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Ferroelectric Properties and Spectroscopic Characterization of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}32\text{PbTiO}_3\text{:Er}^{3+}/\text{Sc}^{3+}$ Crystal

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Abstract: An $\text{Er}^{3+}/\text{Sc}^{3+}$ co-doped $0.68\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.32\text{PbTiO}_3$ ferroelectric single crystal was grown by high-temperature flux method. The remnant polarization P_r is $27.97 \mu\text{C}/\text{cm}^2$ and the coercive field E_c is $8.26 \text{ kV}/\text{cm}$ for $[100]$ oriented crystal. Green (524 and 551 nm) and red (654 nm) emission bands are generated at the 980 nm excitation, which corresponds to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} , respectively. Judd–Ofelt theory has been applied to predict the spectroscopic characteristics of the as-grown crystals. The obtained J–O intensity parameters Ω_t ($t = 2, 4$ and 6) are $\Omega_2 = 0.76 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.0 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 0.55 \times 10^{-20} \text{ cm}^2$. Spectroscopic characteristics, including optical transition probabilities, branching ratio, and radiative lifetime of Er^{3+} in the crystal, are determined. The calculated radiative lifetimes of $^4\text{I}_{13/2}$ and $^4\text{I}_{11/2}$ energy levels are 2.82 ms and 2.61 ms, respectively. These investigations provide possibilities for the crystal $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.32\text{PbTiO}_3\text{:Er}^{3+}/\text{Sc}^{3+}$ to be a new type of multifunctional crystal integrating electricity-luminescence.

Keywords: Judd–Ofelt; PMN-32PT; Er^{3+} ; ferroelectric; crystal; spectroscopic



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1. Introduction

In recent decades, the optical absorption properties of multifunctional materials are of interest for numerous academic and technology research [1–4], a lot of publications dealing with multifunctional material are concerned with the detector, optoelectronic device, and sensor [1–13]. Such research has significantly advanced during the last decade. However, it is still required to design new multifunctional systems to meet the new needs of functional devices [2–4].

Ferroelectric single crystals represented by $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) are well-known multifunctional materials owing to their excellent piezoelectric, ferroelectric properties, and ultra-high electromechanical coupling factors [7–9]. Rare earth (RE) ions as well-known luminescent activators with optical absorption and emission in the infrared and visible wavelength ranges have been widely used as dopants to design luminescent materials. Therefore, doping rare earth ions into relaxer-based ferroelectric single crystals will make the crystals simultaneously possess electrical-mechanical-optical properties, which have potential applications in developing innovative multifunctional devices. Our team members have successfully grown RE ions (Er^{3+} , Ho^{3+} , and Yb^{3+}) doped PMN-PT and PSN-PMN-PT single crystals and investigated their electric and optic properties systematically [14–19]. It is found that the addition of rare-earth ions not only improves the electrical properties of the crystals but also makes them obtain optical absorption and up-conversion luminescence properties. For example, Xi, Z reported that the remnant polarization P_r of PSN-PMN-PT increased from 24.2 to $30.99 \mu\text{C}/\text{cm}^2$ by the modification

of Er^{3+} . Meanwhile, seven optical absorption bands and the up-conversion emissions bands (564 nm and 665 nm) were observed for the Er^{3+} in PSN-PMN-PT [14].

In order to further analyze the optical absorptions and explore the spectral properties of RE ions in PMN-PT crystals, it is necessary to apply Judd–Ofelt [J–O] treatment. Based on the analysis of absorption spectra using the Judd–Ofelt theory, the main spectroscopic characteristics, including optical transition probabilities, branching ratio, and radiative lifetime, can be obtained [20–29]. Therefore, Judd–Ofelt treatment is widely applied to predict the spectroscopic characteristics for laser crystals, luminescent powders, and glass. However, relevant Judd–Ofelt treatment to the ferroelectric crystals PMN-PT doping with RE ions has not been found yet in the previous literature.

In this work, we incorporated rare earth ions $\text{Er}^{3+}/\text{Sc}^{3+}$ into PMN-PT crystal to form a new multifunctional system. It is anticipated that this new multifunctional crystal possesses excellent ferroelectric and luminescence properties. In addition, the spectroscopic characteristics of the new system have been predicted by applying J–O treatment for the first time, which will provide an understanding of the optical properties of Er^{3+} ions in PMN-PT crystal. The research includes the following steps: Firstly, ferroelectric crystal PMN-PT: $\text{Er}^{3+}/\text{Sc}^{3+}$ was grown by a high-temperature flux method. Secondly, SEM image, XRD patterns, hysteresis loops, absorption spectrum, and up-conversion luminescence emission spectra of the as-grown crystals were presented. Finally, we investigated the effect of modification of rare earth ions $\text{Er}^{3+}/\text{Sc}^{3+}$ on the ferroelectric properties of PMN-32PT crystal and the spectroscopic characteristics of Er^{3+} in PMN-PT crystal by applying the Judd–Ofelt treatment.

