Dynamically Tuning the Up-conversion Luminescence of Er\(^{3+}/Yb^{3+}\) Co-doped Sodium Niobate Nano-crystals through Magnetic Field

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In this work, we show here that the up-conversion luminescence of NaNbO\(_3\):Er\(^{3+}/Yb^{3+}\) nano-materials can be modulated by magnetic field and an enhancement of up-conversion intensities by a factor of about 2 for Er\(^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2}\) obtained at 30T and about 5.4 for Er\(^{3+}:^4F_{9/2} \rightarrow ^4I_{15/2}\) obtained at 20T. The increased up-conversion luminescence are mainly interpreted in terms of the enhanced non-radiation transition from \(^4I_{15/2}\) to \(^4I_{11/2}\) of Er\(^{3+}\) ions and the spin-orbital coupling (that is “mixing” effect) in crystal field by an external magnetic field. Meanwhile, we observed continuously spectra broadening with growing the magnetic field intensity, which is ascribed to the “mixing” effect induced by magnetic field and the difference of \(g\) factor of sub-bands. This bi-functional material with controllable optical-magnetic interactions has various potential applications, such as optical detection of magnetic field, etc.

The bi-functional magnetic-optical materials have received growing attention for their potential applications in high accuracy communication, magnetic resonance imaging (MRI), drug targeting or carrier, aircraft guidance and optical detection of magnetic field, due to their ability to be detected at different models, optically and magnetically\(^{1-7}\). Due to conventional magnetic-optical bi-functional materials are produced by coupling optical materials with magnetic ones, making the optical and magnetic phases separation, it is very difficult to realize an interaction between the optical and magnetic properties (e.g., tuning the optical properties using a magnetic field)\(^{8-11}\). Rare-earth (RE) ions doped materials are ideal candidates to realize these functions because they possess rich \(4f\) energy levels in optical frequency, the tunability of magnetic-optical interaction by external magnetic field, and excellent photostability\(^{12-15}\).

Several recent works show that magnetic-optical interactions can be simultaneously observed in various materials by RE doping, for example, Er\(^{3+}\)-doped nano-glass-ceramics\(^8\), YVO\(_4\):Er\(^{3+}\)\(^{16,17}\), Gd\(_2\)O\(_3\):Er\(^{3+}\), Yb\(^{3+}\)\(^{11,12}\), NaGdF\(_3\):Er\(^{3+}\), Yb\(^{3+}\)\(^{13-15}\), Nd\(^{3+}\) co-doped NaGdF\(_3\):Er\(^{3+}\), Yb\(^{3+}\) nano-crystals\(^{21}\), and so on. In this materials, the luminescence intensities of emission bands of RE ions are a gradual decrease (or increase) with increasing (or decreasing) applied magnetic field. In addition, in comparison to those substrates, NaNbO\(_3\) has Perovskite structure and excellent properties such as piezoelectric, ferroelectric, optoelectronics, nonlinear optical, and so on. In addition, we have studied the optical second harmonic generation (SHG) of single NaNbO\(_3\) micro/nano-crystals with various morphologies and sizes, which exhibited strong nonlinear SHG responses\(^22\). Considering its advantages and

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Based on our research foundation, we chose NaNbO₃ as the host material to dope with the classic up-conversion ionic pair, Er³⁺/Yb³⁺, which can convert low-energy infrared photons to high-energy visible light.

