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Enhanced piezoelectricity, bright up-conversion and down-conversion photoluminescence in Er^{3+} doped $0.94(BiNa)_{0.5}TiO_3$–$0.06BaTiO_3$ multifunctional ceramics

Mengli Liu[1], Fengying Lei[1], Na Jiang, Qiaoji Zheng, Dunmin Lin*

College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610066, China

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ABSTRACT

Multifunctional ceramics of $0.94(Bi_{1-x}Er_xNa)_{0.5}TiO_3$–$0.06BaTiO_3$ have been fabricated by an ordinary sintering technique, and their structure, piezoelectricity, ferroelectricity and photoluminescence have been studied. The rhombohedral and tetragonal phases co-exist in the ceramics with $x = 0$–0.036 and the concentration of Er^{3+} has no obvious influence on the crystal structure. The partial substitution of Er^{3+} for Bi^{3+} improves the piezoelectricity of the ceramic. The ceramics with $x = 0$–0.02 possess strong ferroelectricity ($P_r = 26.7$–$29.6\ \mu C/cm^2$) and good piezoelectric properties ($d_{33} = 146$–181 pC/N, $k_p = 21.2$–34.1%, respectively). After the addition of Er^{3+}, the ceramics exhibit the characteristic up/down-conversion emission of Er^{3+} ions. The ceramic with $x = 0.032$ possesses the strongest emissions at approximately 535 nm and 549 nm, which are attributed to ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. The ceramics with low Er_2O_3 levels exhibit simultaneously strong piezoelectricity, ferroelectricity and photoluminescence and thus may have a potential application in multifunctional devices.

1. Introduction

In recent years, there is an increasing demand in the miniaturization and multifunctionalization of electronic and microelectronic devices. Therefore, much interest has been focused on lead-free multifunctional materials with desirable properties because of environmental protection [1]. Among multifunctional materials, the perovskite ferroelectric materials (e.g., Er-doped $(Ba_{0.99}Ca_{0.01})(Ti_{0.98}Zr_{0.02})O_3$ [2], La–$K_{0.5}Na_{0.5}NbO_3$ [3] and Pr^{3+}doped $BaTiO_3$–$CaTiO_3$ [4], etc.) exhibit simultaneously strong piezoelectricity, ferroelectricity and photoluminescence and thus have attracted considerable attention.

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is a ferroelectric compound having Bi^{3+} and Na^+ complex on the A-site of ABO_3 perovskite structure with a rhombohedral symmetry [5]. It is considered as a promising candidate to replace commercial lead-based piezoelectric ceramics because of its large remanent polarization ($P_r = 38.0\ \mu C/cm^2$) [6]. But it also has a high coercive field ($E_c = 73$ kV/cm) [6], making the poling of the ceramics difficult. Thus, the pure BNT ceramic exhibits poor piezoelectricity ($d_{33} = 58$ pC/N) [7]. To reduce the coercive field and improve the piezoelectric properties of the material, a number of BNT-based solid solutions, such as $(Ba_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$ (BNT-BT) [8], $Bi_{0.5}Na_{0.5}TiO_3$-$(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ [9] and $Bi_{0.5}Na_{0.5}TiO_3$–$Bi_{0.5}Li_{0.5}TiO_3$ [10] have been developed and these solid solutions can be easily poled and exhibit enhanced piezoelectricity. As a classic BNT-based material, $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ exhibits excellent piezoelectric properties because of the formation of a rhombohedral–tetragonal morphotropic phase boundary (MPB) [11,12]. On the other hand, in terms of photoluminescence of rare earths, the investigation of up-conversion emission ion (e.g., Er^{3+}, Ho^{3+}, etc.) [2,13] has received an intense attention due to their potential application in various advanced devices, such as solar cells [14], fluorescent labeling, low intensity infrared imaging, up-conversion ultraviolet-tunable lasers and fluorescent temperature sensors. As known, for rare earth-doped up-conversion materials, most of investigations focus on the fluoride glasses owing to its lower vibrational energies and minimization of the quenching of the correlative excited state of the rare-earth ions [15–19]. However, fluoride-containing materials generally exhibit poor stability of thermal, chemical and mechanical properties, which limit their applications. It is well known that the oxide host materials can conquer these fatal flaws and their excellent physicochemical properties are in favor of the

* Corresponding author. Fax: +86 28 84767868.
E-mail address: ddmd222@sicnu.edu.cn (D. Lin).
[1] These authors contributed equally to the work.