2. Materials and Methods

2.1. Crystal Growth

PMN-32PT: $\text{Er}^{3+}/\text{Sc}^{3+}$ single crystals were grown by the high-temperature flux method. The process is as follows: Firstly, MgO and Nb_2O_5 powders with 99.99% purity were mixed at a molar ratio of 1:1 and calcinated at 1000 °C for 6 h to form the columbite precursor MgNb_2O_6 . Secondly, MgNb_2O_6 , PbO , and TiO_2 powders were mixed according to the stoichiometric composition of 0.68PZN-0.32PT, and excessive 80 wt% PbO powders as the solvent of high-temperature solution were added to the mixtures. 2 wt% Er_2O_3 and 2 wt% Sc_2O_3 were also added to the mixtures and wet-milled for 12 hours in the alcohol. Then the slurry mixtures were dried at 80 °C for 24 h in a drying oven; and the dried mixture powders were filled into a platinum crucible which was placed in a corundum pot with the same shape, the space between the platinum crucible and the corundum crucible was filled with Al_2O_3 powders. Thirdly, the crucibles were sealed and placed in the crystal growth furnace with an automatic temperature controller, which was set from room temperature to 1330 °C at the rate of 3 °C/min, held for 12 h, and fell from 1330 °C to 650 °C at the rate of 0.01 °C/min, then cooled to room temperature spontaneously. Finally, the as-grown single crystals PMN-32PT: $\text{Er}^{3+}/\text{Sc}^{3+}$ together with Pt crucible were boiled in nitric acid solution with the concentration of 50% until the crystals were separated from the platinum crucible. The as-grown crystals were obtained after the cleaning process in an ultrasonic cleaner when the crystals were removed from the platinum crucible. Finally, ferroelectric single crystal PMN-32PT: $\text{Er}^{3+}/\text{Sc}^{3+}$ was cut into thin slices along the exposed surface.

2.2. Characterization Procedure

Micro morphology and element content of the as-grown crystal was performed by scanning electron microscope (FEI Quanta 400 FEG) quipped with Energy Dispersive Spectrometer (EDS). The X-ray diffraction (XRD) data were collected on an X-ray Diffractometer (Bruker D8 ADVANCE, Hannover, Germany) with Cu Ka radiation at the room temperature. The ferroelectric hysteresis loops were investigated by aix-ACCT TF2000 analyzer. The UV-VIS-NIR absorption spectra were detected by UV-VIS-NIR spectrophotometer (CARY50000, Agilent, Santa Clara, CA, USA). The up-conversion luminescence spectrum was measured by the Steady-State Spectrometer (FLS980, Edinburgh, England).

3. Results and Discussion

3.1. Macroscopic and Microscopic Morphology of the Crystals

Figure 1a shows the macroscopic morphology of as-grown PMN-32PT:Er³⁺/Sc³⁺ crystals. It can be seen from the figure that the crystals present light yellow, the shape of which is irregular polyhedron or pseudo-cube with the size of 6 mm × 4 mm × 4 mm, similar to that of pure PMN-PT crystals reported in [15]. Figure 1b shows SEM image of PMN-32PT:Er³⁺/Sc³⁺ crystals at 1000 times magnification. There are obvious steps like growth stripes in the local area of the crystal surface, and the step edges are arranged in a linear parallel manner, which also exists in undoped PMN-PT crystal as shown in Figure 1c. The doping of rare earth ions has little effect on the crystal growth, due to the good tolerance of the crystal. Figure 1d shows an SEM image of PMN-32PT:Er³⁺/Sc³⁺ crystals at 5000 times magnification. It can be seen from Figure 1d that there are some corrosion pits with extremely irregular shapes in the crystal. The formation of corrosion pits is caused by the corrosion of wrapped PbO and various salt residues resulting from hot nitric acid during the separation of crystals. An energy dispersive spectrometer (EDS) was carried out at four random locations in the flat region of the crystal surface. Figure 1e,f shows a location and corresponding EDS spectrum. The spectrum shows that Pb, Mg, Nb, Ti, and O are the main elements in the single crystal. In addition, Er and Sc were also found, indicating that Er³⁺ and Sc³⁺ diffuse into the PMN-32PT. Table 1 shows the weight percentage of every element. wt% of Sc³⁺ and Er³⁺ are 0.13% and 2.21%, respectively.