In this work, the effect of external magnetic fields on the magneto-upconversion luminescence (MUL) properties of emission bands of Er³⁺:⁴S₃/₂ → ⁴I₁₅/₂ and ⁴F₉/₂ → ⁴I₁₅/₂ transitions is studied, which results are quite different from the recent reports⁸,¹¹,¹⁶–²¹. For instance, Moshchalkov et al. first showed the tuning of the luminescence of Er³⁺ doped nano-particles ¹⁶,¹⁷, which up-conversion luminescence intensities are always suppressed by magnetic field, possibly due to the enhanced cross-relaxation process, reduced absorption cross, and improved local site symmetry. While in the present, the integrated luminescent intensity of Er³⁺:⁴S₃/₂ → ⁴I₁₅/₂ could increase to approximately 200% of the original value in the applied magnetic field if reached up to 30 T, and the integrated luminescent intensity of Er³⁺:⁴F₉/₂ → ⁴I₁₅/₂ could increase to approximately 540% of the original value in the applied magnetic field if reached up to 20 T. These results are mainly interpreted in terms of the enhanced non-radiation transition from ⁴I₁₁/₂ to ⁴I₁₃/₂ of Er³⁺ ions and the spin-orbital coupling (that is "mixing" effect) in crystal field by an external magnetic field. This remarkable tunability indicates that the studied nano-material can serve as a good optical-magnetic bi-functional material for various potential applications.

Results and Discussion

Phase purity, structure and morphology. High quality NaNbO₃ nano-crystals were prepared by the Pechini sol-gel method. The XRD patterns and TEM image of as-prepared samples are shown in Fig. 1. From Fig. 1(a), we can confirm that all the as-prepared samples have cubic crystal structures, which are consistent with Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 19–1221 (space group: Pm-3m, a = b = c = 0.391 nm), the interrelated crystalline structure is shown in Fig. 1(b). By co-doped Er³⁺/Yb³⁺ ions, no precipitating phase could be detected in the XRD patterns, demonstrating that there is no obvious influence on the phase when doping with Er³⁺/Yb³⁺ ions in NaNbO₃ nano-crystals. As we may know, the ionic radii of Nb⁵⁺, Na⁺, Er³⁺ and Yb³⁺ cations are 0.349, 0.91, 0.89 and 0.87 pm, respectively. When Er³⁺/Yb³⁺ ions substitute the site of Na⁺ or Nb⁵⁺ ions, the values of mismatching ratio of ionic radius are 0.13 and 0.36, respectively. And the ionic radii of Er³⁺/Yb³⁺ ions is smaller than Na⁺ ions and larger than Nb⁵⁺ ions. It could be inferred that Er³⁺/Yb³⁺ ions are more likely to substitute the sites of Na⁺ ions than Nb⁵⁺ ions. Besides, NaNbO₃ is a cubic crystal as shown in Fig. 1(b), Nb⁵⁺ ions occupy the body-centered and Na⁺ ions occupy the eight vertexes of the cube. Therefore,
it is believed that Er$^{3+}$/Yb$^{3+}$ ions prefer to occupy the Na$^+$ sites. Moreover, the TEM image and size distribution of as-prepared NaNbO$_3$ nano-crystals are given in Fig. 1(c,d), it can be seen that the as-prepared NaNbO$_3$ nano-crystals exhibit relatively uniform, well-dispersed nano-particles with narrow size distribution centered around 50 nm.

**MUL properties of Er$^{3+}$/Yb$^{3+}$ co-doped NaNbO$_3$ nano-crystals.** Figure 2 shows the effect of increasing the external magnetic field (up to 40 T) on the MUL properties of Er$^{3+}$/Yb$^{3+}$ co-doped NaNbO$_3$ nano-crystals at 77 K [(a) emission spectra, (b) integrated luminescent intensities].

In the present work, the effect of external pulsed magnetic fields (up to 40 T) on the MUL properties of Er$^{3+}$/Yb$^{3+}$ co-doped NaNbO$_3$ nano-crystals at 77 K [(a) emission spectra, (b) integrated luminescent intensities]. The magnetic field is in a direction parallel to the exciting radiation. The emitted radiation is monitored in the direction parallel to the applied magnetic field as well as the exciting radiation. In the absence of the magnetic field, this sample emits very strong radiation with emission bands of 530–570 nm and 642–685 nm under 976 nm laser excitation (~150 mW power), corresponding to $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of the Er$^{3+}$ ions, respectively.$^{6,17,21}$ Yb$^{3+}$ ions act as the sensitizer for Er$^{3+}$ ions. The integrated luminescent intensity of both emission bands first increases with the applied magnetic fields and then decreases with the applied magnetic fields increasing further. The integrated luminescent intensity of Er$^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2}$ could increase to approximate 200% of the original value in the applied magnetic field reached up to 30 T, and the integrated luminescent intensity of Er$^{3+}:^4F_{9/2} \rightarrow ^4I_{15/2}$ could increase to approximate 540% of the original value in the applied magnetic field reached up to 20 T. It is evident from Fig. 2 that the emissions from the $^4f$ shell electronic transitions ($^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$) of Er$^{3+}$ ions can be efficiently tuned by changing the applied magnetic field at 77 K.

