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Low-Pb High-Piezoelectric Ceramic System (1−x)Ba(Zr_{0.18}Ti_{0.82})O_3−x(Ba_{0.78}Pb_{0.22})TiO_3

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Abstract: Piezoelectric materials, especially Pb-based piezoelectric materials, are widely used in the key components of sensors, actuators, and transducers. Due to the rising concern of the toxicity of Pb, global legislation has been adopted to restrict the use of Pb. Given that the available Pb-free piezoelectric materials cannot replace the Pb-based ones for various reasons, we designed and fabricated a low-Pb piezoelectric solid-solution ceramic system, (1−x)Ba(Zr_{0.18}Ti_{0.82})O_3−x(Ba_{0.78}Pb_{0.22})TiO_3 (denoted as BZ_{0.18}T−xBP_{0.22}T herein). The crystal structure, ferroelectric, dielectric, and piezoelectric properties of the BZ_{0.18}T−xBP_{0.22}T system were systematically studied. With the increase in BP_{0.22}T content, the structure of the samples changed from a rhombohedral phase to a tetragonal phase; the intermediate composition x = 0.5 was located at the morphotropic phase boundary of the system and corresponded to the state with the coexistence of the rhombohedral and tetragonal phases. Moreover, x = 0.5 exhibited the optimum comprehensive properties among all the samples, with a piezoelectric coefficient d_{33} of 240 pC/N, a maximum dielectric temperature Tm of 121.1°C, and a maximum polarization Pm of 15 μC/cm². Our work verifies the validity of the route to design low-Pb high-piezoelectric materials and may stimulate the interests for exploring new low-Pb high-performance ferroelectric and piezoelectric materials.

Keywords: low-Pb; piezoelectric; morphotropic phase boundary; phase transition

1. Introduction

Piezoelectric materials can realize the conversion between elastic energy and electric energy; thus, they are widely used in actuators, sensors, and transducers [1]. Since the discovery of high piezoelectricity in Pb(Zr_{0.52}Ti_{0.48})O_3 (PZT) [2], Pb-based piezoelectric materials, i.e., Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3 (PMN-PT) [3] and Pb(Zn_{1/3}Nb_{2/3})O_3-PbTiO_3 (PZN-PT) [4], have accounted for the majority of the market share [5].

However, with the rising concern regarding the hazards for both human health and the environment caused by the toxic element Pb, the use of Pb in electronic devices is facing fierce circumstance and will be rigidly limited by laws and regulations, such as “Waste Electrical and Electronic Equipment” (WEEE) and “The Restriction of the use of certain Hazardous substances in Electrical and Electronic Equipment” (RoHS). In such a situation, high-performance Pb-free or low-Pb piezoelectric materials are highly desired.

In the last two decades, many Pb-free piezoelectric materials have been introduced, such as (K_{0.5}Na_{0.5})NbO_3 (KNN) [6], (Bi_{1/2}Na_{1/2})TiO_3-BaTiO_3 (BNT-BT) [7], Ba(Zr_{0.2}Ti_{0.8})O_3−x(Ba_{0.7}Ca_{0.3})TiO_3 (BZTBCT) [8], etc. Although much effort has been devoted to this task, it has been admitted that all of the above-mentioned Pb-free materials face various problems; for example, the raw materials (K_2CO_3, Na_2CO_3) used to fabricate KNN are moisture-sensitive [9], the piezoelectricity of BNT-BT is inferior to most Pb-based materials [10], and the maximum dielectric temperature (Tm) is below 100°C (Tm of the optimum composition BZT-0.5BCT is 93°C) [8]. As a result, none of the above Pb-free materials can substitute for Pb-based ones.
Therefore, in the present study, we explore low-Pb high-piezoelectric materials as an alternative. As a comprehensive consideration, such a strategy will not only help people confront the situation of the strict limits on the use of Pb, it will also gain time for the exploration of Pb-free high-performance piezoelectric materials that can completely replace the Pb-based ones.

It has been well acknowledged that the design of morphotropic phase boundary (MPB) is an effective route to obtain high piezoelectricity [11]. At MPB, the coexistence of rhombohedral (R) and tetragonal (T) phases leads to the facilitated rotation and switching of polarization under external stress, thus yielding a high piezoelectric response [8,12]. The end members of such systems should meet the following criteria: (1) one end member undergoes the transition from the cubic (C) to T phase, while the other end member undergoes the transition from the C to R phase; (2) the two end members can form a solid-solution compound; then, a triple-point would exist [13]. We discovered that Zr-doped BaTiO$_3$ [14] and Pb-doped BaTiO$_3$ [15], satisfy the above requirements.

