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Optical, luminescent and optical temperature sensing properties of $(K_{0.5}Na_{0.5})NbO_3$-$ErBiO_3$ transparent ceramics

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The lead-free $0.985(K_{0.5}Na_{0.5})NbO_3$-$0.015ErBiO_3$ (KNN-EB-0.015) ceramic was fabricated by pressureless sintering. It possessed a pure perovskite phase with pseudo-cubic symmetry. Due to the fine-grains, small-sized pores, dense microstructure and relaxor-like characteristics, the ceramic was optically clear, exhibiting the highest transmittances of ~40% and ~71% in the visible and infrared regions, respectively. The photoluminescence (PL) properties of the ceramic were studied, including the up-conversion (UC) green and red emissions, down-conversion near infrared emission as well as the emission lifetimes. The color-tunable (from green to yellow) UC emissions were observed by increasing the temperature, based on the temperature-dependent emission spectra, which also exhibited good thermal stability (52.6% of the initial intensity at 453 K) of the ceramic. Additionally, the temperature sensing properties were investigated using the fluorescence intensity ratio technique. A maximum sensitivity of ~0.0048 K at 603 K was obtained. Combined with the good optical and electrical properties, the KNN-EB-0.015 transparent ceramic could be a promising candidate for multifunctional optoelectronic applications.

1. Introduction

Er^{3+}-activated up-conversion (UC) photoluminescence (PL) materials converting the near-infrared (NIR) excitation to visible (Vis) emission have attracted much interest as the applications in flat displays, optical computing, information processing and other photonic areas [1]. Er^{3+} possesses the ladder-like arranged 4f energy levels and exhibits UC green and red emissions as well as down-conversion NIR (~1.5 μm) emissions upon the excitation of 980-nm laser [2]. The fluorescence intensity ratio (FIR) technique of luminescent materials, which can be applied in harsh environments and fast-moving objects, has been considered as a non-contact and non-invasive thermometry to monitor the temperature change with high accuracy and sensitivity [3–5]. Er^{3+} is also a preferable candidate for optical temperature sensing because the two thermal coupled energy levels ($^2H_{11/2}$ and $^4S_{3/2}$) own suitable energy separation (between 200 cm^{-1} and 2000 cm^{-1}), and the response of two green UC emissions (i.e. $^2H_{11/2}/^4S_{3/2} \rightarrow {}^4I_{15/2}$) to temperature is distinct [6,7].

Besides the activator Er^{3+}, the performance of optical temperature sensors strongly depends on the characteristics of host material. At early times, fluorides and glasses were used as the host materials for FIR technique-based optical temperature sensors [8,9]. As the rapid innovation of optical materials and devices, the ideal host material should have low phonon energy, high stability and non-toxicity [10]. Fluorides are toxic to both human beings and environment although they possess low phonon energy [11], and glasses have main drawbacks including fragility, manufacture difficulty and low laser-induced damage threshold [12], which limit their practical applications. Hence, it is necessary to develop new materials to replace both fluorides and glasses. Oxide ceramics are one kind of good substitutes because of their better chemical durability, mechanical strength, thermal stability [13]. And transparent oxide ceramics possess both these advantages and good light transmission.

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Er^{3+}-doped ferroelectrics have been intensively investigated due to their multifunctional properties (such as ferroelectric and UC PL properties) and multi-property coupling (such as electro-mechano, electro-optic, and mechano-optic couplings) [14]. If they can be fabricated into Er^{3+}-doped transparent ceramics, the characteristic of high optical transmission will widen the multi-functional performance and corresponding applications. $(K_{0.5}Na_{0.5})NbO_3$ (KNN) ceramic is one of the promising lead-free ferroelectric materials owing to the inherent advantages, such as high Curie temperature, large electromechanical coupling coefficient and low anisotropy [15]. The KNN-based transparent ceramics, e.g. (1-x)$(K_{0.5}Na_{0.5})NbO_3$-x$SrTiO_3$ ($0.15 \le x \le 0.25$), $(K_{0.5}Na_{0.5})_{1-x}Li_xNb_{1-x}Bi_xO_3$ ($0.05 \le x \le 0.09$) and $(1-x)(K_{0.5}Na_{0.5})NbO_3$-x$LaBiO_3$ ($0.005 \le x \le 0.06$), exhibit relaxor-like dielectric characteristics, good optical and electric-optic properties [16–18]. However, attributed to the lack of emission centers, the PL properties of KNN-based transparent ceramics have rarely been studied. The combination of rare-earth ions (activator) and KNN-based transparent ceramics (host) will endow the material with new fluorescent features. In this work, $(K_{0.5}Na_{0.5})NbO_3$-$ErBiO_3$ transparent ceramics were fabricated by pressureless sintering. The crystal structure, microstructure, dielectric, UC PL and chromatic properties were investigated. Meanwhile, the temperature-dependent UC emission spectra were measured to study the thermal stability and optical temperature sensing properties.

2. Experimental procedure

$(1-x)(K_{0.5}Na_{0.5})NbO_3$-$xErBiO_3$ (KNN-EB-*x*, x = 0, 0.005, 0.01, 0.015, 0.02, 0.03) ceramics were prepared by pressureless sintering through solid state reaction. The starting raw chemicals were K_2CO_3 (99.9%), Na_2CO_3 (99.5%), Nb_2O_5 (99.99%), Bi_2O_3 (99.99%) and Er_2O_3 (99.99%). The powders were first weighted based on the designed stoichiometric quantities. The following mixing and grinding processes were carried out through ball-milling for 12 h in anhydrous ethanol as the medium. Then the mixture was dried to remove the moisture and calcined at 850 °C for 4 h in an alumina crucible. After that, the calcined powders were ball-milled again for 8 h, baked and then mixed thoroughly with a 5 wt% polyvinyl alcohol (PVA) binder solution. Subsequently, the obtained powders were pressed into disks with 12-mm diameter under the pressure of ~300 MPa. To completely burn out the binder in the samples, the disks were pre-sintered at 800 °C for 2 h with a very slow increasing temperature. Finally, the samples were sintered at 1070–1120 °C for 4 h in air for densification. Before measurement, all the obtained ceramics were thinned down to a thickness of ~0.35 mm and polished with 1-μm diamond paste to make the both surfaces smooth. Silver electrodes were fired at 750 °C for 0.5 h on both surfaces of the ceramic samples to measure the dielectric properties.