In the present work, the effect of external magnetic fields on the MUL properties of emission bands of Er$^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions is quite different from the recent reports.$^{8,11,16-21}$ The main reasons for this result are interpreted as follows: on the one hand, the enhanced non-radiation transition from $^4I_{11/2}$ to $^4I_{13/2}$ of Er$^{3+}$ ions, on the other hand, the combined with "mixing" effect (spin-orbital coupling, Hamiltonian model)$^{3,24}$ and Kramers' degeneracy of Stark sub-levels in crystal field by an external magnetic field. The properties of transitions within the $^4f$ configurations of lanthanide ions are strongly dependent on the environment of the ion in terms of differences in ion size or the ionic dependence of site distortions. Although Er$^{3+}$ ions are in sites with cubic symmetry, the actual site symmetry of Er$^{3+}$ ions in excited-states of $^4S_{3/2}$ and $^4F_{9/2}$ energy levels may be slightly lower due to the charge compensation and differences in ionic radius of Na$^+$ (r = 102 pm) or Er$^{3+}$ (r = 89 pm) ions. This lowering of the site symmetry results in crystal field splitting (Stark sub-levels) of the $^4S_{3/2}$ and $^4F_{9/2}$ energy levels. As we know, the Zeeman splitting behavior is complex. From Fig. 2, we can find that the number of splitting peaks of both $^4S_{3/2}$ and $^4F_{9/2}$ energy levels can't relax the selection rules when applied magnetic fields, and there is no change of the number of splitting peaks applying magnetic field or not. Therefore, it could be suggesting that the Zeeman splitting effect may not be considered.

The "mixing" effect is the mixing of states by magnetic field. This effect exists only in condensed substances, in which the atomic states are split by the crystal field. Furthermore, in order to study the "mixing" effect on Stark sub-levels of the Er$^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions in magnetic field, the peaks of emission bands are fitted by the multi-peak Gaussian fit and are analyzed. The emission band of Er$^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2}$ is fitted for three peaks as 542 nm, 547 nm and 553 nm and the emission band of Er$^{3+}:^4F_{9/2} \rightarrow ^4I_{15/2}$ is fitted for two peaks as 658 nm and 671 nm. We define the rates of the integrated intensities of the peaks at 553 nm and 542 nm of $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition and the peaks at 671 nm and 658 nm of $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition, those are, the indexes $R = I(553 nm, peak3)/I(542 nm, peak1)$ and $R = I(671 nm, peak5)/I(658 nm, peak4)$, which could be used to analyze the "mixing" effect on Stark sub-levels of the Er$^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions in different magnetic fields, as shown in Fig. 3. The "mixing" effect (spin-orbital coupling interaction) could cause an external energy ($\Delta E$) to each non-degenerate energy level in applied magnetic fields, which can be described by the following equation (the related derivation shows in Supplementary)$^{25}$.