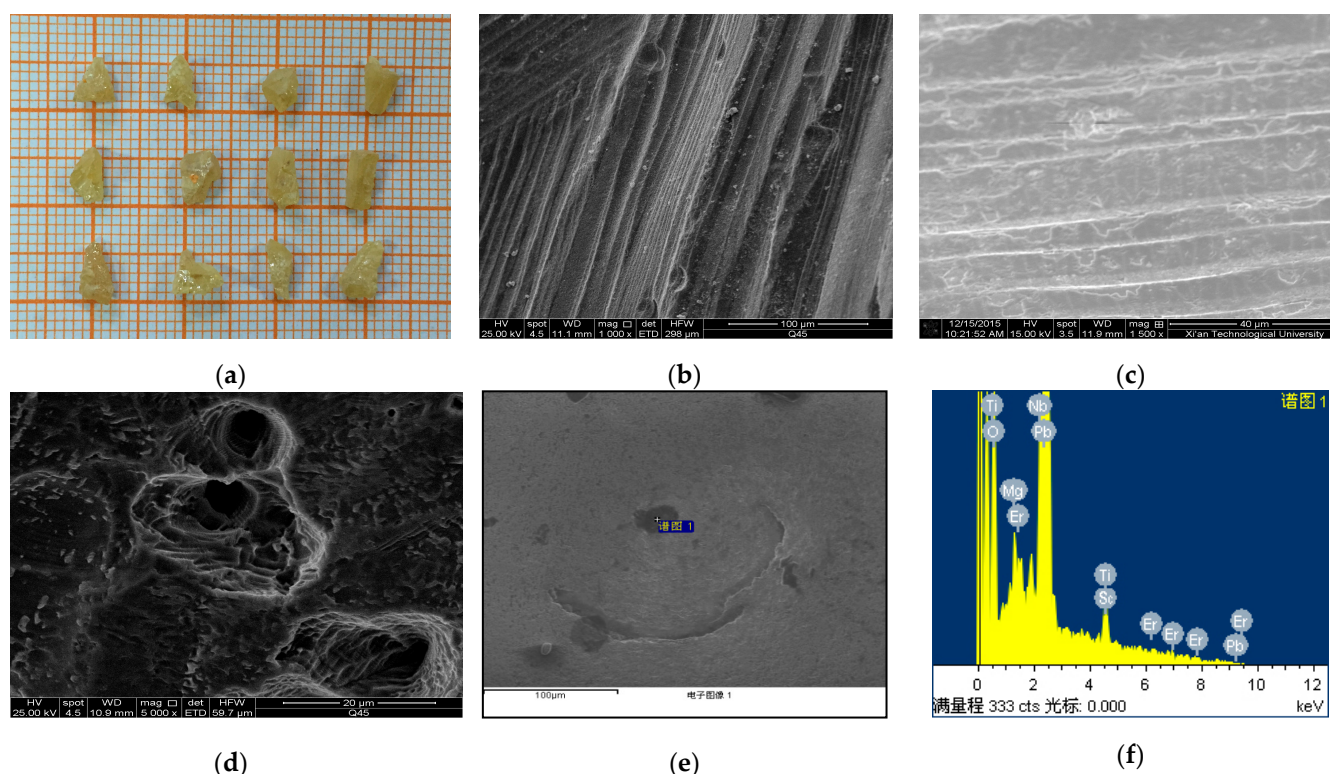


Figure 1. (a) Photograph of crystals PMN-32PT:Er³⁺/Sc³⁺ (b) SEM image of PMN-32PT:Er³⁺/Sc³⁺ (c) SEM image of undoped PMN-32PT (d) SEM image of corrosion pits in crystal PMN-32PT:Er³⁺/Sc³⁺ (5000 × SEM morphology) (e) a location for EDS (f) EDS spectrum of a location on PMN-32PT:Er³⁺/Sc³⁺ crystals surface.

Table 1. The element content of the PMN-32PT:Er³⁺/Sc³⁺ crystal obtained by EDS.

Wt%	O	Mg	Ti	Nb	Pb	Sc	Er
A 1	21.45	1.68	4.02	15.69	54.97	0.24	1.92
A 2	20.17	1.72	3.87	16.71	55.43	0.02	2.12
A 3	19.70	1.53	3.50	15.67	56.73	0.08	2.79
A 4	16.72	1.73	4.27	16.71	58.38	0.17	2.01
Average	19.51	1.67	3.92	16.2	56.37	0.13	2.21

3.2. XRD Patterns

Figure 2a shows the XRD patterns of the exposed flat surface of a PMN-32PT:Er³⁺/Sc³⁺ crystal. It can be seen from the figure that there are only two diffraction peaks corresponding to the crystal planes (100) and (200) at the range of 10°~60°, respectively, and no other impurity peaks, which indicates that the crystal grows basically along the [100] orientation. Figure 2b shows the XRD patterns of PMN-32PT:Er³⁺/Sc³⁺ and PMN-32PT crystals powders for comparison. we can see that the diffraction peak positions are consistent with each other. The doping of rare earth ions does not make the crystal produce a new phase. They both present pure perovskite structure (ABO₃) without pyrochlore phase or any other second phase, which indicates that Er³⁺/Sc³⁺ ions have been diffused into the lattice of the single crystal PMN-32PT. Figure 2c shows the enlarged view of the diffraction peaks of the strongest peak, we can see that the diffraction peak position of the PMN-32PT:Er³⁺/Sc³⁺ crystals is offset to the small angle. This phenomenon can be explained by the Bragg equation: $2d\sin\theta = k\lambda$, where d is the interplanar spacing, θ is the diffraction angle, λ is the wavelength of X-ray, and k is the diffraction order. In the experiment, $\lambda = 1.5406 \text{ \AA}$, for the same k , the larger interplanar spacing, the smaller diffraction angle. When the Mg²⁺ ($r(\text{Mg}^{2+}) = 0.72 \text{ \AA}$) or Nb⁵⁺ ($r(\text{Nb}^{5+}) = 0.64 \text{ \AA}$) ions are replaced by larger Er³⁺ ($r(\text{Er}^{3+}) = 0.88 \text{ \AA}$) ions, d becomes larger and the diffraction angle θ decreases. The deviation of the diffraction peak to a small angle further indicates that Er³⁺ diffuses into the PMN-32PT crystal lattice.

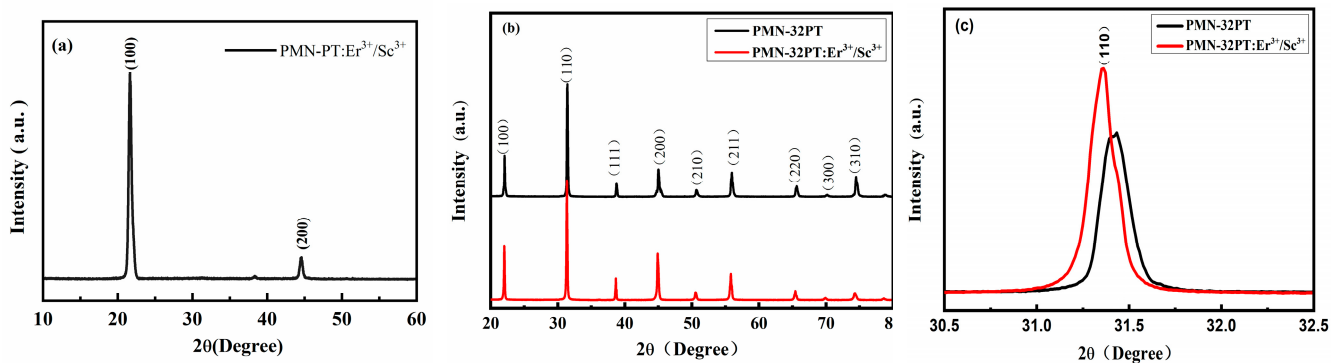


Figure 2. XRD patterns of PMN-32PT:Er³⁺/Sc³⁺ (a) platelet sample. (b) crystal powder (c) zoomed XRD patterns from 30.5° to 32.5°.

