



Comprehensive investigation of Er₂O₃ doped (Li,K,Na)NbO₃ ceramics rendering potential application in novel multifunctional devices



Yongjie Zhao^{a,*}, Yiyao Ge^b, Xiaowen Zhang^b, Yuzhen Zhao^b, Heping Zhou^b, Jingbo Li^a, HaiBo Jin^a

^a Beijing Key Laboratory of Construction Tailorable Advanced Functional Materials and Green Applications, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing, 100081, PR China

^b State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing, 100084, PR China

ARTICLE INFO

Article history:

Received 11 November 2015

Received in revised form

27 April 2016

Accepted 8 May 2016

Available online 10 May 2016

Keywords:

KNN based ceramics

Ferro-/piezoelectrics properties

Photoluminescence properties

ABSTRACT

Multifunctional luminescent materials based on rare earth doped ferro-/piezoelectrics have attracted much attention due to their potential applications in novel multifunctional devices. Herein, we choose Li modified (K_{0.49}Na_{0.51})NbO₃ system benefitting from both of the effect of morphotropic phase boundary and polymorphic phase transition as the target materials, and systematically studied the influence of the doping of Er³⁺ on the phase structure, composition, up-conversion photoluminescence property and so forth. A significantly enhanced ferro-/piezoelectric behavior had been achieved in 0.5% Er₂O₃ doped (Li,K,Na)NbO₃ ceramic. Our results reveal that in addition to the admirable intrinsic piezoelectric properties of (Li,K,Na)NbO₃ ceramic, the donor doping behavior of Er³⁺ could enhance the ferro-/piezoelectric properties and obviously improve the up-conversion photoluminescence property of the matrix materials. These findings show great potential of Er³⁺ doped (Li,K,Na)NbO₃ materials a future application in novel multifunctional devices.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Perovskite oxides have attracted intense interest owing to their excellent physical properties, such as piezoelectricity, ferroelectricity, and ferromagnetism [1–3]. Owing to the controllable phase and crystal structure of perovskite oxides, the approach of ion doping is an efficient method to optimize their intrinsic properties and to realize new functionality [4–6]. For example, the rare earth ions, including Er³⁺, Pr³⁺ and Eu³⁺, have already been introduced into perovskite oxide host matrix to design the photoluminescence (PL) and up-conversion (UC) PL as well as ferroelectric materials [7–13]. The resulting materials possessing two or more desirable properties (such as ferroelectric and PL properties) in a single entity would exhibit more great potentials in sensors, optical-electro integration, coupling devices, and other multifunctional optoelectronic applications. However, as piezoelectric/luminescent multifunctional devices there is still basic demanding for ferroelectric/piezoelectric property. Therefore, in addition of the research

concerning the improvement of luminescence behavior, the piezoelectric/ferroelectric property of the targeted materials should also be taken into consideration. Unfortunately these literature did not render elaborated details about the effect of rare earth doping on the piezoelectricity/ferroelectricity of ceramics. Thus, it is indeed necessary to investigate the influence of rare earth doping on the ferroelectric/piezoelectric property as well as the relationship between the enhancement of piezoelectricity and excellent luminescence effect in rare earth doped lead-free ceramics.

Among the lead-free ceramics with perovskite structure (K,Na)NbO₃ (abbreviated as KNN) has inherent advantages over the other systems [14]. It has a high Curie temperature, good piezoelectric properties, and low anisotropy in electromechanical coupling coefficients. Therefore, combining some features of KNN materials mentioned above, it is possible to design and synthesize highly efficient luminescent ferro-/piezoelectric materials by the introduction of RE ions into KNN host. Recently it is found that there is a mutual enhancement action between the luminescence performance and the ferro-/piezoelectric polarization in rare earth doped lead-free ceramics [9]. Furthermore, considering the effect of morphotropic phase boundary (abbreviated as MPB) and polymorphic phase transition (abbreviated as PPT) on the phase

* Corresponding author.

E-mail address: zhaoyjpeace@gmail.com (Y. Zhao).

structure and ferroelectric behavior of (K,Na)NbO₃ based materials, we choose [Li_{0.04}(K_{0.49}Na_{0.51})_{0.96}]NbO₃ doped with Er³⁺ ion as our targeted materials, the detailed crystal structure, microstructure, ferro-/piezoelectric behavior as well as up-conversion photoluminescence properties have been studied and the related mechanism have been discussed. The characteristics suggests that these ceramics, as a multifunctional material, should be of great reference for the fundamental study of optical–electromechano couplings in many application fields, including future optical–electro-integrated materials and devices, photo-ferroelectric, and mechanical–ferroelectric devices.

2. Experimental section

The [Li_{0.04}(K_{0.49}Na_{0.51})_{0.96}]NbO₃ + *x* mol Er₂O₃ ceramics (abbreviated as KNNLN-*x*Er₂O₃, *x* = 0, 0.25%, 0.5%, 0.75%, 1%) were prepared by conventional solid-state reaction method. Raw materials of Li₂CO₃ (99.8%), K₂CO₃ (99.0%), Na₂CO₃ (99.5%), Nb₂O₅ (99.5%) and Er₂O₃ (99.0%) were mixed according to a pre-determined ratio with the addition of alcohol for 24 h. The mixed raw materials were then dried and calcined at 760 °C for 5 h. Thereafter, calcined powders were remixed, pressed into 10 mm diameter pellets and sintered at 1100 °C for 2 h in air.

