Materials and Design 109 (2016) 609–614

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Enhanced piezoelectric properties in potassium-sodium niobate-based ternary ceramics

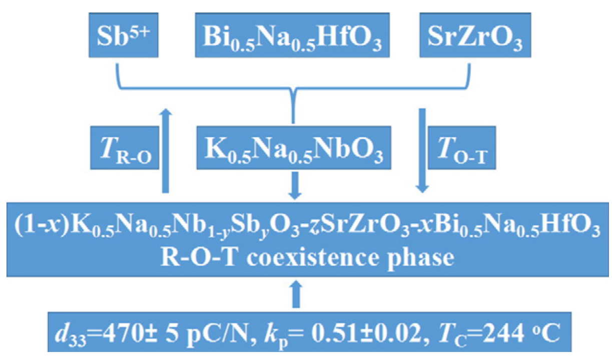
Xiang Lv, Zhuoyun Li, Jiagang Wu *, Jingwen Xi, Meng Gong, Dingquan Xiao, Jianguo Zhu

Department of Materials Science, Sichuan University, Chengdu 610064, PR China

HIGHLIGHTS

- Fabricating the ternary (1-x)$K_{0.5}Na_{0.5}Nb_{1-y}Sb_yO_3$-$zSrZrO_3$-$xBi_{0.5}Na_{0.5}HfO_3$ ceramics by the conventional solid-state reaction method;
- Constructing R-O-T multiphase coexistence in the range of 0.03£x£0.05, 0.04 £y£0.06, 0.01£z£0.025;
- Attaining the high d_{33} (470 ± 5 pC/N) and a relatively high T_C (244 °C).

GRAPHICAL ABSTRACT



Enhanced piezoelectric properties (d_{33} = 470 ± 5 pC/N, k_p = 0.51 ± 0.02, T_C = 244 °C) were obtained in the KNN-based ceramics with an R-O-T phase boundary driven by Sb^{5+}, $Bi_{0.5}Na_{0.5}HfO_3$ and $SrZrO_3$.

ARTICLE INFO

Article history:
Received 8 May 2016
Received in revised form 2 July 2016
Accepted 6 July 2016
Available online 7 July 2016

Keywords:
$(K,Na)NbO_3$
Ternary system
Phase boundary
Electrical properties

ABSTRACT

$(1-x)K_{0.5}Na_{0.5}Nb_{1-y}Sb_yO_3$-$zSrZrO_3$-$xBi_{0.5}Na_{0.5}HfO_3$ (KNNS-SZ-BNH) lead-free ceramics were developed by the conventional solid-state reaction method. Effects of the additives ($Bi_{0.5}Na_{0.5}HfO_3$, $SrZrO_3$ and Sb^{5+}) on their phase structure, microstructure, and electrical properties were investigated. The rhombohedral-orthorhombic-tetragonal (R-O-T) phase boundary can be established in the ceramics with $0.03 \le x \le 0.05$, $0.04 \le y \le 0.06$, and $0.01 \le z \le 0.025$, and then their piezoelectric properties were improved. The ceramics with $x = 0.03$, $y = 0.04$ and $z = 0.01$ possess the optimum piezoelectric properties (d_{33} = 470 ± 5 pC/N, k_p = 0.51 ± 0.02, and T_C = 244 °C). We believe that R-O-T multiphase coexistence is mainly responsible for the enhancement of piezoelectric properties.

1. Introduction

Currently, lead zirconate titanate (PZT) and other lead-based counterparts play a predominant role in the electronic devices market because of their excellent electrical properties. However, high concentration lead over 60% in these materials harms people's health and contaminates the environment during fabrication process. Therefore, it is urgent to develop high-performance lead-free piezoceramics which are comparable to the lead-based ones [1–5].

Pure potassium-sodium niobate (KNN) ceramic possesses a high T_C of 415 °C, which is considered as one of the most promising lead-free materials to replace the lead-based ones. Unfortunately there is an inferior d_{33} (80–160 pC/N), which still cannot meet the demand of practical applications [2–5]. According to the previous reports, the excellent piezoelectric properties of lead-based ceramics were mainly attributed to the formation of morphotropic phase boundary (MPB), where multiphases (i.e., rhombohedral and tetragonal) can easily coexist [6–8]. Therefore, most researchers improved the piezoelectric properties of

* Corresponding author.
E-mail addresses: msewujg@scu.edu.cn, wujiagang0208@163.com (J. Wu).

http://dx.doi.org/10.1016/j.matdes.2016.07.026
0264-1275/© 2016 Elsevier Ltd. All rights reserved.

