Polarization-modified Upconversion Luminescence in Er-Doped Single-Crystal Perovskite $PbTiO_3$ Nanofibers

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Supporting information

EXPERIMENTAL SECTION

The chemistry grade tetrabutyl titanate ($(C_4H_9O)_4Ti$), lead nitrate ($Pb(NO_3)_2$), and erbium nitrate ($Er(NO_3)_3$) were used as the raw materials. The analytical grade potassium hydroxide (KOH) was used as mineralizer. The concentration of Er doping was designed as the molar ratio of Er/(Er +Ti)= 4 %. The 4% Er-doped perovskite $PbTiO_3$ (PTO) particles were synthesized by a hydrothermal method as following: 1.73g tetrabutyl titanate $(C_4H_9O)_4Ti$ was dissolved with $Er(NO_3)_3$ (the concentration of Er doping was designed as the molar ratio of Er/(Er+Ti)= 0, 0.5, 1, 2, 3 and 4 %) in 10 mL of ethylene glycol monomethyl ether. In order to obtain the co-precipitation of Ti and Er hydroxide, approximately 2 mL ammonia was added to the solution. After iltering and washing the co-precipitation with deionized water for five times, the coprecipitation was dispersed into deionized water again with $Pb(NO_3)_2$ (1.82 g), KOH (1.37 g). And then, the feedstock suspended solution was adjusted to 40 mL in a 50 mL stainless-steel Teflon-lined autoclave by introducing deionized water. The

hydrothermal treatment was performed by keeping the autoclave in an oven for hydrothermal reaction at 200 ^{o}C for 12 hours and cooled to room temperature in air naturally, resulting in the formation of Er-doped perovskite $PbTiO_3$ (PTO) particles.

RESULTS AND DISCUSSION

The refined XRD patterns of 4 % Er-doped PTO nanofibers at deferent temperatures are shown in Figure S1. The XRD refinements of the structure of PTO nanofibers were carried out using Rietveld refinement by MAUD software. The refinements of all the samples were started by considering the structure of PTO nanofibers to be in the space group P4mm which published in our previous work.[1] The Pb atom was defined as the origin of the lattice by fixing the atom at the (0, 0, 0) position. And thus, all the other atoms in the lattice of PTO nanofibers were described by only three positional parameters: Ti (1/2, 1/2, 1/2 + δz_{Ti}), O1(1/2, 1/2, 1/2 + δz_{O1}) and O2(1/2, 1/2, 1/2 + δz_{O2}). All the refinements were started by setting δz_{O1} and δz_{O2} equal to zero, whereas δz_{Ti} was given a small positive value to define the positive direction alongthe c axis. Scattering factors of ionized atoms were used in all refinements. The lattice parameters and atomic positions of perovskite PTO nanofibers host have been refined in the refinement procedure. The thermal parameters were kept isotropic during the refinements. Rexp, Rb, Rw and GOF listed in Figure S1 were the measure of the goodness of fitting.