![Figure 2](https://www.nature.com/scientificreports/)
\[ \Delta E = M g \frac{eB}{2m} \]

in which, \( M \) is magnetic quantum number, \( g \) is Lande factor, \( e \) is the electric charge, \( h \) is Planck’s constant, \( m \) is the mass of an electron, \( B \) is the magnetic field intensity. The equation (1) indicates the energy gap between the non-degenerate levels becomes larger with the increase of applied magnetic field, it is beneficial for the transition of the lower non-degenerate level and reduces non-radiative relaxation as a result of increasing the integrated luminescent intensity, which are consistent with the results of the experiment. In relatively weak magnetic field, the integrated luminescent intensities of both the emission bands of \( \text{Er}^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2} \) and \( ^4F_{9/2} \rightarrow ^4I_{15/2} \) transitions (Fig. 2(b)) and the indexes \( R \) values (Fig. 3(b,d)) increase with the applied magnetic fields increasing, this is because the spin-orbit coupling interaction plays a dominant role comparing with interactions between spin (orbit) and magnetic field. In relatively strong magnetic field, the interactions between spin (orbit) and magnetic field are more than the interaction of spin-orbit coupling making spin-orbit coupling interaction vanished, so the integrated luminescent intensities of both the emission bands of \( \text{Er}^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2} \) and \( ^4F_{9/2} \rightarrow ^4I_{15/2} \) transitions and the indexes \( R \) values decrease with further increasing the applied magnetic field. However, due the external energy \( \Delta E \) of non-degenerate energy levels of \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) transition is stronger, the interaction of spin-orbit coupling is larger, there is a delay of the “mixing” effect for this transition as a result of increasing the integrated luminescent intensity of the emission band of \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) transition begins to drop at 30 T, instead of 20 T for \( ^4F_{9/2} \rightarrow ^4I_{15/2} \) transition. \( \text{Er}^{3+} \) ion has an odd number of \( 4f \) electrons (\( 4f^{11} \)), and shows therefore Kramers’ degeneracy in any crystal field. Magnetic field lifts all crystal field degeneracy. Therefore, in strong magnetic field, the sub-levels of both the emission bands of \( \text{Er}^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2} \) and \( ^4F_{9/2} \rightarrow ^4I_{15/2} \) transitions occur degeneracy, and the degeneracy increases with the applied magnetic fields increasing, as shown in Fig. 2(a).

Apart from the transition energies and the intensity changes, it is sometimes possible to determine width of spectral lines in external magnetic fields. We will carefully study the position of emission bands of \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) and \( ^4F_{9/2} \rightarrow ^4I_{15/2} \) transitions of \( \text{Er}^{3+} \) ions in higher magnetic field in the following. Figure 4 shows the normalized emission spectra under different magnetic fields and the dependence of energy change on the magnetic field. A blue shift at short wavelength side from 537 nm to 534 nm and red shift at long wavelength side from 557 nm to 560 nm of the emission band of \( \text{Er}^{3+}:^4S_{3/2} \rightarrow ^4I_{15/2} \) transition and a blue shift at short wavelength side from 650 nm to
to 647 nm and red shift at long wavelength side from 674 nm to 679 nm of the emission band of Er\(^{3+}\):\(4F_{9/2} \rightarrow 4I_{15/2}\) transition can be clearly observed, which depend on the quantum nature of the respective Stark sub-levels. In the presence of the magnetic field, the external torque induced by the magnetic field adds an external energy to each energy level and increases with the strength of the magnetic field. For example, we can clearly observe that blue shift in the short wavelength edge and red shift in the long wavelength edge for Er\(^{3+}\):\(4S_{3/2} \rightarrow 4I_{15/2}\) transition in Fig. 4(a), this is caused by the gaps among the Stark sub-levels of the \(4S_{3/2}\) level which has a larger total momentum expand notably in the magnetic field. The magnetic field induced change of position can be described by the following equation (the related derivation shows in Supplementary)\(^{14,26}\):

\[
\Delta \sigma = \Delta E_2 - \Delta E_1 = \frac{(M g_2 - M g_1) e}{2 \pi mc B} \tag{2}
\]

in which, \(\Delta \sigma\) is the energy change in wave-number (cm\(^{-1}\)), \(\Delta E_1\) and \(\Delta E_2\) are the external energy before and after transition in the magnetic field, respectively.