For the end member Zr-doped BaTiO$_3$, i.e., Ba(Zr$_{0.18}$Ti$_{0.82}$)O$_3$ (BZT), to ensure it satisfies the abovementioned criteria, $m$ was fixed as 0.18. For the end member Pb-doped BaTiO$_3$, i.e., (Ba$_{1-n}$Pb$_n$)TiO$_3$ (BPT), the value of $n$ should guarantee that the BPT undergoes one single transition from a cubic to a tetragonal phase. According to the phase diagram [15], when $n$ exceeds 0.2, this occurs. Therefore, the value of $n$ that satisfies the criterion is not unique and was selected as 0.22 in the present study. However, the value of $n$ should not be too large, which would be contrary to our aim—“low Pb” content. Thus, based on the two end member compounds, we designed the low-Pb solid-solution system (1–$x$)Ba(Zr$_{0.18}$Ti$_{0.82}$)O$_3$–$x$(Ba$_{0.78}$Pb$_{0.22}$)TiO$_3$.

**2. Materials and Methods**

The (1–$x$)Ba(Zr$_{0.18}$Ti$_{0.82}$)O$_3$–$x$(Ba$_{0.78}$Pb$_{0.22}$)TiO$_3$ (denoted as BZ$_{0.18}$T–xBPT hereafter; $x$ represents the mole fraction of (Ba$_{0.78}$Pb$_{0.22}$)TiO$_3$) ceramic samples were prepared with the conventional solid-state reaction method, with the raw chemicals of BaCO$_3$ (99.95%), ZrO$_2$ (98%), TiO$_2$ (99.9%), and PbO (99.9%). Considering that a Pb-induced nonstoichiometric compound usually leads to the formation of an oxygen vacancy [16], excess PbO (5 at%) was added to compensate for the loss of Pb. The calcining was performed at 1200°C in air for 2 h, and the sintering was performed at 1250°C in air for 3 h. The crystal structure was detected using an X-ray diffractometer (XRD, Bruker D8 ADVANCE, Hamburg, Germany). The temperature spectrum of dielectric permittivity was measured using an LCR meter (HIOKI-3532) at 10 kHz in a temperature chamber (Linkam), with the ramp rate of 2°C/min. The ferroelectric properties (Polarization-Electric field loops) were measured using a ferroelectric tester (Radiant Workstation Premier II, Albuquerque, NM, USA) at a frequency of 10 Hz at room temperature (22°C). The piezoelectric coefficient $d_{33}$ was measured using a Berlincourt-type $d_{33}$ meter (ZJ-3A). Before piezoelectric measurements, the ceramic samples were poled at 22°C for 1.5 h under an electric field of 1.0 kV/mm.

**3. Results and Discussion**

**3.1. Structural Characterization**

Figure 1a shows the X-ray diffraction (XRD) patterns for all the BZ$_{0.18}$T–xBPT samples. No reflections of a second phase appeared, demonstrating that all the samples possessed a pure perovskite ABO$_3$ structure [17]. The XRD profile of (200) reflection is shown in Figure 1b. From $x$ = 0 to 0.3, with the increase in BPT content, the reflection of (200) moved toward a higher angle, revealing the lattice constant decreased, which was caused by the smaller ionic radius of Pb$^{2+}$ [15]. No splitting of the (200) reflection suggested a rhombohedral crystal structure [17]. On the other hand, the (200) reflection moving toward a higher angle also implied that the BZ$_{0.18}$T and BPT formed into solid-solution; otherwise, the BPT would distribute mainly at the grain boundary and would not change the lattice parameters [18]. From $x$ = 0.6 to 1.0, the reflection of the (200) split into two peaks, agreeing well with the detected tetragonal crystal structure in Pb-doped
BaTiO$_3$ [15]. By contrast, the intermediate composition, $x = 0.5$, corresponded to the state with the coexistence of $R$ and $T$ phases, coined the MPB composition [8].

\[
\begin{array}{cl}
\text{(a)} & x = 0.0, 0.1, 0.3, 0.5, 0.6, 0.7, 0.9, 1.0 \\
\text{(b)} & x = 0.0, 0.1, 0.3, 0.5, 0.6, 0.7, 0.9, 1.0
\end{array}
\]

Figure 1. XRD profiles (a) and the (200) reflections (b) of the BZ$_{0.18}$T–xBP$_{0.22}$T ceramic powder samples at room temperature (22°C).