Phase structure was examined using an X-ray diffraction meter with a CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) (XRD, D8 Advance, Bruker Inc., Germany). The piezoelectric constant was measured using a Piezo-*d*₃₃ meter (PIEZOTEST, PM300, London, UK). Dielectric properties were measured using a LCR meter (TH2816, Tonghui, Changzhou, China) at 1 KHz. Ferroelectric hysteresis loops were measured at room temperature using a TF2000FE-HV ferroelectric test unit (aix-ACCT Inc., Germany). Up-conversion photoluminescence spectra were recorded using spectrophotometer (LabRAM HR Evolution) under the excitation of a 980 nm laser diode. In order to investigate the variation of structure for KNNLN-*x*Er₂O₃ ceramics, Raman scattering was excited using the 633 nm radiation from He–Ne laser and was collected by a micro-Raman spectrometer in the 100–1000 cm⁻¹ range at different temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of KNNLN-*x*Er₂O₃ ceramics as a function of Er₂O₃ content. It could see that all the ceramics possess the pure perovskite structure. The enlarged (002) and (200) peaks at 2θ around 45.5° of KNNLN-*x*Er₂O₃ were shown in Fig. 1b. Generally speaking, the amplified diffraction peaks {200} could be employed to determine the phase structure of KNN-based ceramics [15]. According to previous relevant research, all the samples here have a coexistence phase structure of major orthorhombic and minor tetragonal phase. As shown in Fig. 1b, with the increase addition of Er₂O₃ to KNNLN ceramic, the variation of 2θ diffraction peaks were apparent at 43–47°, indicating the change of lattice parameter due to the ion substitution of Er³⁺ into perovskite structure. Specifically, the location of diffraction peak (200) would shift toward higher angle with (020) toward lower angle with *x*. Moreover, the amplitude of variation for the former was more obvious than that of the latter, implying the decrease in the cell volume of KNNLN-*x*Er₂O₃ ceramics. Taking the value of Er³⁺ radius ($r = 0.89 \text{ \AA}$) into consideration which lies between the value of Nb⁵⁺ and K⁺/Na⁺ radius, thus it would be a amphoteric dopant. Two kinds of ion substitution may occur at the same time. Macro speaking, just one kind of ion substitution could be dominant and bring about a series of according changes. However, only if the substitution of Er³⁺ for A site ions hold a dominant position, accordingly the shrinkage of cell volume would be induced as illustrated in above XRD results.

Fig. 2 depicted the SEM micrographs of the surface microstructure obtained from the as-sintered KNNLN-*x*Er₂O₃ ceramics. The bimodal grain size distributions were shown in all these measured ceramics, more homogeneous and smaller grains have been involved into a pure KNNLN ceramic (as indicated in the inset of Fig. 2a). It could be easily found that the average grain size first rose and then dropped with increasing Er₂O₃ content, showing a maximum value at *x* = 0.5%. However, the grain size was refined as the Er₂O₃ content further increased to 1%. Meantime, some larger grains (about 10 μm) began to form for the ceramics with *x* = 0.5%. It is consistent with the other reports that the formation of large grain could be caused by the existence of liquid phase for KNN-based ceramics [16–18]. A large amount of liquid phase (as

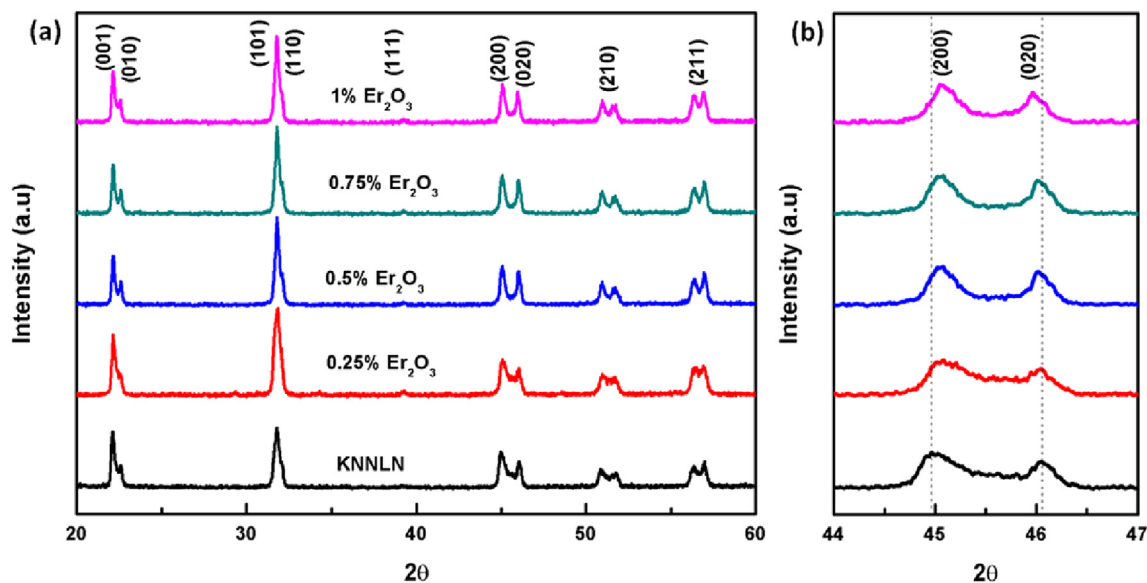


Fig. 1. The XRD patterns of KNNLN-*x*Er₂O₃ ceramics. (a) $2\theta = 20\text{--}60^\circ$, (b) $2\theta = 44\text{--}47^\circ$.

Download English Version:

<https://daneshyari.com/en/article/1605454>

Download Persian Version:

<https://daneshyari.com/article/1605454>

[Daneshyari.com](https://daneshyari.com)