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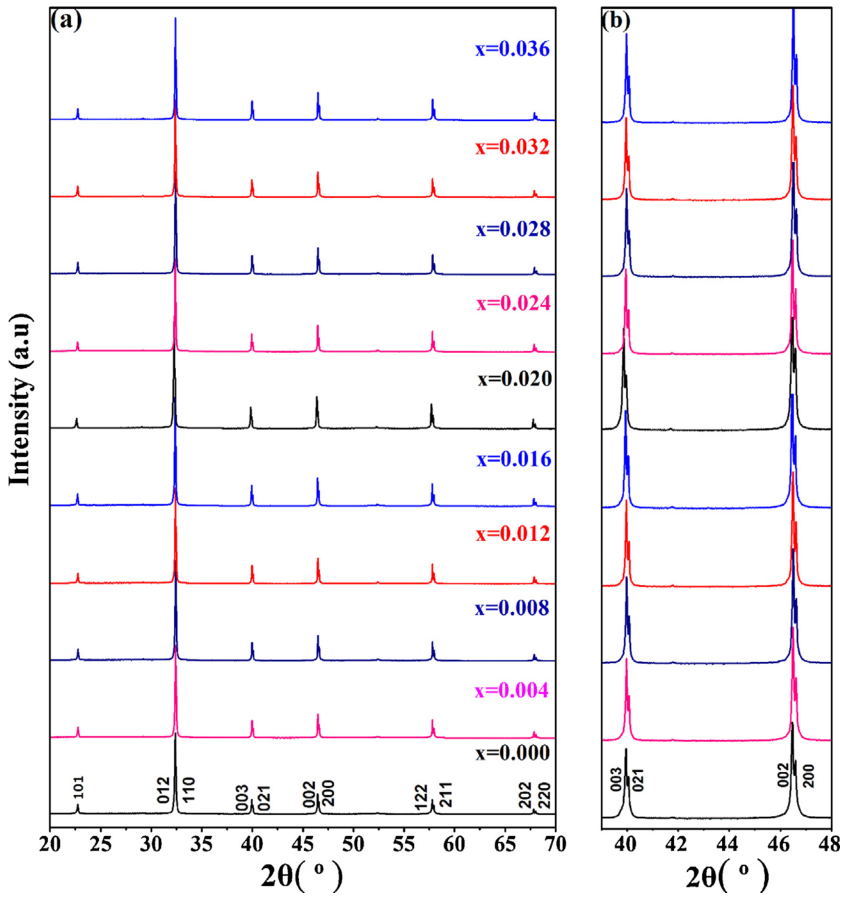

Fig. 1. XRD patterns of the $0.94(Bi_{1-x}Er_xNa)_{0.5}TiO_3$–$0.06BaTiO_3$ ceramics.

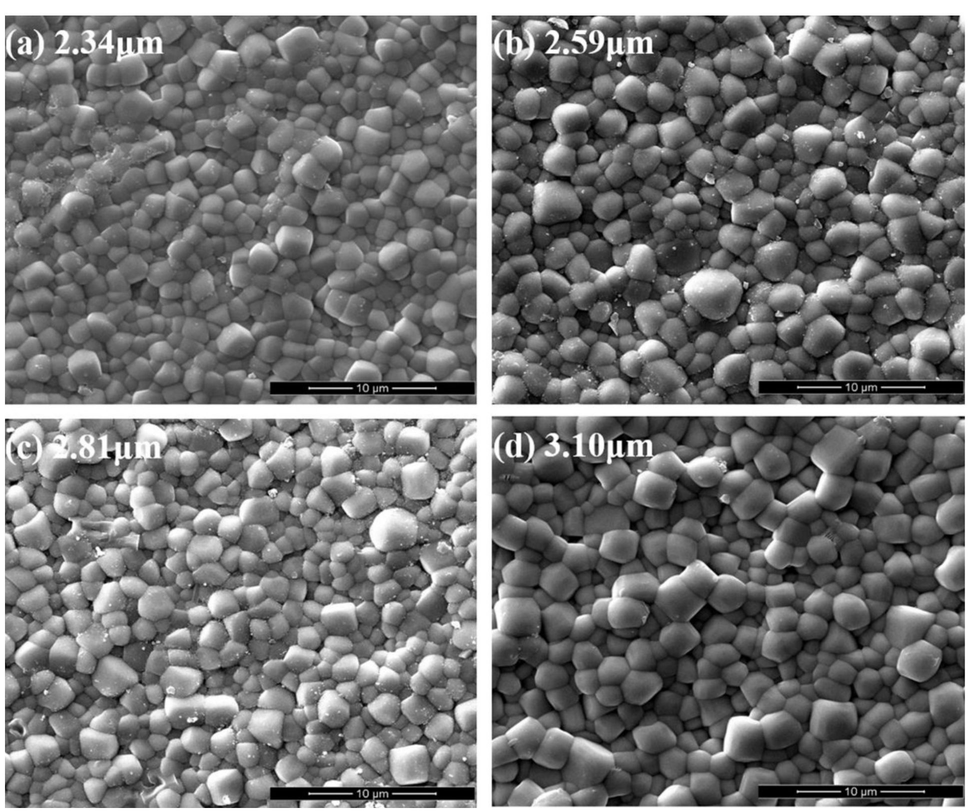

Fig. 2. SEM micrographs of the $0.94(Bi_{1-x}Er_xNa)_{0.5}TiO_3$–$0.06BaTiO_3$ ceramics sintered at 1200 °C for 2 h: (a) $x = 0$; (b) $x = 0.012$; (c) $x = 0.024$ and (d) $x = 0.036$.