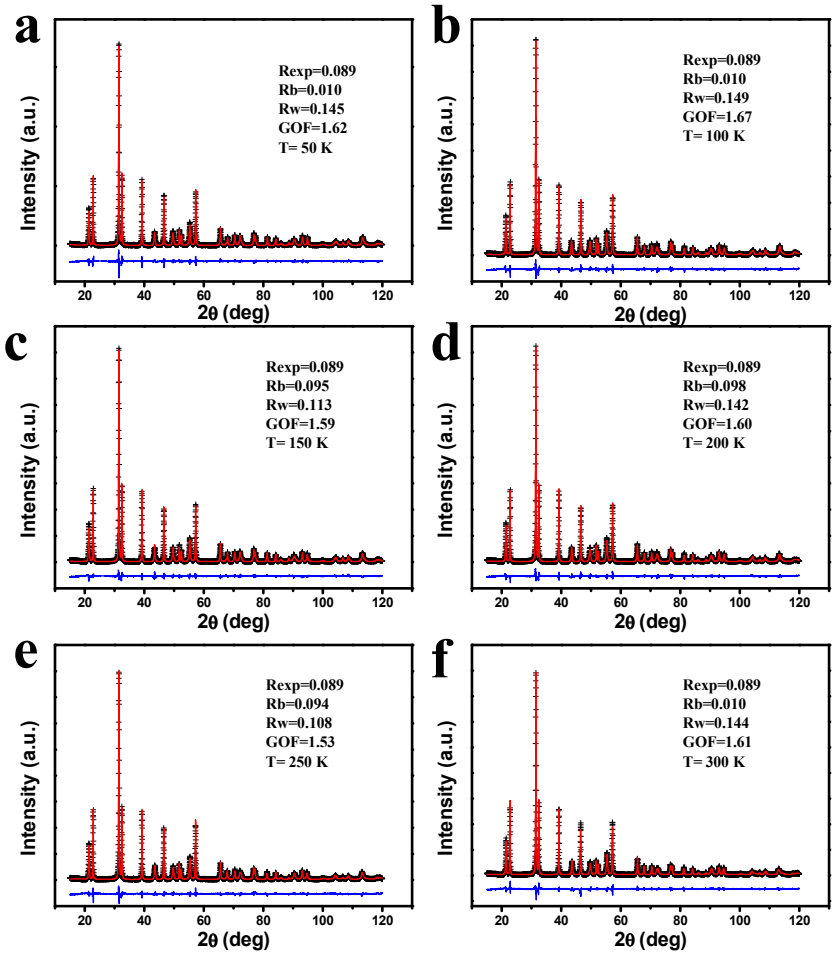

Figure S1. XRD patterns for $PbTiO_3$ at different temperatures with refined data obtained by Rietveld method. Experimental points are given as (+) and refined data are shown as solid line. Difference between refined and experimental data is shown as bottom line.

Figure S2 and Figure S3 show the evolutions of upconversion lifetime decays for the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ emissions of 4 % Er-doped perovskite PTO nanofibers at 50 K, 100 K, 150 K, 200 K, 250 K and 300 K, respectively. The measured upconversion lifetime decay curves at all temperatures could be adequately modeled to a single exponential decay (fit R^2 <1). The calculated value of lifetime of $^4S_{3/2}$ and $^4F_{9/2}$ level are derived to be 128.04±0.47 μs and 278.10±1.07 μs at 50 K, and the values are kept basically as the temperature increased.

