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Dielectric properties of $BiAlO_3$-modified (Na, K, Li)NbO_3 lead-free ceramics

Xiaojun Sun[a], Jianming Deng[a], Laijun Liu[a,*], Saisai Liu[a], Danpin Shi[a], Liang Fang[a], Brahim Elouadi[b]

[a] *Guangxi Universities Key Laboratory of Non-ferrous Metal Oxide Electronic Functional Materials and Devices, Key laboratory of Nonferrous Materials and New Processing Technology, Ministry of Education, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China*
[b] *Laboratory of Chemical Analysis Elaboration and Materials, Engineering (LEACIM), Université de La Rochelle, Avenue Michel Crépeau, 17042 La Rochelle Cedex 01, France*

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ABSTRACT

$(1-x)K_{0.45}Na_{0.49}Li_{0.06}NbO_{3-x}BiAlO_3$ ($(1-x)$KNLN-xBA) solid solution has been synthesized by a conventional solid state reaction. Crystal structure, microstructure, dielectric properties of the $(1-x)$KNLN-xBA ceramics were investigated. With the increase of BA, the unit cell volume shrinks. The average grain size decreases from >20 μm to ~1 μm and the morphology of grains changes from irregular to cubic. The dielectric peak of ferroelectric-paraelectric translation is suppressed and shifts to low temperature with the increase of BA. A good dielectric temperature stability was obtained in the samples $x=0.08$ and $x=0.10$, corresponding to operating temperature range 454.4–660.4 K and 405.6–630.7 K (±10% variation), respectively. High-temperature dielectric relaxation behavior was discussed. The activation energy of oxygen vacancies first decreased and then increased with the increase of BA, which was attributed to both the concentration of oxygen vacancies and lattice distortion.

1. Introduction

The rapid growth of electronic industry needs the miniaturization of component in mixed-signal integrated circuits, which calls for the development of new materials with high dielectric permittivity and better thermal stability [1]. Many attempts have been made in recent years toward solving the above-mentioned issues. The typical ceramics are $BaZrO_3$ [2], $0.7BaTiO_3$–$0.3BiScO_3$ [3], $0.4(Ba_{0.8}Ca_{0.2})TiO_3$–$0.6Bi(Mg_{0.5}Ti_{0.5})O_3$ [4], which have received much attention. However, high sintering temperature keeps them from the multilayer ceramic capacitors (MLCC) technique. Recently, niobate-based ferroelectric compositions have attracted much more attention owing to their relatively good dielectric stability and low sintering temperature [5–9].

$K_{0.5}Na_{0.5}NbO_3$ (KNN) is a possible alternative for high temperature applications because of their relatively high Curie temperature (T_C) 693 K. However, the phase transition from orthorhombic to tetragonal at 473 K deteriorates the thermal stability of electrical properties [10]. Furthermore, it is difficult to obtain dense KNN ceramics due to the high volatility of alkaline elements at high temperatures, resulting in apparently poor electric properties. Therefore, excess alkaline elements were added to the A-site for compensating alkali metal loss during pyrolysis process at high temperatures [11].

In order to solve performance degradation of the KNN near the phase transformation, an alternative way is to shift the phase transition temperature (T_{O-t}) of orthorhombic–tetragonal to room temperature. The dielectric properties of $(1-x)K_{0.5}Na_{0.5}NbO_{3-x}LiNbO_3$ has been reported by Naama Klein et al. [12]. The T_{O-t} shifts to low temperature with increasing x while T_C shifts to high temperatures. $K_{0.45}Na_{0.49}Li_{0.06}NbO_3$ (KNLN) shows a high T_C, unfortunately, the dielectric permittivity of the KNLN is only 500 at room temperature.

