



Pb(Er_{1/2}Nb_{1/2})O₃–Pb(Zn_{1/3}Nb_{2/3})O₃–PbTiO₃ Single Crystals with High Curie Temperature

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Abstract: In this work, $0.15Pb(Er_{1/2}Nb_{1/2})O_3-0.63Pb(Zn_{1/3}Nb_{2/3})O_3-0.22PbTiO_3$ (15PEN-63PZN-22PT) single crystals with a pure perovskite structure are obtained through the flux method. The phase structure, dielectric, ferroelectric properties and upconversion photoluminescence of the crystals are studied. The ternary crystals along the [110] orientation have a high Curie temperature ($T_c = 250$ °C) and large coercive field ($E_c = 11.0597$ kV/cm) which are higher than those of crystals reported previously. Furthermore, the PEN-PZN-PT crystals are produced with a strong green light excited by a 980 nm laser. Being in the range 298–478 K, the emission intensity of all peaks decreases with increase in temperature. The absolute quantum yield (QY) for the crystals is 0.00059%. These excellent properties provide new possibilities for multifunctional materials of optoelectronic devices.

Keywords: PEN–PZN–PT; perovskite; high Curie temperature; upconversion luminescence

1. Introduction

In recent years, due to their remarkable piezoelectricity and dielectricity, relaxor ferroelectric materials have been widely investigated [1–5]. Pb($Zn_{1/3}Nb_{2/3}$)O₃– $xPbTiO_3$ (PZN–xPT) ferroelectric crystals with a composition near the morphotropic phase boundary (MPB) show a prominent piezoelectricity of $d_{33} = 2000-2500$ pC/N and electromechanical coupling factors of $k_{33} = 90\%-92\%$ [6–9]. These remarkable electric performances make PZN–9PT single crystals a promising candidate for electromechanical devices, including underwater sonar, sensors, and medical imaging, etc. [10,11].

However, the Curie temperature ($T_c \sim 170$ °C) and coercive field ($E_c \sim 3.5$ kV/cm) of PZN-9PT single crystals are relatively low [12–14]. All of these shortcomings make PZN-PT unsuitable for high-power applications and high temperature working environments.

Lately, to meet the needs of high power and high temperature application-, the coercive field and the Curie temperature of PZN-PT-based crystals have been increased to some extent by forming ternary solid solution systems such as Pb(Ni_{1/3}Nb_{2/3})O₃-Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ (PNN-PZN-PT) [15,16], Pb(In_{1/2}Nb_{1/2})O₃-Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ (PIN-PZN-PT) [17], Pb(Lu_{1/2}Nb_{1/2})O₃-Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ (PLN-PZN-PT) [18], and Pb(Yb_{1/2}Nb_{1/2})O₃-Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ (PYN-PZN-PT) [19]. A. Salak prepared Pb(Er_{1/2}Nb_{1/2})O₃ (PEN) ceramics with a perovskite structure under high temperature and high pressure condition without precedent [20]. The ceramics display an antiferroelectric phase at room temperature which transforms into a paraelectric phase when the temperature rises to about 347 °C [20]. PZN–PT together with PEN can form a ternary solid solution which contributes a lot to the increase in the coercive field



and Curie temperature of the crystals. Furthermore, PEN can achieve upconversion luminescence. Hence, PZN–PT modified by PEN may have potential application in optical-electrical devices.

In this paper we incorporate PEN into PZN–PT single crystals to form a new system. It is anticipated that the new material possesses a high coercive field and Curie temperature, as well as good electric and optical properties. Firstly, we design the components of PEN–PZN–PT crystals using linear rules and grow PEN–PZN–PT single crystals using the flux technique. Secondly, we investigate the structure and electric (dielectric and ferroelectric) and optical (optical absorption, upconversion (UC) luminescence, and absolute quantum yield (QY) properties of PEN–PZN–PT crystals.

2. Experiments

The composition of 15PEN–63PZN–22PT crystals is determined by the linear rule, with the linear rule being that in a ternary system, the two components near the MPBs in PZN–9PT and PEN–50PT are connected by a straight line, and most compositions on a straight line have an MPB structure [21]. The crystals were obtained by the traditional flux method. In order to eliminate the pyrochlore phase and thereby increase the yield of perovskite, the precursors $ZnNb_2O_6$ (ZN) and $ErNbO_4$ (EN) were pre-synthesized at 1050 °C for 6 h and 1150 °C for 10 h, respectively [22]. The raw materials ZN, EN, PbO, and TiO₂ powder, with a PbO excess of 70 wt.%, were wet-milled with ethanol for 10 h. After drying, the mixed raw material was first loaded into a platinum crucible and then the filled platinum crucible was placed in a corundum (Al₂O₃) crucible. Following this, the gap between the two crucibles was filled with alumina powder. Then, the corundum crucible was put into an ultrahigh temperature furnace and the crystals were grown according to the preset processes. After the crystal growth was completed, the platinum crucible was boiled in dilute nitric acid at a concentration of 50% and the crystals were separated.