3.2. Dielectric Permittivity versus Temperature Spectrum

Based on the XRD results in Figure 1, several typical compositions were selected for further investigation, $x = 0, 0.1, 0.5, \text{and} 0.7$. Figure 2 shows the temperature spectrum of the dielectric permittivity ($\varepsilon$ at 10kHz) for the selected typical compositions (for $\varepsilon$ measured at multiple frequencies, please refer to Figures S1–S4). For $x = 0.0$ (BZ$_{0.18}$T), which exhibited an $R$ phase at room temperature, there appeared only one dielectric peak at 56.6°C, indicating the transition from the $C$ to $R$ phase and agreed well with a previous report [14]; for $x = 0.7$, which exhibited a $T$ phase at room temperature, there also appeared only one peak indicating the transition from the $C$ to $T$ phase [15]. For the intermediate compositions $x = 0.1$ and $x = 0.5$, there appeared two dielectric peaks, of which the one at a higher temperature indicated the $C$-$T$ transition, and the other one at a lower temperature indicated the $T$-$R$ transition. The doped BP$_{0.22}$T increased both the maximum dielectric temperature ($T_m$) and the $T$-$R$ transition temperature. Compared with the other compositions, $x = 0.5$ possessed both relatively large dielectric permittivity and good temperature stability. The observed composition-dependent dielectric behavior was consistent with those of the previously reported ferroelectric MPB systems, i.e., BZT-BCT [8] and BHT-BCT [13].

\[
\begin{array}{c}
\text{Temperature (°C)} \\
\text{ε (10³)}
\end{array}
\]

Figure 2. Dielectric permittivity versus temperature curves (10 kHz) for the selected compositions $x = 0, 0.1, 0.5, \text{and} 0.7$ of BZ$_{0.18}$T–xBP$_{0.22}$T. Compared with a normal paraelectric–ferroelectric transition [15], the shapes of the dielectric peak at $T_m$ for the BZ$_{0.18}$T–xBP$_{0.22}$T samples expanded to a broader temperature
range, and this is the typical feature of a diffuse phase transition [19]. In the paraelectric phase, the inverse dielectric permittivity \( (1/\varepsilon) \) for ferroelectric materials obeys the Curie–Weiss Law [19]:

\[
\frac{1}{\varepsilon} = \frac{T - T_C}{C}
\]

(1)

where \( T_C \) is the Curie temperature, and \( C \) is the Curie–Weiss constant.

The inverse dielectric permittivity versus temperature curves of the typical compositions \( x = 0, 0.1, 0.5, \) and \( 0.7 \) are listed in Table 1. Generally, the diffuse phase transition behaviors, and \( \gamma = 2 \) indicates the complete diffuse phase transition behavior, commonly regarded as relaxor behavior [19].

Figure 3. The inverse dielectric permittivity (10 kHz) versus temperature curves and corresponding fitted \( \ln(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m}) \) versus \( \ln(T - T_m) \) curves (inset) for the selected compositions \( x = 0 \) (a), 0.1 (b), 0.5 (c), and 0.7 (d) of BZ\(_{0.18}\)T–xBP\(_{0.22}\)T. The blue lines denote the linear fitting of \( \frac{1}{\varepsilon} \sim T \) above \( T_C \), and the green lines denote the linear fitting of \( \ln(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m}) \sim \ln(T - T_m) \) at high temperature regime.

The plots of \( \ln(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m}) \) versus \( \ln(T - T_m) \) curves are shown in the insets of Figure 3. The fitted parameters, \( T_C, T_m, \) and \( C \) and the estimated values of \( \gamma \) for \( x = 0, 0.1, 0.5, \) and 0.7 are listed in Table 1.

The composition \( x = 0.1 \) exhibited the strongest diffuse phase transition behavior, which can be understood from two aspects: (1) on one hand, as can be seen in Figure 2, the transition peak corresponded to the convergence of the \( C-T \) and \( T-R \) transitions; (2) on the other hand, for the solid-solution system \( (1-x)\text{BZT}-x\text{XBPT}, \) while the content of the BPT was low (i.e., \( 0 < x \leq 0.1 \)), the solution can be regarded as Pb and Ti co-doped BZT. Although Pb\(^{2+}\) and Ba\(^{2+}\) are of equal valence, their ionic radii are different. Substitution of Zr\(^{4+}\) with Ti\(^{4+}\) is of the same type. Therefore, co-doping of Pb\(^{2+}\) and Ti\(^{4+}\) would probably result in a relaxor-like state [21].
Table 1. The dielectric parameters of BZ$_{0.18}$T–xBP$_{0.22}$T (x = 0.0, 0.1, 0.5, 0.7) at 10 kHz.