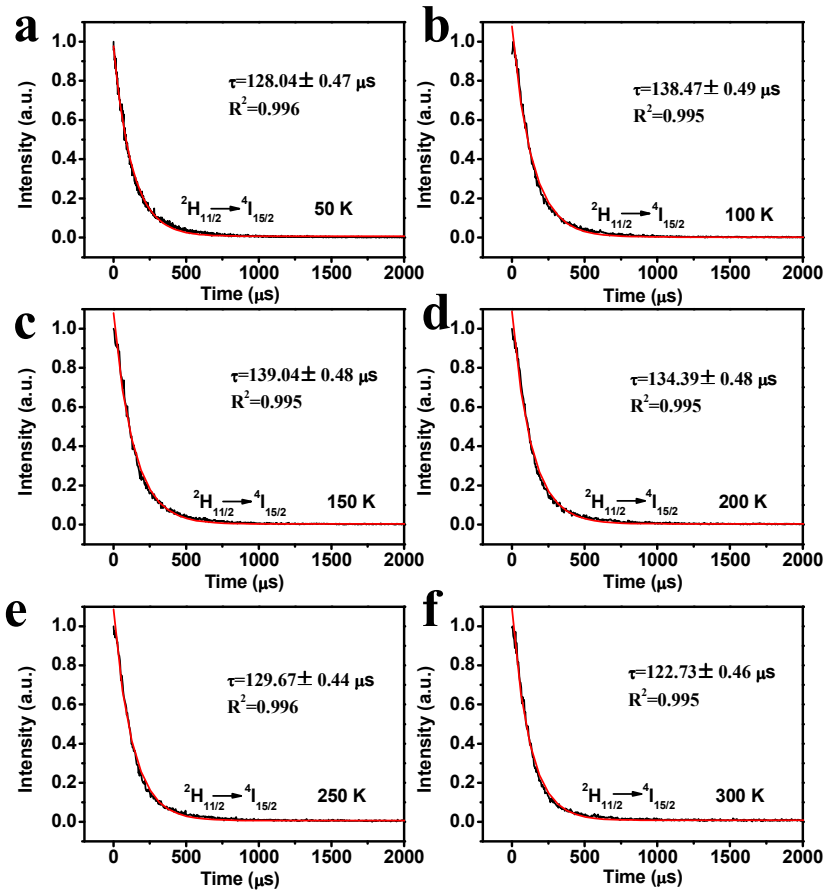

Figure S2. Evolution of upconversion lifetime decays for the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ emissions of 4 % Er-doped perovskite PTO nanofibers at (a) 50 K, (b) 100 K, (c) 150 K, (d) 200 K, (e) 250 K and (f) 300 K, respectively. The upconversion lifetime decays could be adequately modeled to a single exponential decay (at all temperatures) as indicated by the parameters shown in the illustrations.

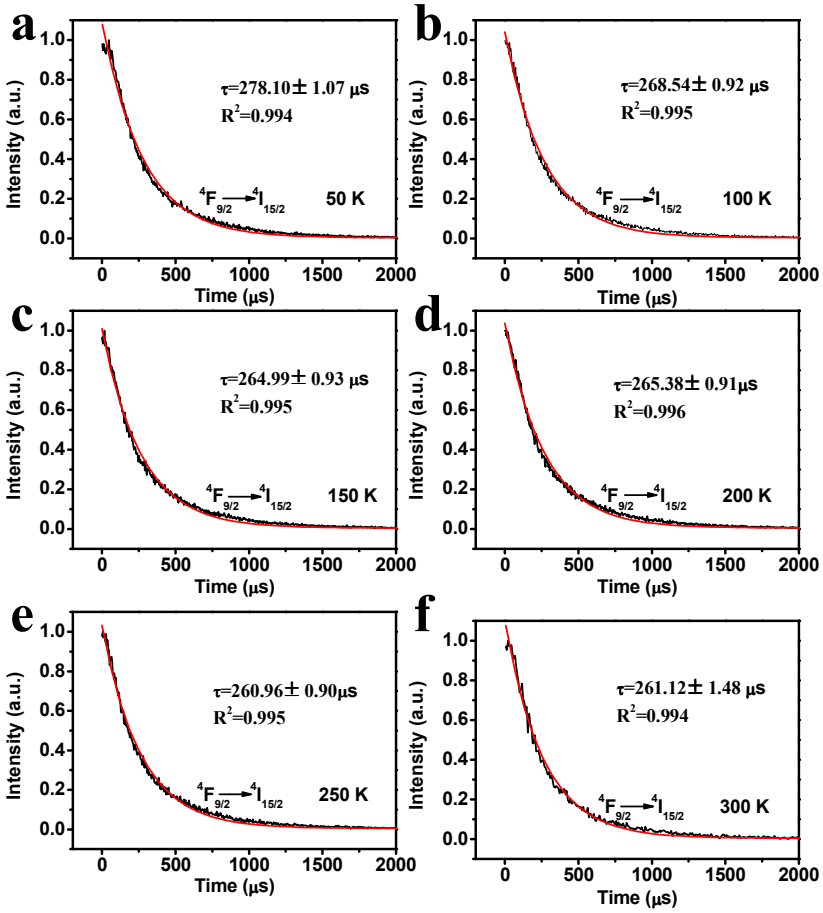

Figure S3. Evolution of upconversion lifetime decays for the $^4F_{9/2}\rightarrow{}^4I_{15/2}$ emissions of 4 % Er-doped perovskite PTO nanofibers at (a) 50 K, (b) 100 K, (c) 150 K, (d) 200 K, (e) 250 K and (f) 300 K, respectively. The upconversion lifetime decays could be adequately modeled to a single exponential decay (at all temperatures) as indicated by the parameters shown in the illustrations.

