BiFeO$_3$-doped (Na$_{0.5}$K$_{0.5}$)NbO$_3$ lead-free piezoelectric ceramics

Xueyi Sun$^1$, Jun Chen$^1$, Ranbo Yu$^1$, Xianran Xing$^{1,2}$, Lijie Qiao$^3$ and Guirong Liu$^1$

$^1$ Department of Physical Chemistry, Ministry of Education of China, University of Science and Technology Beijing, Beijing 100 083, People’s Republic of China
$^2$ State Key Laboratory for Advanced Metals and Materials, Ministry of Education of China, University of Science and Technology Beijing, Beijing 100 083, People’s Republic of China
$^3$ Key Laboratory of Environmental Fracture, Ministry of Education of China, University of Science and Technology Beijing, Beijing 100 083, People’s Republic of China

E-mail: xing@ustb.edu.cn

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Abstract
Lead-free piezoelectric ceramics (1 − x)(Na$_{0.5}$K$_{0.5}$)NbO$_3$-xBiFeO$_3$ (x = 0.07) were synthesized by the solid-state reaction. Differential scanning calorimetry (DSC) measurements revealed that an increase in the amount of BiFeO$_3$ dopant resulted in a decrease in the orthorhombic-tetragonal and tetragonal-cubic phase transition temperature of the material. One percent BiFeO$_3$ additive suppressed grain growth, which not only benefits the sintering of ceramics but also enhances the piezoelectric and ferroelectric properties, where $d_{33} = 145$ pC/N, $k_p = 0.31$, $Q_m = 80$, $P_i = 11.3$ $\mu$C cm$^{-2}$ and $E_c = 16.5$ kV cm$^{-1}$. As $x_{BF} > 0.01$, both piezoelectric and ferroelectric properties decreased rapidly with an increasing amount of dopant.

Keywords: piezoelectrics, lead free, ferroelectrics

(Some figures in this article are in colour only in the electronic version)

1. Introduction

To conquer the toxicity of widely used PZT-based piezoelectric materials, many lead-free materials, including Bi-based [1, 2], BaTiO$_3$-based [3, 4], and alkaline niobate-based compounds [5–8], have been studied. Among these materials, the perovskite structure (Na,K)NbO$_3$ forms a morphotropic phase boundary, similar to the PZT, with the ratio of sodium to potassium near 1 : 1. It shows excellent characteristics such as a high Curie point and relatively high piezoelectricity. However, a dense ceramic body for (Na,K)NbO$_3$ is difficult to obtain by ordinary sintering. In order to resolve this problem, two methods have been used. One is to develop new techniques such as hot-pressing [9], spark plasma sintering [10] and reactive template grain growth [11], but all of these techniques are relatively high in cost. The other is to modify (Na,K)NbO$_3$ ceramics by using dopant to form solid solutions. So far, doped materials have been grouped into two perovskite compounds (Na,K)NbO$_3$-A$^{2+}$B$^{5+}$O$_3$ and (Na,K)NbO$_3$-A$^{2+}$B$^{4+}$O$_3$. For example, (Na,K)NbO$_3$-LiNbO$_3$ [12, 13], (Na,K)NbO$_3$-LiTaO$_3$ [14], (Na,K)NbO$_3$-LiSbO$_3$ [15, 16], and (Na,K)NbO$_3$-BaTiO$_3$ [17] have been studied and found to show better sintering characteristics and piezoelectric properties than nondoped materials.

BiFeO$_3$ a rhombohedrally distorted perovskite-type $A^{3+}B^{3+}$O$_3$ structure with the space group $R$3c has a high Curie temperature of about 820–850 °C. It has been successfully applied to PZT ceramics to form a solid solution in order to lower the hot-pressing temperature and improve the piezoelectric properties [18].

In the present study, we attempt to prepare (1 − x)(Na$_{0.5}$K$_{0.5}$)NbO$_3$-xBiFeO$_3$ by the traditional solid-state reaction method and obtain improved piezoelectric,
ferroelectric and ceramic sintering properties of the as-prepared material with a suitable BiFeO₃ dopant.

2. Experiment

The traditional solid-state reaction was used to prepare \((1-x)(Na_{0.5}K_{0.5})NbO_3-xBiFeO_3\) (abbreviated to KNN-BF100x) ceramics. Analytical reagent oxides and carbonates (\(Na_2O_2\), \(Bi_2O_3\), \(Fe_2O_3\), \(K_2CO_3\) and \(Na_2CO_3\)) were used as starting materials. They were accurately weighed in the desired composition and milled for 10 h by planetary milling with zirconia balls and alcohol media. After calcination at 900 °C for 5 h, the powders were ground in mortar and pressed into pellets of 11 mm in diameter and 1 mm in thickness using 5 wt.% PVA as binder. After burning off the PVA, the pellets were sintered at 1100 °C for 3 h. Silver paste was fired on both sides of the samples as the electrodes for the piezoelectric measurements. The ceramic samples were poled in 100 °C silicon oil under 3 kV mm⁻¹ for 15 min.