3.3. Hysteresis Loops

Polarization versus Electric field (P - E) hysteresis loop is a common characteristic of all ferroelectric materials. Figure 3a shows P - E hysteresis loops of the PMN-32PT:Er³⁺/Sc³⁺ crystals along [100] at room temperature. It can be seen from the figure that the hysteresis loop tends to be saturated as the applied electric field increases from 2 to 14 kV/cm. When the electric field increases to 14 kV/cm, the P - E hysteresis loop is saturated. The obtained remnant polarization (P_r) is 27.97 $\mu\text{C}/\text{cm}^2$ and the coercive field E_C is 8.26 kV/cm, which is higher than that of PMN-32PT crystal ($P_r \sim 19.43 \mu\text{C}/\text{cm}^2$, $E_C \sim 3.83 \text{ kV}/\text{cm}$) shown in Figure 3b. The E_C is also higher than that of PMN-32PT:Er³⁺ ($E_C \sim 6.37 \text{ kV}/\text{cm}$) and PMN-32PT:Ho³⁺ ($E_C \sim 4.31 \text{ kV}/\text{cm}$) crystals reported in literature [16] and [17]. The enhancement of the coercive field is attributed to the domain wall pinning by defects [17]. The

higher coercive field makes the ferroelectric single crystals PMN-32PT:Er³⁺/Sc³⁺ become a potential material for high-power piezoelectric device applications.

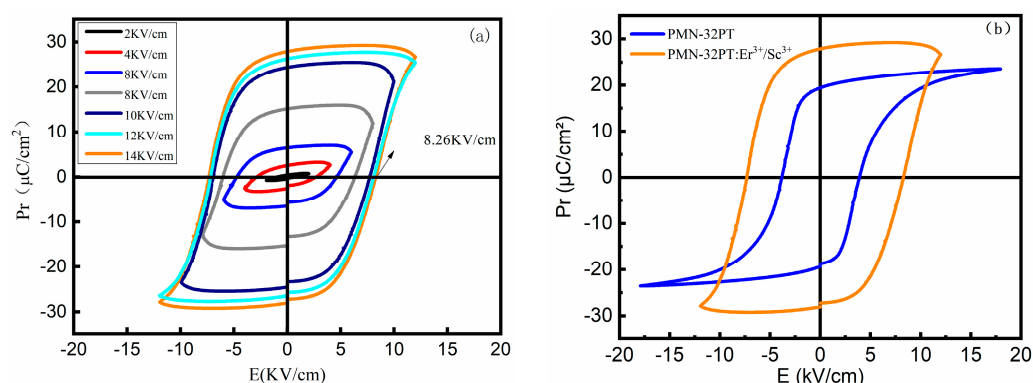


Figure 3. Polarization versus electric field (P - E) hysteresis loops of PMN-32PT:Er³⁺/Sc³⁺ crystal (a) P - E hysteresis loops at different electric fields (b) P - E hysteresis loops of the crystals PMN-32PT:Er³⁺/Sc³⁺ and PMN-32PT at saturated state.

3.4. UV-VIS-NIR Absorption

Figure 4 shows the unpolarized absorption spectra of PMN-32PT:Er³⁺/Sc³⁺ and PMN-32PT crystals in the range of 450~1800 nm at room temperature. It can be seen from the figure that there are no absorption bands for pure PMN-32PT, but seven optical absorption bands are explored for PMN-32PT:Er³⁺/Sc³⁺ crystal. The center wavelengths of the seven bands are located at 491 nm (⁴I_{15/2} → ⁴F_{7/2}), 524 nm (⁴I_{15/2} → ²H_{11/2}), 551 nm (⁴I_{15/2} → ⁴S_{3/2}), 654 nm (⁴I_{15/2} → ⁴F_{9/2}), 801 nm (⁴I_{15/2} → ⁴I_{9/2}), 973 nm (⁴I_{15/2} → ⁴I_{11/2}), 1541 nm (⁴I_{15/2} → ⁴I_{13/2}). The obtained absorption spectra are very similar to that of solely Er³⁺-doped PMN-32PT [16] and PSN-PMN-PT [14], which have a similar crystal structure. However, it is completely different from that of other laser crystals such as Yb₃Al₅O₁₂, KY(WO₄)₂, Gd₃Ga₅O₁₂ [20–22]. It seems that it is necessary to apply the Judd–Ofelt treatment for analysis of absorption spectrum and predict the spectroscopic characteristics for the PMN-32PT:Er³⁺/Sc³⁺ crystal. It is also necessary to do the same work on the solely Er-doped PMN-32PT crystals for comparison. In our previous work, we have reported the absorption spectrum of the solely Er³⁺-doped PMN-32PT crystal [16], but relevant Judd–Ofelt treatment was not carried out. In this paper, the absorption spectra of PMN-32PT:Er³⁺/Sc³⁺ and PMN-32PT:Er³⁺ are analyzed by using the Judd–Ofelt theory.