| Composition | T$_C$ (°C) | T$_m$ (°C) | C (°C) | γ |
|-------------|------------|------------|--------|---|
| 0.0         | 48.8       | 56.4       | 3.63 × 10$^6$ | 1.763 |
| 0.1         | 54.6       | 56.0       | 1.14 × 10$^7$ | 1.945 |
| 0.5         | 85.0       | 121.1      | 6.10 × 10$^6$ | 1.790 |
| 0.7         | 130.0      | 168.6      | 1.21 × 10$^6$ | 1.780 |

It should be noted that the T$_m$ of the MPB composition of the BZ$_{0.18}$T–xBP$_{0.22}$T system, x = 0.5, was 121.1°C, nearly thirty degrees higher than that of the famous MPB composition BZT-0.5BCT (93°C) [8]. This means that the upper limit of working temperature for BZ$_{0.18}$T-0.5BP$_{0.22}$T is higher than that of BZT-0.5BCT, proving the validity of designing low-Pb high-piezoelectric materials via the MPB mechanism.

3.3. Ferroelectric and Piezoelectric Properties

The polarization (P)—ferroelectric field (E) hysteresis loops are shown in Figure 4. With the increase in BP$_{0.22}$T content from x = 0 to x = 0.5, the maximum polarization P$_m$ and remnant polarization P$_r$ first increased and then decreased, both reaching the maximum value at x = 0.5, which is clearly seen in Figure 5a,b, respectively. Generally, the enhancement of polarization results mainly from two factors: (1) the increase in the intrinsic spontaneous polarization [22] and (2) the facilitation of the ferroelectric domain switching [23]. As for the BZ$_{0.18}$T–xBP$_{0.22}$T system, both factors may contribute to the observed increase in polarization. On one hand, the increasing content of BP$_{0.22}$T is essentially equal to the increasing substitution of BaTiO$_3$ by PbTiO$_3$. PbTiO$_3$ possesses a larger c/a ratio, which results in a larger ionic polarization [24]; so the introduction of BP$_{0.22}$T (within a certain amount) leads to the increase in intrinsic spontaneous polarization [15].

On the other hand, when the volume fraction of BP$_{0.22}$T reaches a certain content, as 50 at% (x = 0.5) in the present study, the material locates at the MPB that corresponds to the state where the R phase and T phase coexist. The thermodynamic state at MPB has been well illustrated as the flattening of the Landau energy landscape with near-zero energy barrier between different neighboring phases [25,26]. At MPB, the ferroelectric domain can be switched under a lower field (although the coercive field E$_C$ of x = 0.5 was not the minimum among all the compositions) [12]. Therefore, the maximum polarization was obtained at x = 0.5. From x = 0.5 to 1.0, the greater potential well depths of PbTiO$_3$ gradually dominated and caused the domain switching to become more difficult as evidenced by the changing trend of E$_C$ (Figure 5c) [27]; so, the polarization decreased monotonously as the content increased from x = 0.5 to 1.0.

As for the minimum E$_C$ appearing at x = 0.3, it was probably due to the observed “invisible phase boundary” in such MPB-involved systems [28]. For the triple-point MPB involved system, the MPB derives from its starting point—the triple-point where three phases coexist [13]. Such phase coexistence naturally gives rise to the minimum energy barrier within the whole diagram; so, the MPB that derives from it yields a large response under small external fields. The minimum E$_C$ appearing at x = 0.3 suggested that the triple point of the system corresponded to the composition x = 0.3, similar to a previously reported (1−x)Ba(Ti$_{0.8}$Hf$_{0.2}$)O$_3$−x(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ system [28,29]. In addition, from x = 0.3 to 1.0, E$_C$ increased monotonously; this phenomenon was ascribed to the abovementioned greater potential well depths of PbTiO$_3$ [30]. This could also explain the difference between the BZ$_{0.18}$T–xBP$_{0.22}$T system and the BZT-BCT system; for the BZT-BCT, the lowest E$_C$ was observed at the MPB composition BZT-0.5BCT [8].
The measured piezoelectric coefficients $d_{33}$ of all the samples are shown in Figure 5d. Among all the available compositions, there were two peak values, one at $x = 0.1$ and the other at $x = 0.5$. The physical basis of the enhanced piezoelectricity at the MPB is the unique thermodynamic state with low energy barriers between neighboring ferroelectric states [12]. $x = 0.5$ was the MPB composition of the system, corresponding to the state of two-phase coexistence with a low energy barrier, which endowed it with a relatively low $E_C$ and high polarization, as well as transverse instability under external stimuli [26]. Thus, exhibiting a large $d_{33}$ value (240 pC/N), even exceeding that of the undoped PZT ceramics (160–190 pC/N) [31]. It should be emphasized that two-phase coexistence does not guarantee high piezoelectricity, although enhancement of piezoelectricity is usually observed, as evidenced in BNT-BT materials [10]. The increase in $d_{33}$ of $x = 0.5$ compared with other off-MPB compositions originates from the thermodynamic feature of MPB, which inherits partly from the triple point where three phases coexist with near-zero energy barriers. Therefore, in principle, the energy barrier of the MPB is lower than that of the polymorphic boundary (PB), and naturally the piezoelectric properties at the MPB are superior to those at the PB [32].