lead-free ceramics by designing and constructing multi-phases coexistence [2–5,9–11]. It is well known that a pure KNN ceramic often undergoes a paraelectric-ferroelectric phase transition and two ferroelectric-ferroelectric phase transitions with the decrease of ambient temperature, that is, cubic to tetragonal (T_C ~415 °C), tetragonal to orthorhombic ($T_{O\text{-}T}$ ~210 °C), and orthorhombic to rhombohedral ($T_{R\text{-}O}$ ~− 150 °C) [2,4,5]. Thus, in order to obtain multiphases coexistence in KNN ceramics at room temperature, it is necessary to shift their $T_{T\text{-}O}$ and/or $T_{O\text{-}R}$ to room temperature.

In the past decades, numerous efforts have been used to construct phase boundaries in KNN-based ceramics [2,4,5,11–19]. These results show that $T_{T\text{-}O}$ and/or $T_{O\text{-}R}$ of KNN ceramics can be effectively shifted to room temperature by doping some additives (i. e., Li^+, Sb^{5+}, Ta^{5+}, $Bi_{0.5}Na_{0.5}ZrO_3$ and so on) [3,12–15]. Previous results indicated the addition of Sb^{5+} can strongly affect the phase structure and electrical properties of KNN ceramics [13,14], that is, the addition of Sb^{5+} can effectively increase their $T_{R\text{-}O}$ and decrease $T_{O\text{-}T}$. However, the improvement of piezoelectric properties is limited due to the finite solid solubility between KNN and Sb^{5+}. Therefore, new phase boundaries of KNN ceramics cannot be realized by only doping Sb^{5+}, and other additives must be doped if new phase boundaries are wanted. Recently, phase boundaries (i.e., orthorhombic-tetragonal (O-T) phase boundary, rhombohedral-tetragonal (R-T) phase boundary) of KNN ceramics have been established by doping $SrZrO_3$ or $Bi_{0.5}Na_{0.5}HfO_3$ or $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}ZrO_3$ [16–21]. Then, a series of d_{33} values (250–460 pC/N) were observed when the compositions locate at the region of phase boundaries. For example, a high d_{33} value of 419 pC/N was found in the region of R-T phase boundary through with the addition of both Sb^{5+} and $Bi_{0.5}Na_{0.5}HfO_3$ [20]. A large d_{33} value of 460 pC/N was also observed in the KNN ceramics modified by Sb^{5+} and $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}ZrO_3$ because of an R-T phase boundary [21]. In addition, the addition of $SrZrO_3$ improved the piezoelectric performance of KNN-based ceramics by constructing phase boundaries [16–19].

In this work, Sb^{5+}, $SrZrO_3$, and $Bi_{0.5}Na_{0.5}HfO_3$ were chosen as the additives, and then the $(1-x)K_{0.5}Na_{0.5}Nb_{1-y}Sb_yO_3$-$z$$SrZrO_3$-$x$$Bi_{0.5}Na_{0.5}HfO_3$ ceramics were fabricated by the conventional solid-state reaction method. Effects of $Bi_{0.5}Na_{0.5}HfO_3$, $SrZrO_3$ and Sb^{5+} on their phase structure, microstructure, and electrical properties were investigated. The results demonstrate that the electrical properties of KNN ceramics can be well improved by developing ternary material system.

2. Experimental procedure

In this work, $(1-x)K_{0.5}Na_{0.5}Nb_{1-y}Sb_yO_3$-$z$$SrZrO_3$-$x$$Bi_{0.5}Na_{0.5}HfO_3$ {(x = 0–0.06 with y = 0.04, z = 0.01), (y = 0–0.08 with x = 0.03, z = 0.01) and (z = 0–0.03 with x = 0.03, y = 0.04)} ceramics were fabricated by the conventional solid-state reaction method. Raw materials were K_2CO_3 (99%), Na_2CO_3 (99.8%), Nb_2O_5 (99.5%), Sb_2O_3 (99.99%), $SrCO_3$ (99%), HfO_2 (99%), Bi_2O_3 (99.999%), and ZrO_2 (99%). The detailed fabrication processes can be easily found in our previous work [13,20]. In addition, the detailed measurement procedures for properties (e.g., crystal structure, dielectric, ferroelectric, and piezoelectric) can be also found in our previous references [13,20].