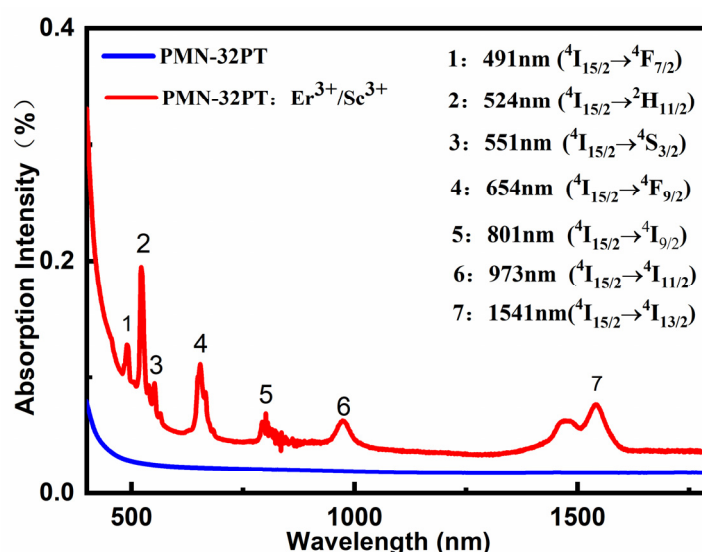


Figure 4. The absorption spectra of PMN-32PT and PMN-32PT:Er³⁺/Sc³⁺ crystals.

3.5. Judd–Ofelt Analysis

The analyses of the optical unpolarized absorption spectra of laser crystals by using the Judd–Ofelt theory have been reported in much literature [20–29]. Firstly, the Judd–Ofelt model was applied to the unpolarized absorption bands to determine their experimental oscillation strength. The experimental oscillation strength (f_{exp}) associated with a $4f-4f$ transition from the ground state (J) to an excited state (J') can be obtained from analysis of the $\int D(\lambda)d\lambda$ of absorption bands using the following formula:

$$f_{exp}(J \rightarrow J') = \frac{mc^2}{\pi e^2 \bar{\lambda}^2 N_0} \times \frac{1}{0.43L} \int D(\lambda)d\lambda \quad (1)$$

where m is the electron mass, c is the speed of light in vacuum, e is the electron charge, N_0 is the erbium concentration, L is the thickness of the sample, $\bar{\lambda}$ is the mean wavelength of the specific absorption band, and $D(\lambda)$ is optical density. From the absorption spectra shown in Figure 4, only seven optical absorption bands from the ground state $^4I_{15/2}$ of erbium ions in the total spectrum were explored. The values of experimental polarized oscillator strengths f_{exp} of these seven bands were obtained from Formula (1). The results are listed in Table 2 along with the values of the main parameters.

Table 2. f_{cal} , f_{exp} , δ_{rsm} and Ω_t ($t = 2, 4$ and 6) of Er^{3+} in the PMN-32PT:Er³⁺/Sc³⁺ crystal.

S' L' J'	$\bar{\lambda}$ /nm	$\int D(\lambda) d\lambda \times 10^{-6}$	$f_{exp} \times 10^{-6}$	$f_{cal} \times 10^{-6}$	δ_{rsm}
$^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$	491	2.0559	4.3567	4.4312	0.38×10^{-6}
$^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$	524	3.0401	5.6767	5.6909	
$^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$	551	1.1167	1.8647	1.9435	
$^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$	654	3.5541	4.2279	4.2733	
$^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$	801	1.4307	1.1346	0.7911	
$^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$	973	2.5978	1.3961	0.7232	
$^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$	1541	11.3843	2.4423	2.4424	
$\Omega_2 = 0.76 \times 10^{-20} / \text{cm}^2; \Omega_4 = 1.0 \times 10^{-20} / \text{cm}^2; \Omega_6 = 0.55 \times 10^{-20} / \text{cm}^2$					

On the other hand, the theoretical oscillator strength of the magnetic/electric dipole transition (f_{cal}^{md} and f_{cal}^{ed}) can be obtained by the Formulas (3) and (4), and the theoretical oscillator strength f_{cal} is the sum of them, they are given by the followings:

$$f_{cal}(J \rightarrow J') = f_{cal}^{ed}(J \rightarrow J') + f_{cal}^{md}(J \rightarrow J') \quad (2)$$

$$f_{cal}^{ed}(J \rightarrow J') = \frac{8\pi^2 mc}{3h\bar{\lambda}(2J+1)} \times \frac{(n^2+2)^2}{9n} \sum_{t=2,4,6} \Omega_t \left| \langle 4f^N(SL)J || U^{(t)} || 4f^N(S'L')J' \rangle \right|^2 \quad (3)$$

$$f_{cal}^{md}(J \rightarrow J') = \frac{hn}{6mc\bar{\lambda}(2J+1)} \times \left| \langle 4f^N(SL)J || L + 2S || 4f^N(S'L')J' \rangle \right|^2 \quad (4)$$

where J and J' are the angular momentums of the initial and final level, respectively; h is the Planck constant; n is the average refractive index which can be express as $n = (2n_o + n_e)/3$. The values of $n_o(\lambda)$ and $n_e(\lambda)$ used here were derived from reference [12]; $U^{(t)}$ ($t = 2, 4$ and 6) are the reduced matrix elements of the unit tensor operator; $(L + 2S)$ is the magnetic dipole operator which depends on ΔJ given in [28]. Because of the magnetic dipole selection rules: $\Delta l = 0$; $\Delta S = 0$; $\Delta L = 0$; $\Delta J = 0, \pm 1$; $\Delta M = 0, \pm 1$; the magnetic dipole transitions only contribute here to the $^4I_{15/2} \rightarrow ^4I_{13/2}$ absorption band. Ω_t ($t = 2, 4$, and 6) are Judd–Ofelt parameters, which characterize the efficiency of interaction of the earth ions with the field environment. The J–O parameters Ω_t ($t = 2, 4$, and 6) were evaluated from

least-square fitting the measured f_{exp} values to the calculated ones f_{cal} . The quality of the fitting can be evaluated by root mean square (RMS) deviation δ_{rms} by the following:

$$\delta_{rms} = \sqrt{\frac{\sum (f_{exp}^i - f_{cal}^i)^2}{N - 3}} \quad (5)$$

where N is a number of is absorption bands. In this paper $N = 7$. Table 2 shows the f_{cal} and f_{exp} that result from the above-mentioned analysis together with the δ_{rms} and the effective J–O parameters Ω_t ($t = 2, 4$ and 6) for the PMN-32PT:Er³⁺/Sc³⁺ crystals. We can see that the values of theoretical oscillator strength f_{cal} are practically closed to those of experimental oscillator strength f_{exp} and the δ_{rms} between which is 0.38×10^{-6} for PMN-32PT:Er³⁺/Sc³⁺. Based on our previous work reported in the literature [10], Judd–Ofelt analysis was also carried out for absorption spectra of PMN-32PT:Er³⁺ in this paper and the calculated results are shown in Table 3. The first column of Table 4 shows the δ_{rms} of Er³⁺ in some laser crystals for comparison. It can be seen that the obtained δ_{rms} is lower than that of several laser crystals containing Er³⁺ [22–24,26]. The low RMS deviation indicates that our fitting is effective. The obtained effective J–O parameters Ω_t ($t = 2, 4$ and 6) are $\Omega_2 = 0.76 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.0 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 0.55 \times 10^{-20} \text{ cm}^2$ for the crystals PMN-32PT:Er³⁺/Sc³⁺ and $\Omega_2 = 1.77 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.50 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 0.79 \times 10^{-20} \text{ cm}^2$ for PMN-32PT:Er³⁺. As well known, Judd–Ofelt parameters Ω_t ($t = 2, 4$, and 6) are important for the investigation of the local structure and bonding in the vicinity of rare-earth ions. They characterize the interaction of rare-earth ions with the host crystals. In addition, the spectroscopic quality factor, defined by Ω_4/Ω_6 , is critically important in predicting the stimulated emission for the active laser medium. For comparative study, the J–O parameters and Ω_4/Ω_6 of other crystals are also listed in Table 4. In this work, the values of Ω_4/Ω_6 are 1.82 and 1.90 for PMN-32PT:Er³⁺/Sc³⁺ and PMN-32PT:Er³⁺, respectively, which are smaller than that of LiNbO₃ [26–28]. Still, it is larger than that of other crystals reported in the literature [20–25]. The high spectroscopic quality factor Ω_4/Ω_6 indicates the ferroelectric single crystal PMN-32PT:Er³⁺/Sc³⁺ and PMN-32PT:Er³⁺ can be promising laser crystal.

Table 3. f_{cal} , f_{exp} , δ_{rms} and Ω_t ($t = 2, 4$ and 6) of Er³⁺ in the PMN-32PT:Er³⁺ crystal.

S' L' J'	λ / nm	$\int D(\lambda) d\lambda \times 10^{-6}$	$f_{exp} \times 10^{-6}$	$f_{cal} \times 10^{-6}$	δ_{rsm}
$^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$	491	3.1470	6.3522	6.4768	0.18×10^{-6}
$^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$	522	6.2087	11.0882	11.0951	
$^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$	551	1.7890	2.8571	2.8171	
$^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$	654	5.6328	6.4086	6.3404	
$^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$	801	1.5232	1.1728	1.1944	
$^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$	973	2.7991	1.4358	1.1051	
$^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$	1541	15.3654	3.1487	3.1487	
$\Omega_2 = 1.77 \times 10^{-20} / \text{cm}^2$; $\Omega_4 = 1.50 \times 10^{-20} / \text{cm}^2$; $\Omega_6 = 0.79 \times 10^{-20} / \text{cm}^2$					

Table 4. The J-O intensity parameters Ω_t ($t = 2, 4$ and 6) of Er^{3+} in different crystals.

Crystal	$\delta_{rms} \times 10^{-6}$	$\Omega_2 \times 10^{-20}/\text{cm}^2$	$\Omega_4 \times 10^{-20}/\text{cm}^2$	$\Omega_6 \times 10^{-20}/\text{cm}^2$	Ω_4/Ω_6	Reference
$\text{Yb}_3\text{Al}_5\text{O}_{12}:\text{Er}^{3+}$	0.39	0.27	0.90	1.16	0.78	[20]
$\text{KY}(\text{WO}_4)_2:\text{Er}^{3+}/\text{Yb}^{3+}$	0.27	6.33	1.35	1.90	0.71	[21]
$\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Er}^{3+}/\text{Pr}^{3+}$	0.70	5.13	6.30	7.57	0.83	[22]
$\text{LuAl}_3(\text{BO}_3)_4:\text{Er}^{3+}$	0.88	8.33	3.83	3.55	1.08	[23]
GSAG: Er^{3+}	0.75	1.94	1.58	1.41	1.12	[24]
$\text{K}_2\text{YF}_5:\text{Er}^{3+}$	0.29	1.22	0.65	0.46	1.41	[25]
$\text{LiNbO}_3:\text{Er}^{3+}/\text{Yb}^{3+}$	0.98	7.23	3.14	1.42	2.21	[26]
$\text{LiNbO}_3:\text{Er}^{3+}/\text{Mg}^{2+}$	0.34	2.36	0.76	0.30	2.53	[27]
$\text{LiNbO}_3:\text{Er}^{3+}$	/	6.19	2.17	0.97	2.23	[28]
PMN-32PT: Er^{3+}	0.18	1.77	1.50	0.79	1.90	This work
PMN-32PT: $\text{Er}^{3+}/\text{Sc}^{3+}$	0.38	0.76	1.0	0.55	1.82	This work

Based on the obtained J-O parameters Ω_t ($t = 2, 4$, and 6), the radiative transition probability $A(J \rightarrow J')$ of the electric and magnetic dipole transitions from an excited manifold J' to a lower manifold J can be calculated by followings:

$$A_{ed}(J', J) = \frac{64\pi^4 e^2}{3h(2J'+1)\lambda^3} \left[n \left(\frac{n^2+2}{3} \right)^2 \sum_{t=2,4,6} \Omega_t \left| \langle 4f^N(SL)J \| U^{(t)} \| 4f^N(S'L')J' \rangle \right|^2 \right] \quad (6)$$

$$A_{md}(J', J) = \frac{4\pi^4 e^2 h}{3m^2 c^2 (2J'+1)\lambda^3} \left[n^2 \left| \langle 4f^N(SL)J \| L + 2S \| 4f^N(S'L')J' \rangle \right|^2 \right] \quad (7)$$

$$A(J', J) = A_{ed}(J', J) + A_{md}(J', J) \quad (8)$$

Branching ratios β and radiative lifetimes τ_r were calculated according to the following.