$BiAlO_3$ (BA) has a perovskite structure with rhombohedral symmetry at room temperature, a large spontaneous polarization of about 76 μm/cm², and a high Curie temperature of about (~800 K) [13,14]. Furthermore, good dielectric properties can be obtained in the $(1-x)BaTiO_{3-x}BiAlO_3$ system [15]. In this work, the BA doped the KNLN ceramics were prepared for obtaining high dielectric properties and a good temperature stability in terms of temperature coefficient of dielectric permittivity. Furthermore, in order to reveal the dielectric loss mechanism above T_C, the high-temperature dielectric relaxation was also focused on.

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[*] Corresponding author. Fax: +86 773 5896672.
E-mail address: ljliu2@163.com (L. Liu).

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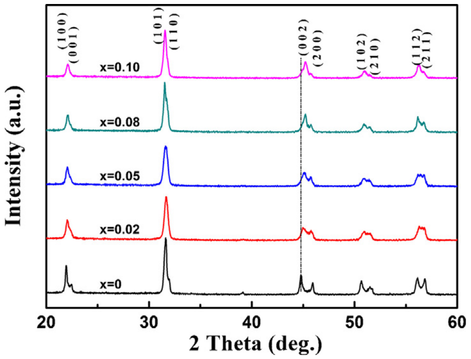

Fig. 1. XRD patterns of the (1-*x*)KNLN-*x*BA ceramics.

Table 1
Phase, lattice parameters and cell volume of the$(1-x)$KNLN-*x*BA ceramics.

Sample	Phase	*a* (Å)	*b* (Å)	*c* (Å)	*V* ($Å^3$)
$x=0.00$	Orthorhombic + Tetragonal	3.9516	5.6850	5.7574	129.340
		3.9648	3.9648	4.0432	63.558
$x=0.02$	Tetragonal	3.9730	3.9730	4.0264	63.554
$x=0.05$	Tetragonal	3.9658	3.9658	4.0247	63.483
$x=0.08$	Tetragonal	3.9750	3.9750	4.0140	63.425
$x=0.10$	Pseudo-cubic	3.9673	3.9673	3.9673	62.446

2. Experimental procedures

$(1-x)K_{0.45}Na_{0.49}Li_{0.06}NbO_{3-x}BiAlO_3$ ($x=0.00$, 0.02, 0.05, 0.08 and 0.10) ceramics were prepared from constituent oxides and carbonates by the conventional solid state reaction. Appropriate oxide and carbonate powders Na_2CO_3 (99.8%), K_2CO_3 (99%), Li_2CO_3 (98%), Nb_2O_5 (99.99%), Al_2O_3 (95%) and Bi_2O_3 (99%) were used as starting materials. The powders were separately dried in an oven at 393K for 48 h before weighting. Firstly, Na_2CO_3, K_2CO_3, Li_2CO_3 and Nb_2O_5 were thoroughly weighted in the stoichiometric ratio of $K_{0.45}Na_{0.49}Li_{0.06}NbO_3$ and mixed in a nylon jar for 8 h using ZrO_2 balls in ethyl alcohol. 3mol% excess Li was added to compensate the evaporation of alkali oxides. The mixture was calcined at 1123 K for 2 h. Secondly, the equal molar Bi_2O_3 and Al_2O_3 was added into $K_{0.45}Na_{0.49}Li_{0.06}NbO_3$ powder according to the stoichiometry of $(1-x)K_{0.45}Na_{0.49}Li_{0.06}NbO_3$-$x$$BiAlO_3$. The mixture was mixed in a nylon jar for 8 h using ZrO_2 balls in ethyl alcohol, then calcined again at 1123 K for 2 h. Thirdly, the calcined power was grinded for 8 h and added 5 wt% PVA as binder, then uniaxially pressed at 350 MPa into discs of 12 mm in diameter. Finally, the discs were sintered at 1333 K for 4 h in a sealed alumina crucible in air.