The equation (2) indicates the energy gap between the Stark sub-levels becomes larger with the increase of magnetic field, the upper sub-bands shift to higher position in the energy level diagram while the lower sub-bands move to lower position, resulting in broadening of emission bands. For the Er\(^{3+}\):\(4S_{3/2} \rightarrow 4I_{15/2}\) and \(4F_{9/2} \rightarrow 4I_{15/2}\) transitions in NaNbO\(_3\) nano-crystals, the relationships between the change of the emission band position and the magnetic field intensity are shown in Fig. 4(b,d). The influence of the energy change on the magnetic field intensity is nonlinear in the applied magnetic fields, which is slightly mismatch with the linear relationship according to equation (2). This nonlinear dependence could be attributed to the variation of the Lande \(g\) factor with the increase of magnetic field\(^{14,15}\). The detailed mechanism remains to be revealed in further studies.

The up-conversion emission intensity \(I_{UP}\) is proportional to the \(n\)th power of infrared excitation intensity \(I_{IR}\), that is:

\[
I \propto I_{IR}^n \tag{3}
\]

where \(n\) is the number of pumping photons required to excite rare earth ions from the ground state to the emitting state\(^{27,28}\). The dependence of up-conversion emission intensities on the pumping light intensities is measured and the ln-ln plot is drawn in Fig. 5. We find that the \(n\) values for the \(4S_{3/2} \rightarrow 4I_{15/2}\) and \(4F_{9/2} \rightarrow 4I_{15/2}\) emission bands are 1.77 and 1.92, respectively. It indicates that the occurrence of \(4S_{3/2} \rightarrow 4I_{15/2}\) emission and \(4F_{9/2} \rightarrow 4I_{15/2}\) emission

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Figure 4. (a,c) Emission spectra of \(4S_{3/2} \rightarrow 4I_{15/2}\) (a) and \(4F_{9/2} \rightarrow 4I_{15/2}\) (c) transitions of Er\(^{3+}\) ions in NaNbO\(_3\) nano-crystals at different magnetic fields at 77 K. (b,d) Dependence of energy change on the magnetic field for the transition \(4S_{3/2} \rightarrow 4I_{15/2}\) emission band center at 611 nm (b) and \(4F_{9/2} \rightarrow 4I_{15/2}\) emission band center at 671 nm (d).
can be attributed to a two-photon process. The two-photon process corresponds to the up-conversion emission can be described as follows: under a 976 nm laser diode excitation, the Yb3+ ion is excited to the 2F5/2 state via an incoming pump photon, and then goes back to the ground state by transferring its energy to the Er3+ ion in the ground state, this promotes Er3+ ion from the ground state 4I15/2 transit to the excited state 4I11/2. Meanwhile, some of the exited ions relax rapidly to the low-lying level of 4I13/2. A second 976 nm photon or energy transfer from an Yb3+ ion can then populate the 4F7/2 level of the Er3+ ion. Then a non-radiative decay takes place in the Er3+ ion through the populated state to the 4S3/2 level, and then the green 4S3/2 → 4I15/2 emissions occur. Alternatively, the ion can further relax and populate the 4F9/2 level, which can lead to the red 4F9/2 → 4I15/2 emission.

To get more information about the up-conversion luminescence processes of Er3+ ions in NaNbO3:Er3+/Yb3+ nano-crystals, the decay curves of 4S3/2 → 4I15/2 and 4F9/2 → 4I15/2 transitions of the Er3+ ions are measured under the excitation 976 nm. As shown in Fig. 6, the decay curves of Er3+ (λexc: 976 nm) can be well fitted into a single exponential function as

\[ I = I_0 + A \exp \left( -t/\tau \right) \]

where \( I \) and \( I_0 \) are the luminescence intensity at time \( t \) and 0, respectively, \( A \) is constant, \( t \) is the time, and \( \tau \) represents the lifetime for the exponent. The lifetimes of 4S3/2 and 4F9/2 states of Er3+ ions for NaNbO3:Er3+/Yb3+ nano-crystals are 40 and 61 μs, respectively.