The calculated electric and magnetic dipole spontaneous emission probabilities, radiative lifetimes, and branching ratios of Er^{3+} ions in crystals PMN-32PT: $\text{Er}^{3+}/\text{Sc}^{3+}$ and PMN-32PT: Er^{3+} are summarized in Table 5. The radiative transitions of $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (654 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (551 nm), and $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (524 nm) have larger fluorescence branching ratios in visible wavelength regions. The fluorescence branching ratios of them are 81%, 73%, and 70%, respectively. Moreover, the radiative lifetimes of $^4\text{I}_{13/2}$ and $^4\text{I}_{11/2}$ levels for the PMN-32PT: $\text{Er}^{3+}/\text{Sc}^{3+}$ crystals are estimated to be 2.82 ms and 2.61 ms, respectively, which are longer than those of PMN-32PT: Er^{3+} , $\text{KY}(\text{WO}_4)_2:\text{Er}^{3+}/\text{Yb}^{3+}$ [21], $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Er}^{3+}/\text{Pr}^{3+}$ [22], and $\text{Lu}_2\text{O}_3:\text{Er}^{3+}$ [29] shown in Table 6, indicating excellent energy storage capability for the PMN-32PT: $\text{Er}^{3+}/\text{Sc}^{3+}$ crystals.

$$\beta = \frac{A_{J'J}}{\sum_{J'} A_{J'J}} \quad (9)$$

$$\tau = \frac{1}{\sum_{J'} A_{JJ'}} \quad (10)$$

Table 5. Spectroscopic parameters of Er³⁺ in PMN-32PTcrystal.

S'L'J' → SLJ	λ/nm	PMN-32PT:Er ³⁺ /Sc ³⁺					PMN-32PT:Er ³⁺				
		A_{ed}/s^{-1}	A_{md}/s^{-1}	A/s^{-1}	τ/ms	β	A_{ed}/s^{-1}	A_{md}/s^{-1}	A/s^{-1}	τ/ms	β
⁴ I _{13/2} → ⁴ I _{15/2}	1540	286	68	355	2.82	1.00	420	68	488	2.05	1.00
⁴ I _{11/2} → ⁴ I _{15/2}	973	344	0	344	2.61	0.90	525	0	525	1.75	0.92
→ ⁴ I _{13/2}	2642	17	21	38		0.10	26	21	47		0.08
⁴ I _{9/2} → ⁴ I _{15/2}	793	556	0	556	1.60	0.89	852	0	852	1.04	0.89
→ ⁴ I _{13/2}	1635	61	0	61		0.10	97	0	97		0.10
→ ⁴ I _{11/2}	4287	3	4	7		0.01	5	4	9		0.01
⁴ F _{9/2} → ⁴ I _{15/2}	654	4505	0	4505	0.18	0.81	6684	0	6684	0.12	0.81
→ ⁴ I _{13/2}	1137	858	0	858		0.16	1275	0	1275		0.15
→ ⁴ I _{11/2}	1995	159	0	159		0.03	237	0	237		0.03
→ ⁴ I _{9/2}	3731	28	0	28		0.01	37	0	37		0.00
⁴ S _{3/2} → ⁴ I _{15/2}	551	2876	0	2876	0.25	0.73	4169	0	4169	0.17	0.73
→ ⁴ I _{13/2}	860	759	0	759		0.19	1102	0	1102		0.19
→ ⁴ I _{11/2}	1275	233	0	233		0.06	339	0	339		0.06
→ ⁴ I _{9/2}	1816	86	0	86		0.02	119	0	119		0.02
→ ⁴ F _{9/2}	3539	11	0	11		0.00	16	0	16		0.00
² H _{11/2} → ⁴ I _{15/2}	524	9417	0	9417	0.08	0.69	18,360	0	18,360	0.04	0.70
→ ⁴ I _{13/2}	789	2720	0	2720		0.20	5309	0	5309		0.20
→ ⁴ I _{11/2}	1126	938	0	938		0.07	1835	0	1835		0.07
→ ⁴ I _{9/2}	1527	398	0	398		0.03	743	0	743		0.03
→ ⁴ F _{9/2}	258	77	0	77		0.01	151	0	151		0.01
→ ⁴ S _{3/2}	9605	2	0	2		0.00	3	0	3		0.00

Table 6. Radiative lifetimes of Er³⁺ in laser crystal.