Ground crystal powder and crystal wafers with polished parallel surfaces were prepared. The phase structure of the crystals was measured using an X-ray diffractometer (XRD-6000, Tokyo, Japan) with Cu target K α (λ = 1154 nm). Micro morphology of the crystals was performed using a scanning electron microscope (SEM, Quanta 400F, FEI, Holland) and an energy dispersive system (EDS) spectrum was used to measure the elemental homogeneity of the crystals. The silver paste was spread evenly on the surface of the crystals and fired at 550 °C for 40 min to obtain electrodes. The dielectric constant behavior was tested using an E4980/GJW-I system (Agilent E4980A, Agilent, NM, USA) equipped with a temperature control system from 25 °C to 400 °C. Polarization–electric field hysteresis loops of the crystals were performed using a ferroelectric testing system (Radiant Precision Premier II, Radiant Technologies, Inc. Albuquerque, NM, USA) at room temperature. To realize the luminescence characteristics of the sample, the UC photoluminescence and absolute quantum yield of the crystal powder were explored through photoluminescence spectrometry (FLS980, Edinburgh, UK).

3. Results and Discussion

Figure 1a shows an XRD profile of the crystal powder at room temperature. The results indicate that there is no pyrochlore or any other secondary structure, indicating that all the XRD diffraction peaks of the crystals belong to a pure perovskite structure (ABO₃). Figure 1b shows an XRD pattern of the exposed surface of the crystal sample; two strong diffraction peaks were detected, corresponding to the (110) and (220) crystal planes, respectively, indicating that the crystal surface direction is a strict [110] orientation [23]. An SEM image of the surface of the crystal sample is shown in Figure 1c. The surface of the crystals is uneven; a large number of irregular pits and parallel growth steps can be observed. Figure 1d shows an energy dispersive system of four random points on the surface of the crystals. After comparing the mass percentages of the elements at four different locations, we were able to arrive at the conclusion that the crystal sample shows excellent element homogeneity. The calculated composition of the grown crystals is 12PEN–45PZN–43PT, which deviates from the nominal composition due to element segregation during the crystal growth process.



Figure 1. XRD profiles of (**a**) crystal powder and(**b**) [110]-oriented crystals. (**c**) An SEM image of the crystals. (**d**) An energy dispersive system (EDS) spectrum of crystals.

Figure 2 shows the dependence of the dielectric constant (ε') and dielectric loss (tan δ) on the temperature of unpolarized crystals at different test frequencies (1 kHz to 1 MHz). The dielectric peak at 250 °C (T_c) is associated with the phase transition between ferroelectric and paraelectric phases, which is a significant improvement compared to the PZN–9PT system ($T_c \sim 170$ °C) [24] and the PEN–PMN–PT ternary system ($T_c \sim 207$ °C) [25]. Obviously, the existence of PEN can increase the Curie temperature of the PZN–PT system, due to the fact that Er^{3+} ions, which have a relatively large atomic radius, occupy the B position of the system, which makes the perovskite tolerance factor decrease in this system, and the rhombohedral or tetragonal phase to be relatively more stable.



Figure 2. The dependence of the dielectric constant (ε') and dielectric loss (tan δ) on the temperature of [110] crystals at different frequencies (1 kHz to 1 MHz).

Polarization–electric field (*P*-*E*) hysteresis loops of crystals under different electric fields at room temperature are shown in Figure 3. At an electric field of 50 kV/mm, the residual polarization P_r and coercive field E_c are 14.88 μ C/cm² and 33.92 kV/cm, respectively. The E_c is about nine times higher than that of the PZN–9PT system, indicating that the ternary solid solution is an effective method with which to improve the coercive field for PZN–9PT crystals [23]. The higher coercive field gives the crystals potential application in high power piezoelectric devices [26].



Figure 3. Polarization-electric field (*P*-*E*) hysteresis loops for crystals under different electric fields at room temperature.

Figure 4 shows an optical absorption spectrum of the PEN–PZN–PT crystals for the wavelength range 200 to 1800 nm. The transition absorptions of Er^{3+} from the ground state ${}^{4}\text{I}_{15/2}$ to the excited states ${}^{4}\text{F}_{7/2}$, ${}^{2}\text{H}_{11/2}$, ${}^{4}\text{F}_{9/2}$, ${}^{4}\text{I}_{11/2}$, and ${}^{4}\text{I}_{13/2}$ were detected at 491 nm, 522 nm, 654 nm, 971 nm, and 1470 nm, respectively. The optical absorption spectrum of the 15PEN–63PZN–22PT crystals is similar to that of the Er^{3+} doped ferroelectric material reported previously [27].



Figure 4. The optical absorption spectrum of the 15PEN-63PZN-22PT crystals.