The crystal structures were determined using an x-ray diffractometer (Mac Science, M21XVHF22). The morphologies of the samples were studied by field-emission scanning electron microscopy (FE-SEM, LEO1530). The piezoelectric constant \(d_{33}\) was measured using a quasi-static method (China Academy of Acoustics, ZJ-3). The P-E hysteresis loop was measured at room temperature using a ferroelectric tester (aixACCT, TF Analyzer 2000) at 50 Hz. The electromechanical coupling coefficients \(k_p\) and mechanical quality factor \(Q_m\) were calculated by a resonance-antiresonance method with an impedance analyzer (Agilent, HP4194A). The phase transition of samples was determined by differential scanning calorimetry (TA, DSC TA-Q200) with a heat rate of 20 °C min⁻¹.

3. Results and discussion

Figure 1 shows the XRD patterns of KNN-BF powders calcined at 900 °C for 5 h. The phase structure of the samples with \(x_{BF} < 0.07\) of dopant was a single perovskite phase. With \(x_{BF} = 0.07\), a second phase, \(K_2Nb_2O_7\), appeared. With increasing BF content, the splitting between two diffraction peaks of (001) and (100) near 22° as well as (002) and (200) near 45° gradually disappears, indicating the phase transition from an orthorhombic to a pseudocubic phase. A MPB between the ferroelectric orthorhombic and the pseudocubic phase was determined to be at approximately 0.01 ≤ \(x\) ≤ 0.03.

The DSC heating curves of KNN-BF were measured to reveal the phase transition temperatures (figure 2). According to the phase diagram [19], the KNN solid solution was orthorhombic at room temperature and it underwent two phase transitions from the orthorhombic to the tetragonal phase (O–T) at 190 °C and from the tetragonal to the cubic phase \((T_c)\) at 400 °C. Figure 2 indicates endothermic peaks at 189 °C and 414 °C for KNN. At \(x_{BF} = 0.01\), the transition temperature \(T_c\) decreased from 414 °C to 374 °C and the O–T transition temperature decreased from 189 °C to 97 °C. With the BiFeO₃ content increasing, KNN-BF exhibited similar behavior but the peak of phase transitions became obscure compared with the undoped KNN. Thus, the O–T transition temperature is difficult to determine exactly above room temperature.

The SEM micrograph of KNN-BF powders showed cubic shapes (see figure 3(a)) and BiFeO₃ obviously suppressed the grain growth of the ceramics from about 1 μm at \(x_{BF} = 0\) to about 100 nm at \(x_{BF} = 0.01\) (see figure 3(b)). The driving force for grain growth originated from the surface energy of grains, which was released during the grain growth. When the dopant BiFeO₃ concentration was higher than the critical one \((x_{BF} = 0.01)\), the energy required for grain growth could not be supplied. In the present case, the particle size of the 0.01-BiFeO₃-doped sample was smaller than that of KNN, which benefited the sintering of the ceramics.

Figures 3(c) and (d) show the SEM micrographs of the fracture surface of KNN-BF ceramics sintered at 1100 °C for 3 h. For pure KNN ceramics, the sizes of grains were still of micron order, and the grain boundary was clear, and many
distinct pores existed even in the grain boundary sintered at 1100 °C (see figure 3(c)). The loose structure and high porosity were due to the phase stability of KNN ceramics, which is limited to 1140 °C [19]. Therefore, the high sintering temperature was not suitable and the grains did not grow sufficiently to pure KNN. According to Powell’s suggestion that the liquid phase might be caused by impurities in the bodies, the adding of BF might induce additional liquid-phase sintering. The liquid phase was inferred to be formed in the specimens (see figure 3(d)) and to have assisted the
densification of the ceramics during the sintering with the doping of BF.

Figure 4(a) shows $d_{33}$ of KNN-BF ceramics as a function of the content of BF, with the highest $d_{33}$ of about 145 pC/N occurring at $x_{BF} = 0.01$. When $x_{BF} > 0.01$, $d_{33}$ rapidly decreased with increasing $x_{BF}$. This phenomenon was ascribed to the ferroelectric nature. Figure 4(b) shows the P-E hysteresis loop of KNN-BF ceramics at room temperature. As could be seen, the remanent polarization $P_r$ and the coercive field $E_c$ of KNN-BF depended on the amount of BiFeO$_3$. For $x_{BF} = 0.01$, the KNN-BF possessed higher $P_r$ and $E_c$ than those of pure KNN. For $x_{BF} > 0.01$, $P_r$ of KNN-BF was lower than that of pure KNN and $E_c$ was similar to the $E_c$ of pure KNN. Piezoelectric ceramics with higher remanent polarization $P_r$ exhibits higher piezoelectric properties. Higher remanent polarization indicates a higher degree of orientation of the ferroelectric domain near the MPB composition. This is the reason why $d_{33}$ of KNN-BF at $x_{BF} = 0.01$ is the highest. The $k_p$, $c_r$, tan $\delta$ and $Q_m$ of KNN-BF at $x_{BF} = 0.01$ were 0.31, 265, 0.046 and 80, respectively.

4. Conclusion

The effects of BiFeO$_3$ dopant on the ferroelectric properties and microstructure were investigated in the KNN-BF system. BiFeO$_3$ ($x_{BF} = 0.01$) could suppress the grain growth, which not only benefits the sintering of ceramics but also enhances the piezoelectric and ferroelectric properties. The optimum piezoelectric and ferroelectric properties are $d_{33} = 145$ pC/N, $k_p = 0.31$, $Q_m = 80$, $P_t = 11.3$ $\mu$C cm$^{-2}$ and $E_c = 16.5$ kV cm$^{-1}$.

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