Figure 5. Pump power dependence of up-conversion emissions for the \(^4\!S_{3/2} \rightarrow \!^4\!I_{15/2}\) and \(^4\!F_{9/2} \rightarrow \!^4\!I_{15/2}\) transitions of the Er3+ ions (excited by 976 nm laser diode) in Er3+/Yb3+ co-doped NaNbO3 nano-crystals.

Figure 6. The up-conversion luminescence dynamic curves for the \(^4\!S_{3/2} \rightarrow \!^4\!I_{15/2}\) and \(^4\!F_{9/2} \rightarrow \!^4\!I_{15/2}\) transitions of the Er3+ ions (excited by 976 nm laser diode) in Er3+/Yb3+ co-doped NaNbO3 nano-crystals at room temperature.
two Kramers doublets, which are characterized by the projections \( \pm 1/2 \) and \( \pm 3/2 \) of the total momentum \( J = 3/2 \), and the \( 4F_{9/2} \) multiplet splits into five Kramers doublets, which are characterized by the projections \( \pm 1/2 \), \( \pm 3/2 \), \( \pm 5/2 \), \( \pm 7/2 \) and \( \pm 9/2 \) of the total momentum \( J = 9/2 \) (in which, some Stark sub-levels are crystal field degeneracy). When an external magnetic field is applied, the non-radiation transition from \( 4I_{11/2} \) to \( 4I_{13/2} \) of \( \text{Er}^{3+} \) ions is enhanced and the “mixing” effect is occurred by magnetic field, which could affect the transition energies and determine the intensity and width of spectral lines.

Conclusions
In conclusion, magnetic-optical bi-functional \( \text{NaNbO}_3: \text{Er}^{3+}, \text{Yb}^{3+} \) nano-crystals have been successfully synthesized by the Pechini sol-gel method, consisting of a luminescent center \( \text{Er}^{3+} \) ion. Up-conversion luminescence properties of \( \text{NaNbO}_3: \text{Er}^{3+}, \text{Yb}^{3+} \) nano-crystals is efficiently tuned by applying a magnetic field at low temperature. The broadening of up-conversion spectra were observed with magnetic field, which could be ascribed to the ‘mixing’ effect induced by magnetic field and the difference of \( g \) factor of sub-bands. The enhanced up-conversion luminescence with the rise of magnetic field intensity was observed, which could be mainly owing to the non-radiation transition from \( 4I_{11/2} \) to \( 4I_{13/2} \) of \( \text{Er}^{3+} \) ions is enhanced and the “mixing” effect in crystal field is occurred by an external magnetic field. This bi-functional material with controllable optical-magnetic interactions has potential applications in high accuracy communication, magnetic resonance imaging (MRI), drug targeting or carrier, aircraft guidance and optical detection of magnetic field.

Methods
Materials synthesis. Nano-crystals of sodium niobate (\( \text{NaNbO}_3 \)) co-doped with lanthanide (\( \text{Ln} = \text{Er}, \text{Yb} \)) (the dopants 2% \( \text{Er}^{3+} \), 20% \( \text{Yb}^{3+} \) with respect to \( \text{Na}^{+} \) ions in the structure) were successfully prepared using the Pechini sol-gel method. The starting materials were sodium carbonate (\( \text{Na}_2\text{CO}_3 \), A.R.), lanthanide nitrate (\( \text{Ln(NO}_3)_3 \cdot x\text{H}_2\text{O} \), 99.99%), ammonium niobium oxalate (\( (\text{NH}_4)_3[\text{NbO(C}_2\text{O}_4)_3] \), A.R.), citric acid (CA, A.R.) and ethylene glycol (EG, A.R.). 0.1 mol% of CA was added to 10 mL of water under stirring and under heating at 90°C in a crucible. After dissolution of CA, a proper amount of (\( (\text{NH}_4)_3[\text{NbO(C}_2\text{O}_4)_3] \)) was dissolved in water and then stoichiometric quantities of \( \text{Na}_2\text{CO}_3 \) and \( \text{Ln(NO}_3)_3 \cdot x\text{H}_2\text{O} \) were added to the transparent solution and then EG was also added in the solution. The final mixtures were stirred thoroughly and heated at 120°C for 6 h until transparent brown or yellow gels were obtained. Finally, to obtain the \( \text{NaNbO}_3: \text{Er}^{3+}, \text{Yb}^{3+} \) nano-crystals, the gel precursors were calcined at 700°C for 5 h in a muffle furnace in atmosphere.

