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Lithium-modified $(K_{0.5}Na_{0.5})NbO_3$–$BiAlO_3$ lead-free piezoelectric ceramics with high Curie temperature

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ABSTRACT

Lead-free piezoelectric ceramics based on the perovskite solid solution $0.995(K_{0.5}Na_{0.5})_{1-x}Li_xNbO_3$–$0.005BiAlO_3$ were prepared using conventional solid-state sintering techniques. According to the analysis of X-ray diffraction patterns, a pure perovskite phase structure could be achieved in the studied composition range of $0 \le x \le 0.08$. As the lithium content increased, the crystal structure gradually transitioned from orthorhombic to tetragonal symmetry. Furthermore, an orthorhombic–tetragonal phase boundary could be observed in ceramics with the compositions of $0.03 \le x \le 0.05$. The ceramics with compositions close to the orthorhombic–tetragonal phase boundary exhibited enhanced piezoelectric activity, possessing the largest values of piezoelectric constant d_{33}, and planar and thickness electromechanical coupling coefficients, of 182 pC/N, 0.375, and 0.460, respectively. Additionally, it was found that these ceramics with excellent piezoelectric properties also possessed a high Curie temperature (~ 450 °C), indicating that they would be suitable for application in elevated-temperature piezoelectric devices.

1. Introduction

Alkali niobate (K, Na)NbO_3 (KNN)-based lead-free piezoelectric ceramics are regarded as some of the most promising candidates to replace commercial Pb(Zr, Ti)O_3 (PZT)-based piezoelectric ceramics, due to their high Curie temperature (T_C) and excellent piezoelectric properties [1,2]. However, pure KNN ceramics possess poor piezoelectric properties, partly because of their processing difficulties, such as a narrow sintering window, the volatilization of K and Na, a poling barrier resulting from high loss tangent, and the evolution of secondary phases [3]. Therefore, many attempts have been made to solve these issues in the past decade, among which was the development of novel KNN-based solid solutions by adding other components into KNN. A special emphasis has been placed on constructing a phase boundary at room temperature in these solid solutions, including the orthorhombic–tetragonal (O–T) phase boundary [4–6], rhombohedral–orthorhombic (R–O) phase boundary [7–9], and rhombohedral–tetragonal (R–T) phase boundary [10–15]. It has been widely believed that the involved phase boundaries play a large part in their improved piezoelectricity [1], as a result of more spontaneous polarization states originating from the coexistence of two kinds of ferroelectric phases [16]. Many of these KNN-based ceramics exhibit obviously enhanced piezoelectric properties at compositions near the phase boundary, some of them even displaying properties comparable to those of the PZT–based ceramics. However, most of these modified ceramics have a T_C of < 300 °C, which is remarkably low in comparison with that of pure KNN (~ 420 °C), and hence they cannot be used in elevated-temperature fields. Therefore, the development of new KNN-based ceramics exhibiting both high performance and a high T_C is a necessity.

A novel ABO_3-type compound, $BiAlO_3$ (BA) has recently begun to attract increasing attention, owing to its high T_C and potentially excellent electrical properties [17–26]. However, both experimental and theoretical studies have revealed that the phase structure of BA is extremely unstable at ambient temperatures and pressures [23–26]. On the other hand, theoretical calculations have also determined that the BA has a perovskite-like structure with rhombohedral symmetry, a very large spontaneous polarization, and a high T_C [25]. Therefore, BA has been widely used to form new solid solutions by incorporating it into other stable perovskite compounds, such as alkali niobate $(K_{0.5}Na_{0.5})NbO_3$. And, with a BA content of less than 5%, a pure perovskite structure could be achieved for the formed solid solutions $(K_{0.5}Na_{0.5})NbO_3$–$BiAlO_3$ by using a conventional solid-state sintering method [22]. Interestingly, it was found that both the R–O and O–T phase transition temperatures (T_{R-O} and T_{O-T}) of KNN could be brought close to room temperature via the addition of certain amounts of BA [22]. However, the sinterability of KNN-based ceramics deterio-

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rated severely with just a slight increase in the BA content, which resulted in an extremely fine grain size. In addition, the T_C (~ 372 °C) of KNN-BA was not high enough to use in many high-temperature fields [22].

It is widely reported that lithium can have a great effect on the phase transition temperatures and electrical properties of KNN-based piezoelectric ceramics [27,28]. Therefore, in this current work, lithium-modified KNN-based ceramics, with the general chemical formula $0.995(K_{0.5}Na_{0.5})_{1-x}Li_xNbO_3$–$0.005BiAlO_3$ (KNL$_x$N–BA), were projected and prepared by conventional solid-state sintering techniques. A study was conducted on the impact of lithium content on the crystal structure, microstructure, and electrical properties of KNL$_x$N–BA ceramics. It was found that the ceramics possessed an O-T phase boundary in the composition range of $0.03 \le x \le 0.05$, near which an enhanced piezoelectric activity, as well as a high T_C (~ 450 °C), was observed.