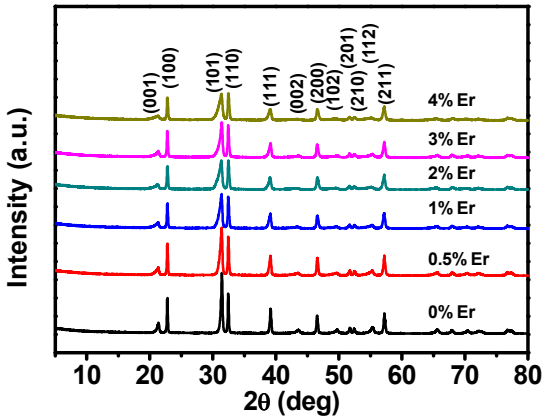

Figure S4. XRD patterns of 0 mol%, 0.5 mol%, 1 mol %, 2 mol %, 3 mol%, 4 mol% Er-doped perovskite PTO particles.

The X-ray diffraction patterns of Er-doped perovskite PTO particles at are shown in Figure S4. By indexing, all of the diffraction patterns of the sample measured at different temperatures are consistent with the tetragonal perovskite-structured $PbTiO_3$ without any impurity phases (Joint Committee on Powder Diffraction Standards [JCPDS] Card No. 06-0452).[2]

As the designed Er^{3+} doping concentration increases from 0 mol% to 4 mol%, the XRD peaks of Er-doped perovskite PTO particles gradually shift towards lower angle, implying that doping-introduced lattice expansion occur Er-doped perovskite PTO particles. According to the sequence of Shannon effective ionic radii (i.e., r(Ti^{4+} 60.5 pm VI)<r(Er^{3+} 89 pm VI, 100.4 pm VIII)<r(Pb^{2+} 129 pm VIII), the Er^{3+} ions occupied Ti^{4+} sites in perovskite PTO particles.[3]