It is interesting that when $x = 0.1$, neither the end member composition nor the composition at phase boundary also showed a peak value of $d_{33}$ of 186 pC/N, comparable to the performance of undoped PZT ceramic. This should be attributed to the strongest diffuse phase transition behavior detected for the composition $x = 0.1$ (Table 1), as discussed above. In fact, tuning the normal ferroelectric transition to a diffuse phase transition has been regarded one of the efficient routes to obtain large piezoelectricity [33,34]. Overall,
the composition $x = 0.5$ exhibited the optimum comprehensive properties regarding the polarization, the coercive field, and the piezoelectricity.

![Figure 5](https://www.mdpi.com/xxx/s1){fig}

**Figure 5.** Composition dependence of the maximum polarization $P_m$ (a), remnant polarization $P_r$ (b), coercive field $E_c$ (c), and the piezoelectric coefficient $d_{33}$ (d) for $BZ_{0.18}$-$xBP_{0.22}$. The lines in the figure are guide for the eye.

Finally, it should be noted that Pb has an increased migration ability during the formation of ferroelectric materials with their content, thus affecting the properties and microstructure of the samples [35–37]. Although the Pb-induced nonstoichiometric and imperfection factors are beyond the scope of the current work, this issue should and will be seriously considered in the future.

4. Conclusions

In conclusion, considering that the worldwide laws and regulations that restrict the content of Pb in functional materials are about to be implemented, and that the currently reported Pb-free piezoelectric materials are far from commercial fabrication, we propose to design low-Pb high-piezoelectric material as an effective alternative. Based on the MPB mechanism, a new MPB-involved system, $BZ_{0.18}$-$xBP_{0.22}$, was fabricated. The optimum composition (also the MPB composition), $x = 0.5$, exhibited a high piezoelectricity of 240 pC/N and a high $T_m$ of 121.1°C. Our result verifies the validity of obtaining good piezoelectricity via fabricating a low-Pb MPB system with one end member of a Pb-free compound and the other end member of a Pb-based compound. We believe that low-Pb piezoelectric materials that can completely replace Pb-rich materials are coming soon.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/ma15144760/s1](https://www.mdpi.com/article/10.3390/ma15144760/s1), Figure S1: Dielectric permittivity versus temperature curve (100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz) of $x = 0$. Figure S2: Dielectric permittivity versus temperature curve (100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz) of $x = 0.1$. Figure S3: Dielectric permittivity versus temperature curve (100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz) of $x = 0.5$. Figure S4: Dielectric permittivity versus temperature curve (100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz) of $x = 0.7$. 


Author Contributions: Conceptualization, C.Z. and S.Y.; methodology, J.L.; investigation, J.L., X.Z. and T.Y.; writing—original draft preparation, C.Z., J.L. and Y.Z.; writing—review and editing, Y.Z. and C.Z.; supervision, S.Y.; funding acquisition; S.Y., C.Z. and J.L. contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key R&D Program of China (Grant Number 2021YFB3501401), the National Natural Science Foundation of China (Grant Numbers 91963111, 51601140), the Key Scientific and Technological Innovation Team of Shaanxi Province (Grant Number 2020TD-001), the Innovation Capability Support Program of Shaanxi (Grant Numbers 2018PT-28, 2017KTP-04), the Fundamental Research Funds for the Central Universities (China) and the World-Class Universities (Disciplines), and the Characteristic Development Guidance Funds for the Central Universities (China).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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