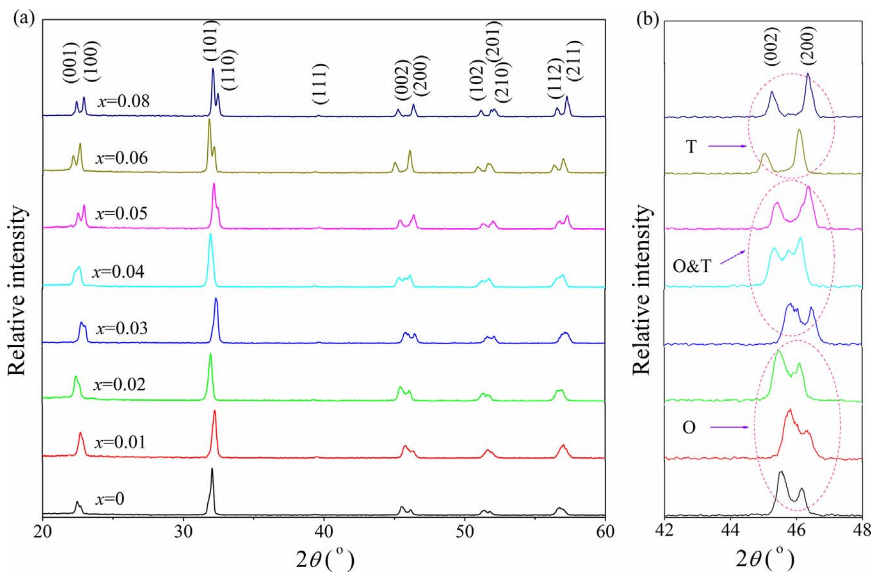

Fig. 1. XRD patterns of the KNL$_x$N–BA ceramics in the 2θ range of (a) 20–60° and (b) 42–48°.

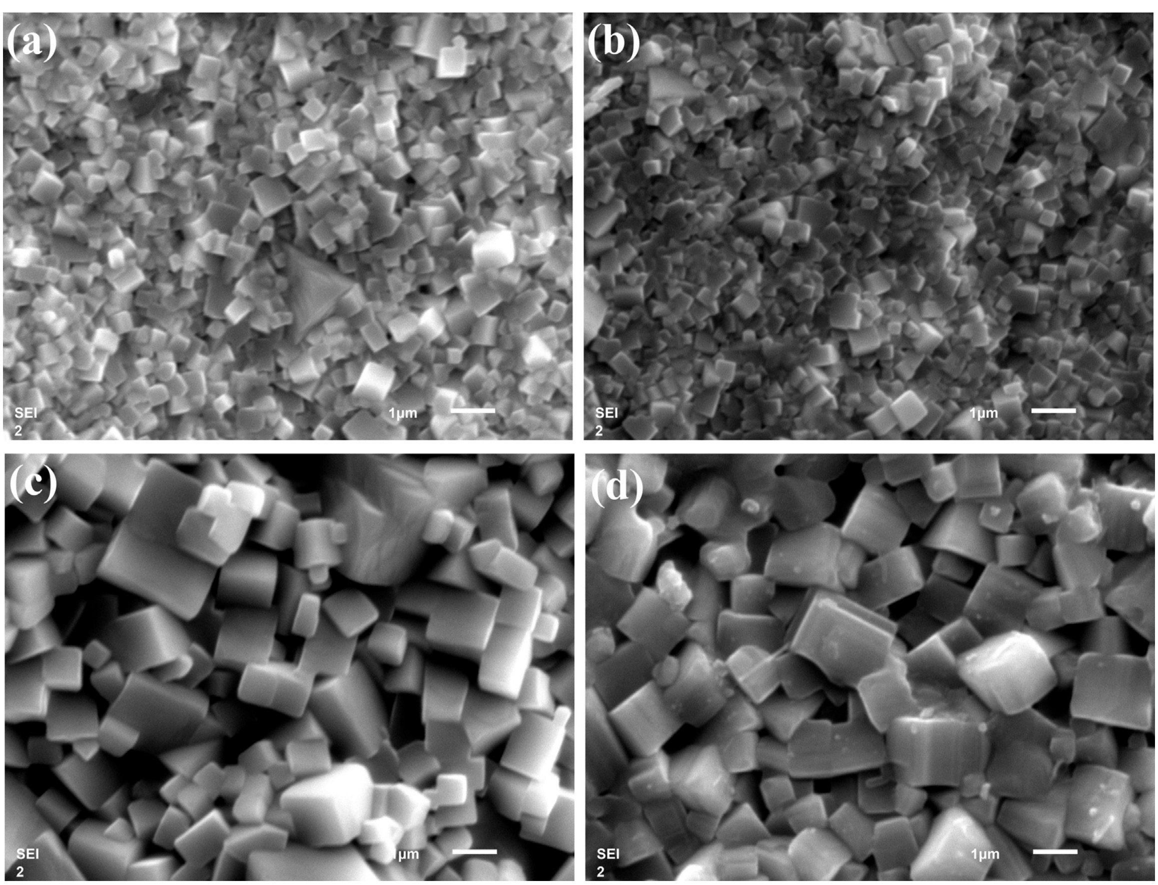

Fig. 2. SEM surface micrographs of the KNL$_x$N–BA ceramics: (a) x=0, sintered at 1100 °C; (b) x=0.04, sintered at 1090 °C; (c) x=0.05, sintered at 1080 °C; and (d) x=0.06, sintered at 1080 °C.