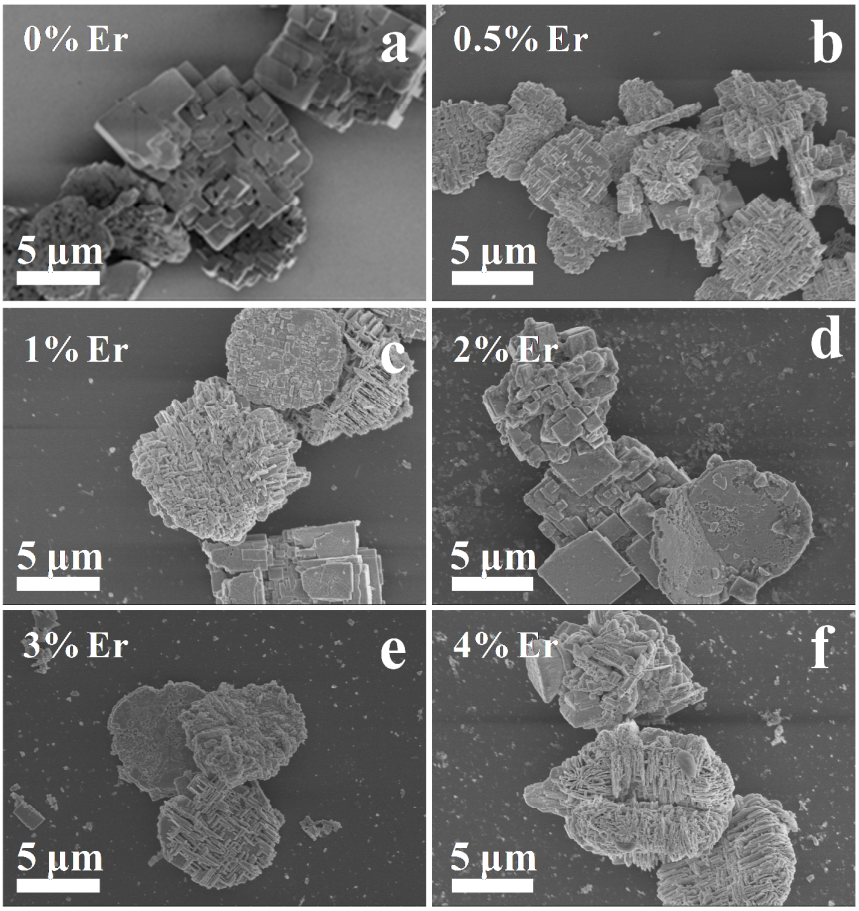

Figure S5. SEM images of (a) 0 mol%, (b) 0.5 mol%, (c) 1 mol %, (d) 2 mol %, (e) 3 mol%, (f) 4 mol% Er-doped perovskite PTO particles, respectively.

Figure S5 shows the scanning electron microscope (SEM) images of Er-doped perovskite PTO particles, which displays that the average size of these particles are around 5 µm.

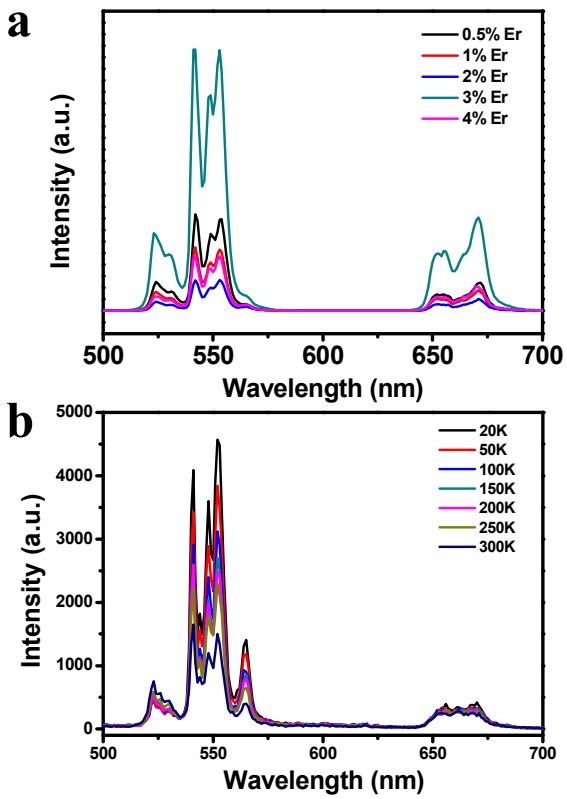

Figure S6. Upconversion Photoluminescence spectra of (a) Er-doped perovskite PTO particles with different doping concentrations measured at room temperature, (b) Temperature dependence of the UC PL emission of 4 mol% Er-doped perovskite PTO particles under excitation at 980 nm.

The Upconversion (UC) photoluminescence (PL) emission spectra of Er-doped perovskite PTO particles with different Er doping concentrations measured at room temperature under infrared excitation (980 nm) are shown in Figure S6(a). The strong UC green emission around 524 nm and 555 nm as well as the weak red UC emission around 670 nm correspond to the characteristic $^{2}H_{11/2}\rightarrow{}^{4}I_{15/2}$, $^{4}S_{3/2}\rightarrow{}^{4}I_{15/2}$ and $^{4}F_{9/2}\rightarrow{}^{4}I_{15/2}$ emissions of Er^{3+} ions.[5] The UC PL intensity increases with increased Er^{3+} doping concentration and no apparent shifts of the emission peaks are observed. The enhancement might attribute to the increased the energy transfer (ET) process between Er^{3+} ions with the increased Er^{3+} doping concentration.[5] The UC emission spectra of 4 % Er-doped perovskite PTO particles under excitation at 980 nm at different temperatures are shown in Figure S6(b). Obviously, the UC PL emission intensity of Er-doped perovskite PTO particles can be obviously enhanced when

decreasing the measuring temperature, corresponding to that of Er-doped $BaTiO_3$ powders and different to that of Er-doped PTO nanofibers (Figure 4).

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