loss were calculated to be 1.7% and 4.14%, respectively. Furthermore, the piezoelectric coefficient (d_{33}) was tested. Consistent with the pseudo-cubic structure feature shown in Figure 2b, the d_{33} values were ~14 pC/N, which was not very high, indicating that this is the intrinsic feature of the 87BNT-6BT-7KNN ceramic.

Figure 6. The P-E hysteresis loops (a), I-E hysteresis loops (b), bipolar (c) and unipolar (d)S-E curves of 16 samples in the library and corresponding evolution of the ferroelectric properties (P_s, P_r and E_c) and normalized strain (S_max/E_max) (e) at room temperature.
As shown in Figure 6a, the $P-E$ loop of 87BNT-6BT-7KNN was slim, similar to the quasi-linear hysteresis loop, which is the typical characterization of relaxor ferroelectric. The saturated polarization ($P_s$) was up to 25.9 $\mu$C/cm$^2$, but the residual polarization ($P_r$) was only about 3.6 $\mu$C/cm$^2$. This is because the electric field induced polarization is not stable for relaxor ferroelectric and a depolarization process would be observed in the $I-E$ loop curves while the electric field decrease to zero (Figure 6b). The bipolar and unipolar electric induced $S-E$ curves were measured and shown in Figures 6c-d. Consistent with the $P-E$ loop, they also show typical characterization of the relaxor ferroelectric. A positive strain was observed and the normalized strain ($d_{33}^*$) was calculated to be $\sim$290 pm/V. Note both the $P-E$ loops and electric induced $S-E$ curves show good consistence among the 16 samples of the library, the $P_s$, $P_r$, $E_c$ and $d_{33}^*$ are collected and depicted in Figure 6e. The excellent consistence results are reflected in the low CV values of 0.94%, 8.4%, 6.1%, 3.3% for $P_s$, $P_r$, $E_c$ and $d_{33}^*$, respectively. Combined with previous analysis on density, phase, morphology, composition, dielectric, piezoelectric and ferroelectric properties, the great consistency of the measured parameters values of the HT prepared samples and quite small CV values confirm that HT process developed in this work is feasible in the study of lead-free piezoelectric ceramics.

4. Conclusions
A high-throughput (HT) technology was explored to prepare multi-composition lead-free piezoelectric ceramics. The validity of HT process was investigated by preparing a 87BNT-6BT-7KNN lead-free ceramic library. The samples prepared by HT method showed high homogeneity in density, phase composition, morphology and chemical composition. Meanwhile, the low CV values of the dielectric, piezoelectric and ferroelectric properties demonstrated the excellence of consistency. The experimental results demonstrated the feasibility of the HT method developed in this work for searching new high performance lead-free piezoelectric ceramics.

Acknowledgements
The authors would like to acknowledge the financial supports from the National Natural Science Foundation of China (NSFC Grant No. 51802330) and the Joint Funds of the National Natural Science Foundation of China and Guangdong Province (Grant No. U1501246).

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