Figure 5a displays an upconversion photoluminescence (UC PL) spectrum of the crystals excited by a 980 nm laser at different temperatures. Three broad emission bands located at 527 (green), 563 (green), and 680 (red) nm were detected which are consistent with the energy level transitions of Er^{3+} from the excited states ${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$, and ${}^{4}F_{9/2}$ to the ground state ${}^{4}I_{15/2}$, respectively [28]. In the temperature range 298–478 K, no difference in the location of the emission band can be observed as the temperature increases, but the luminescence intensity is significantly weakened. Figure 5b shows the emission intensity differences among the centers at 527, 551, 563 (green), and 680 (red) nm. It can be observed that 551 and 563 nm have the same downward trend and that no downward trend is observed at 527 nm, indicating that heating has little effect on the concentration of electrons at the ${}^{2}\text{H}_{11/2}$ level, while the concentration of electrons at the ${}^{4}\text{S}_{3/2}$ and ${}^{4}\text{F}_{9/2}$ levels have a strong dependence on temperature [29].



Figure 5. (a) Upconversion photoluminescence (UL PL) ($\lambda_{ex} = 980$ nm) spectra of the crystals at different temperatures. (b) The dependence of luminescence intensity on temperature located at different wavelengths.

Quantum yield is the fraction of molecules that return to the ground state by emission of fluorescence out of the total number of excited molecules. The higher the quantum yield, the higher the efficiency of the fluorescent materials. The absolute QY of the crystals was excited using a 980 nm laser, with the results shown in Figure 6. The absolute quantum yield up conversion of the crystal can be computed using the formula:

$$QY = A^{em} / [(A^{scat}_{ref} - A^{scat}_{sample}) * k_{\text{Red}-PMT/NIR-PMT}]$$

where *A* is the fluorescence peak area, A^{em} is the area of the emission peak after spectral correction, and A^{scat}_{ref} and A^{scat}_{sample} represent the area of the Rayleigh scattering peak of the reference sample and

the measured sample, respectively. $k_{\text{Red-PMT/NIR-PMT}}$ denotes the proportion between the sensitivities of the red and near-infrared detectors. An integral calculation was performed to obtain the QY of the PEN–PZN–PT crystals, which was found to be 0.00059%. This value is higher than the quantum yield of the reported rare earth Er^{3+} modified glass system [30,31], and the glass-based material cannot obtain the same excellent electrical properties. Hence, the PEN–PZN–PT crystals have potential application in optical-electrical devices.



Figure 6. (**a**) The quantum yield (QY) emission spectra of the crystals under 980 nm excitation. (**b**) The QY scatter spectra of the crystals under 980 nm excitation.

Figure 7 shows a possible luminescence mechanism and an energy level diagram of the PEN–PZN–PT crystals at 980 nm excitation. Firstly, the Er^{3+} located at the ground state ${}^{4}I_{15/2}$ are excited to ${}^{4}I_{11/2}$ through the ground state absorption (GSA) process and undergo small proportion relaxation to ${}^{4}I_{13/2}$ by non-radiative (NR) transitions. The Er^{3+} at ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$ level start absorbing photons and then get to the ${}^{4}F_{7/2}$ and ${}^{4}F_{9/2}$ levels through excited state absorption (ESA). Then, the Er^{3+} at ${}^{4}I_{11/2}$ are excited to the ${}^{4}F_{7/2}$ level through energy transfer (ET): ${}^{4}I_{11/2} + {}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2} + {}^{4}F_{7/2}$. Afterwards, the Er^{3+} at the ${}^{4}F_{7/2}$ level reach the ${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$, and ${}^{4}F_{9/2}$ levels by non-radiative transition. Finally, the Er^{3+} ions return to the ground state, with (${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$) $\rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ emitting green and red light, respectively. The above mechanism is a two-photon excitation process, which is consistent with other materials doped with Er^{3+} [32,33].



Figure 7. Energy level diagram of the crystals and possible luminescence mechanism under 980 nm excitation. Legend: ESA, excited state absorption; ET, energy transfer; GSA, ground state absorption; NR, non-radiative.

4. Conclusions

In this work, PEN–PZN–PT crystals with a pure perovskite structure were first obtained using the high-temperature flux method. The electric properties of the crystals have been greatly improved. The Curie temperature T_c increased from 170 °C for the PZN–9PT crystals to 250 °C for the PEN–PZN–PT crystals. The coercive field E_c of the PEN–PZN–PT crystals reached 33.92 kV/cm, which is about nine times higher than that of the PZN-9PT system. Furthermore, PEN–PZN–PT crystals produce a UC with a strong green light when excited by a 980 nm laser. The luminescence intensity of all the emission peaks decreased across an increasing temperatures range of 298 to 478 K. In addition, the absolute QY for the crystals was found to be 0.00059%. The results make PEN–PZN–PT crystals a potential candidate for optoelectronic devices.

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