The phase structures of the ceramics were characterized using X-ray diffraction (XRD) analysis with CuK_α radiation (SmartLab, Rigaku Co.). The X-ray photoelectron spectroscopy (XPS) spectrum was obtained using a photoelectron spectroscope (Kratos Axis Ultra DLD). The optical transmittance of the ceramics was examined in the range of 200–900 nm using a UV–Vis spectrophotometer (UV-2550, Shimadzu Co.) and in the range of 1.5–10 μm by an IR spectrophotometer (MAGNA-IR 760, Nicolet Instrument Co.). The microstructures of the ceramics were measured by a scanning electron microscope (SEM) (JSM-6490, JEOL Ltd.). The “Nano Measurer” software was utilized to analyze the grain size from the SEM data based on 150 grains (manually determined). The temperature and frequency dependence of dielectric constant (ε_r) and dielectric loss (tan δ) were measured using an impedance analyzer (HP 4194A, Agilent Technologies Inc.). The PL emission spectra were recorded by a spectro-fluorometer (F-7000, Hitachi) under the excitation of a continuous 980-nm diode laser with the fixed power of 30 mW. The luminescent decay curves were measured by the 980-nm pulsed signals (with a repetition rate of 100 Hz and duty circle of 10%), which was regulated by an external Transistor-Transistor Logic (TTL) signal produced by a function generator (AFG3251, Tektronix). The temperature of sample was measured by a Pt-100 thermocouple located at a heating stage controlled by a TP94 temperature controller (Linkam Scientific Instruments Ltd.).

3. Results and discussion

Among the KNN-EB-*x* ceramics, attributing to the highest optical transmittance (See Fig. S1 in the supplementary materials), the KNN-EB-0.015 transparent ceramic (sintered at 1090 °C) was selected as the material for following characterizations. Fig. 1 shows the XRD pattern of the KNN-EB-0.015 ceramic. It possesses pure perovskite structure (PDF#79-1482), suggesting that Er and Bi ions have diffused into the KNN lattice. In the expanded XRD pattern at 2θ ~45.5° (inset of Fig. 1), only one sharp (200) diffraction peak can be observed, demonstrating that the KNN-EB-0.015 ceramic has a pseudo-cubic phase. As the pure KNN ceramic owns an orthorhombic phase (See Fig. S2 in the supplementary materials), the introduction of $ErBiO_3$ can bring phase transition from orthorhombic to pseudo-cubic phase with *x* increasing from 0 to 0.015. The high-symmetric pseudo-cubic phase of the KNN-EB-0.015 ceramic contributes to its high transmittance, which will be discussed in the following section. $(K_{0.5}Na_{0.5})NbO_3$ has the ABO_3 (A = K/Na, B = Nb) structure, and Er^{3+} occupies the A site according to the ionic radius of K^+ (1.64 Å), Na^+ (1.39 Å), Er^{3+} (1.24 Å) with the coordination number (CN) of 12. It has been testified from the XPS data (See Fig. S3 in the supplementary materials) that the valence state of Bi ion is trivalent in the KNN-EB-0.015 ceramic. The smaller ions Er^{3+} and Bi^{3+} (1.38 Å, CN = 12) are suggested to introduce into the A site based on the similar ionic radius of K^+ and Na^+, resulting in the lattice contraction and shift towards higher angles of the XRD peaks (See Fig. S2 in the supplementary materials).

As shown in the optical transmittance of Fig. 2, the KNN-EB-0.015 ceramic exhibits a wide optical transmission window in the range of Vis to IR region. A photograph of the ceramic is given (inset of Fig. 2) and the letters under the ceramic can be clearly resolved. The observed transmittance increases steadily from zero at ~420 nm, reaches ~40% at ~750 nm, ~45% at ~900 nm (NIR region),

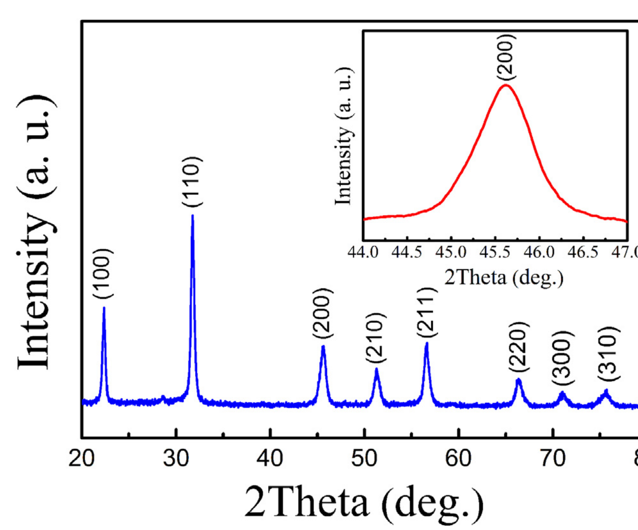

Fig. 1. XRD pattern of the KNN-EB-0.015 ceramic. The inset is the expanded XRD pattern at 2θ ~45.5°.