3. Results and discussions

Fig. 1(a), (c) and (e) show the composition dependence of phase structure of the ceramics. All ceramics display a pure perovskite structure without secondary phases, and the phase structure is also strongly dependent on the doping content. The expanded XRD patterns of the ceramics in the range of 44–47° were also depicted [Fig. 1(b), (d) and (f)]. As shown in Fig. 1(b), the intensity ratio (2:1) between the left peak and the right one was observed in the ceramics with $x = 0$, indicating the involvement of an orthorhombic symmetry [14–19]. With an increase of x, the intensity of the left peak gradually reduces and the intensity of the right one increases, then a tetragonal-like symmetry was observed

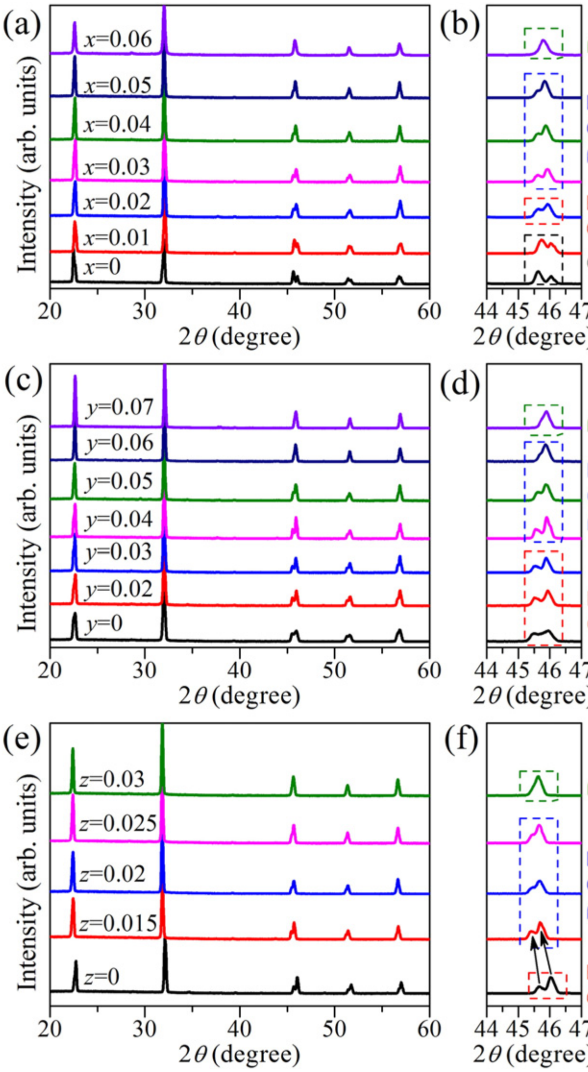


Fig. 1. XRD patterns of the ceramics as a function of (a) (x, y = 0.04, z = 0.01), (c) (x = 0.03, y, z = 0.01), and (e) (x = 0.03, y = 0.04, z); amplified patterns in the range of 44–47° as a function of (b) (x, y = 0.04, z = 0.01), (d) (x = 0.03, y, z = 0.01) and (f) (x = 0.03, y = 0.04, z).

in the composition range of $0.02 \le x \le 0.05$. However, only one diffraction peak was observed in the ceramics with $x = 0.06$, suggesting a rhombohedral phase [16,19]. There is a similar changing tendency in the ceramics with different y and z values, as shown in Fig. 1(d) and (f). In addition, an obvious peak shift (marked by the arrows) was observed in Fig. 1(f). After the addition of $SrZrO_3$, the characteristic peaks are shifted to a lower angle. According to the Bragg's law, $2d\sin\theta = n\lambda$, where d is the interplanar spacing, θ is the angle of diffraction and λ is the wavelength of incident ray. Thus, this phenomenon could be caused by replacing A site (K: 0.138 nm, Na: 0.102 nm) with Sr^{2+} (0.118 nm). The difference of ion radius between Na^+ and Sr^{2+} (~0.016 nm) is inferior to the one between K^+ and Sr^{2+} (~0.02 nm), which means that Sr^{2+} prefers to replace Na^+. After replacing Na^+ with Sr^{2+}, d increases, leading to the decrease of $\sin\theta$ or θ.

The temperature dependence of dielectric constant (ε_r-T) curves of the samples were conducted to judge their phase structure (Fig. 2). As shown in Figs. 2(a)–(d), there are two obvious abnormal dielectric peaks in the ceramics with $x = 0$, which respectively correspond to their $T_{R\text{-}O}$ and $T_{O\text{-}T}$ [14–19]. With an increase of x, $T_{R\text{-}O}$ increases and $T_{O\text{-}T}$ decreases. Then, only one abnormal dielectric peak was observed in the ceramics with $x = 0.03$, suggesting that both $T_{R\text{-}O}$ and $T_{O\text{-}T}$ were shifted to the same temperature. With the further increase of x, there