The crystal structure was determined by x-ray diffraction (XRD) using a X-ray diffractometer (X'Pert PRO, PANalytical, Netherlands) with Cu *Kα* ($\lambda=0.15418$ nm) radiation. The microstructure was

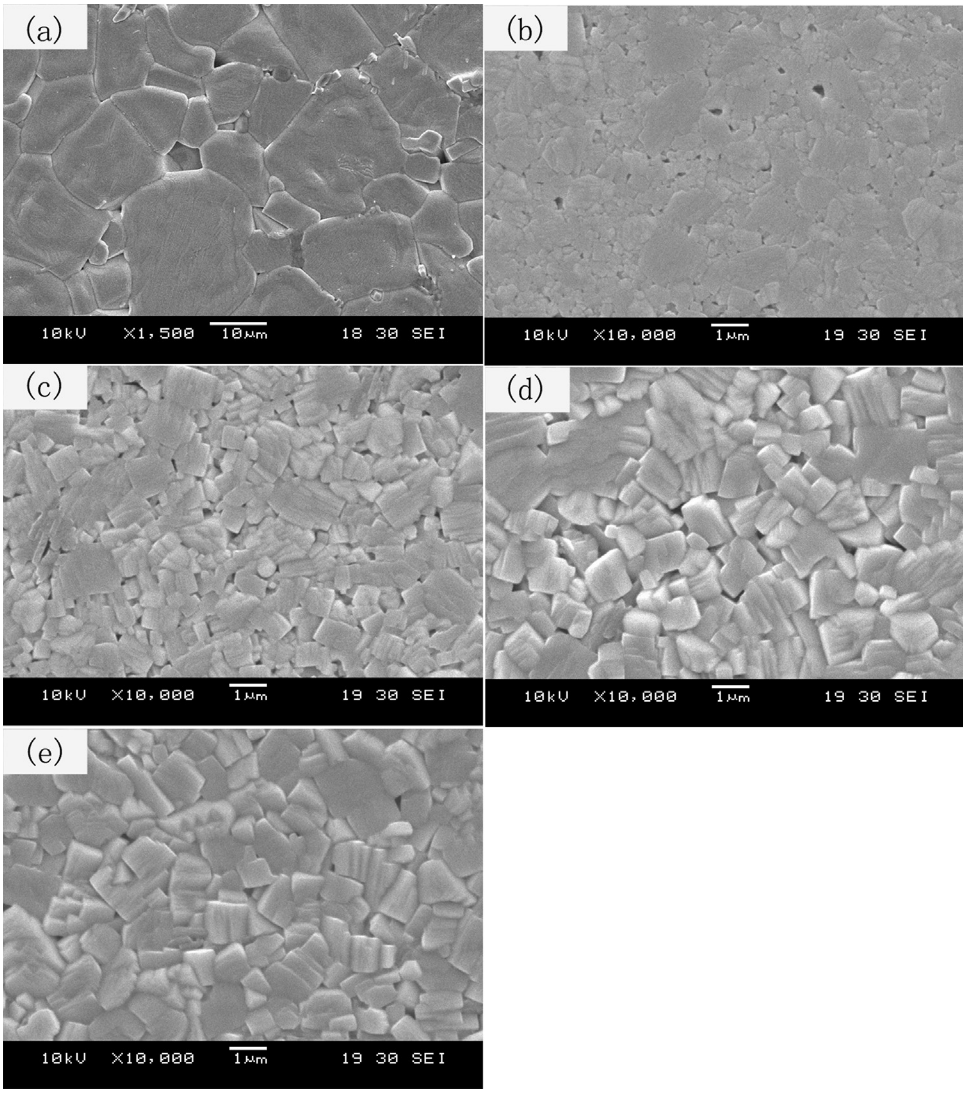

Fig. 2. SEM photographs of the surface of the $(1-x)$KNLN-*x*BA ceramics, (a) $x=0.00$, (b) $x=0.02$, (c) $x=0.05$, (d) $x=0.08$ and (e) $x=0.10$.