Crystal	⁴ I _{13/2}	⁴ I _{11/2}	⁴ I _{9/2}	⁴ F _{9/2}	⁴ S _{3/2}	² H _{11/2}	Reference
Yb ₃ Al ₅ O ₁₂ :Er ³⁺	6.238	4.906	4.548	0.573	0.384	0.517	[20]
LiNbO ₃ :(1%mol) Er ³⁺	2.505	1.877	1.841	0.246	0.211	0.030	[27]
KY(WO ₄) ₂ : Er ³⁺ /Yb ³⁺	2.45	1.79	2.29	0.23	0.15	0.05	[21]
Lu ₂ O ₃ :Er ³⁺	1.36	2.52	5.22	0.71	0.37	0.12	[29]
Gd ₃ Ga ₅ O ₁₂ :Er ³⁺ /Pr ³⁺	0.78	0.62	0.60	0.07	0.05	0.04	[22]
PMN-32PT:Er ³⁺	2.05	1.75	1.04	0.12	0.17	0.04	This work
PMN-32PT:Er ³⁺ /Sc ³⁺	2.82	2.61	1.60	0.18	0.25	0.07	This work

3.6. Up-Conversion Emission

Figure 5a shows the up-conversion emission spectra of Er³⁺/Sc³⁺ co-doped PMN-32PT crystals irradiated by a 980-nm laser with different pump power. Three emission bands are generated, corresponding to ²H_{11/2} → ⁴I_{15/2} (524 nm), ⁴S_{3/2} → ⁴I_{15/2} (551 nm), ⁴F_{9/2} → ⁴I_{15/2} (654 nm) transitions. These assignments are coinciding with the J-O analysis because these dipole transitions have large fluorescence branching ratios and high radiative quantum efficiencies. It can be seen from the spectrum that the green light has undergone Stark level splitting, 551 nm splitting into 540 nm, 551 nm, and 565 nm. This is due to the fact that each spectral branch of rare earth ions has a 2J+1 degeneracy, if the symmetry of the crystal field is low, then the degeneracy of the energy level will be canceled or partially canceled, resulting in energy level splitting. Figure 5b shows the dependence of emission intensities on pump power used to investigate the up-conversion mechanism and the number of photons in the up-conversion process. The up-converted emission intensity I_{up} is proportional to IR excitation intensity I_{IR} , $I_{up} \propto I_{IR}^m$ where m is the number of pumping photons. The dependence emission intensity on pump power is quadratic and obtained m values are 1.92 2.21 and 2.27 for ⁴F_{9/2} → ⁴I_{15/2} (654 nm), ⁴S_{3/2} → ⁴I_{15/2} (551 nm), and ²H_{11/2} → ⁴I_{15/2} (524 nm), respectively. These values are close to 2, which indicates that two excitation photons contribute to one UC photon.

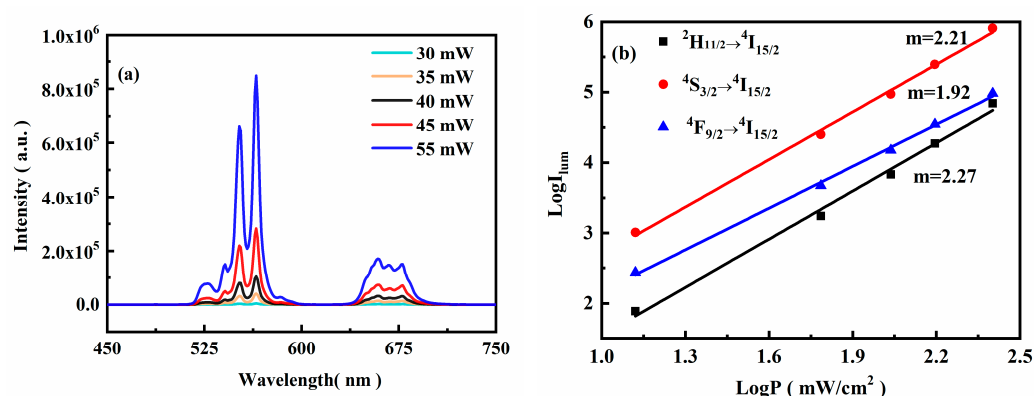


Figure 5. (a) UC emission spectra of PMN-32PT:Er³⁺/Sc³⁺ crystals at 980 nm excitation with different pump power (b) Power dependence of the up-conversion emission intensities.

Finally, it should be stressed that all of the preceding results and discussion concentrate on the spectroscopic properties of Er³⁺. As no absorption and emission bands corresponding to Sc³⁺ are generated, spectroscopic properties of Sc³⁺ cannot be investigated by Judd–Ofelt treatment. However, comparison results of the Judd–Ofelt analysis carried out for Er³⁺ doped PMN-32PT and Er³⁺/Sc³⁺ co-doped PMN-32PT crystals are given in Table 6, where the longer radiative lifetime for PMN-32PT:Er³⁺/Sc³⁺ crystal indicated that Sc³⁺ ion doping improves the optical quality of the PMN-32PT:Er³⁺ crystal, but the molecular mechanism needs to be further investigated.

4. Conclusions

PMN-32PT:Er³⁺/Sc³⁺ single crystals were grown by using the high-temperature flux method. The coercive field E_C of PMN-32PT crystal was enhanced from 3.83 kV/cm to 8.26 kV/cm by Er³⁺/Sc³⁺ ions modification. Moreover, seven optical absorption bands of Er³⁺ are explored in the PMN-32PT crystal field. Based on the analysis of absorption spectra using the Judd–Ofelt theory, the main spectroscopic characteristics, including optical transition probabilities, branching ratio, and radiative lifetime, have been obtained. The obtained J–O intensity parameters Ω_t ($t = 2, 4$ and 6) are $\Omega_2 = 0.76 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.0 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 0.55 \times 10^{-20} \text{ cm}^2$ for PMN-32PT:Er³⁺/Sc³⁺ single crystals, and the spectroscopic quality factor, Ω_4/Ω_6 , is 1.82. The investigations have shown that PMN-32PT:Er³⁺/Sc³⁺ looks promising for laser applications. Combined with the ferroelectric properties of the host crystal, Er³⁺/Sc³⁺ co-doped PMN-32PT crystal is expected to become a new type of multifunctional crystal integrating electricity–light.

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