Characterization methods. The crystal structure and phase purity of as-prepared samples were investigated by X-ray diffraction (XRD) (Bruker, D8 ADVANCE analysis with Cu Kα radiation operated at 40 kV and 40 mA, \( \lambda = 0.15418 \text{nm, scanning step 0.02°, scanning speed 0.1 s per step} \)). The morphology and size distribution of the samples were observed by high-resolution transmission electron microscopy (HRTEM, JEOL 2100 F). The up-conversion emissions at room temperature were measured with a high-resolution spectrofluorometer (FLS920, Edinburgh Instruments, Livingston, UK) equipped with a 976 nm laser diode as excitation source. 800 nm long-pass (LP) filter (Andover, Salem, NH) was used to cut off the short wavelength lights of the

Figure 7. Energy levels of \( \text{Er}^{3+} \) ions (a) and the crystal field splitting of energy levels of \( 4S_{3/2} \) (b) and \( 4F_{9/2} \) (c) of the \( \text{Er}^{3+} \) ion in \( \text{NaNbO}_3 \) nano-crystals.
simulated laser source. The up-conversion luminescence lifetimes were collected with a spectrometer (Omni-λ 3007, Zolix, Beijing, China) with a digital oscilloscope (TDS 2012B, Tektronix, Beaverton, OR) and a pulse laser diode as excitation source (LE-LS-976-5000TFCA, LEO Photoelectric, Shenzhen, China).

The MUL spectra under pulsed magnetic field were measured using a similar fiber optical system reported previously. Schematic for the MUL experiments in pulsed magnetic fields is shown in Fig. 8. The pulsed magnetic field up to 40 T was generated by a liquid nitrogen-cooled resistive coil magnet with a pulsed duration of 290 ms and the falling side of 270 ms, which was applied to the sample. The sample was placed into the center of the magnetic field through an optical probe. A laser beam irradiated by 976 nm radiation from a diode laser was launched into the probe through a multimode fiber and directly illuminated on the sample. The MUL spectrum was collected by the same fiber. The MUL signal was recorded by an EM-CCD (Andor, DU970P) through a monochromator (Andor, SR500). All measurements were investigated at room temperature, except that the measurement of MUL spectrum in magnetic field was cooled to 77 K.

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Acknowledgements
This work has been supported by the National Natural Science Foundation of China (Grant NO. 61435010, 51132004, 51072054, 61475047), Natural Science Foundation of Guangdong Province (Grant NO. S2011030001349), the Guangdong Natural Science Foundation for Distinguished Young Scholars (2014A030306045), the Pearl River S&T Nova Program of Guangzhou (2014J2200083), the Science and Technology Innovation Commission of Shenzhen (KQTD2015032416270385, JCYJ20150625103619275, JCYJ20160308092249215), Natural Science Foundation of SZU (Grant NO. 827/000010), and the Postdoctoral Science Foundation of China (No. 2016MS92526). The authors are grateful to Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology for the magneto-upconversion luminescence (MUL) measurement.

Author Contributions
G.D. proposed and guided the overall project. Q.X. and Y.Z. performed all the experiments and analyzed the results. All the authors discussed the results. Q.X. and G.D. wrote the manuscript, with discussion from H.Z., J.H. and J.Q.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Xiao, Q. et al. Dynamically Tuning the Up-conversion Luminescence of Er$^{3+}$/Yb$^{3+}$ Co-doped Sodium Niobate Nano-crystals through Magnetic Field. Sci. Rep. 6, 31327; doi: 10.1038/srep31327 (2016).

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