Photoluminescence

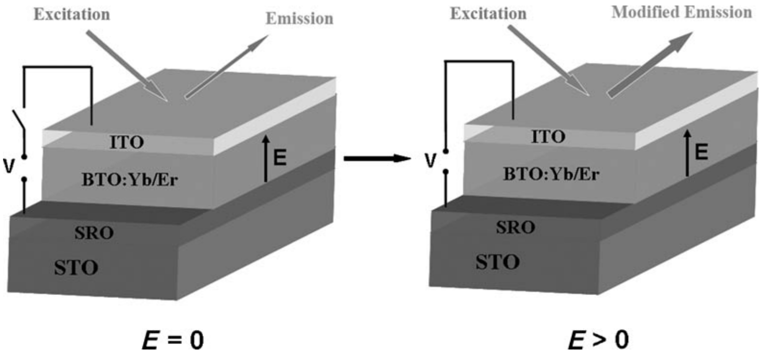
DOI: 10.1002/anie.201101374

Electric-Induced Enhancement and Modulation of Upconversion Photoluminescence in Epitaxial $BaTiO_3$:Yb/Er Thin Films**

Jianhua Hao,* Yang Zhang, and Xianhua Wei

Spectroscopic tuning and enhancement of upconversion photoluminescence (PL) are highly desirable for understanding the physical processes of energy transition and for widespread applications, such as laser mediums, optical waveguides, display lighting, and biomedicine.[1–5] To date, modification of the upconversion PL in phosphors excited by a given excitation source can normally be achieved through a conventional chemical approach, that is, changing the composition of host materials and/or doping ions,[6–8] thus giving only a limited understanding of the detailed process of luminescence and applications. For instance, the variation of the PL in different hosts can be ascribed to the different crystal field around dopant ions of various symmetries. Low symmetry hosts typically exert a crystal field containing more uneven components around the dopant ions compared to high symmetry counterparts.[9] However, the tuning of PL by chemical way is essentially an irreversible and ex-situ process. Therefore, it is unlikely to know from the kinetic process how the luminescence changes with structural symmetry through the conventional approach. Moreover, it is almost impossible to isolate the pure crystal-field effect from other extrinsic effects present in different samples such as chemical inhomogeneities and defects. Hence, it is much needed to find a pathway in varying the host's symmetry in the same material, leading to the modification of PL. In particular, an enhancement of upconversion still presents a significant challenge, although a breakthrough of plasmon-enhanced upconversion through very precise manipulation was recently presented.[10,11] To date, there are no reports of an established approach to modulate upconversion emission in an in-situ and real-time way.

The unique crystal structure of ferroelectric materials provides us an opportunity to couple variables including electric field and temperature to crystal symmetry in a single compound. Approaches through the use of ferroelectric characteristics have recently proven successful in controlling the ferromagnetism, spin polarization, and photovoltaic effects.[12–16] Comparatively, ferroelectric control of luminescence has not been exploited. Therefore, it is of great interest to take advantage of the properties of ferroelectric host in combination with the luminescent doping ions acting as sensitive probes for the structure and symmetry. PL in the specific materials system should be modulated in reversible, real-time and dynamical way under ferroelectric control that can be realized by electrically changing the structural symmetry. Herein, $BaTiO_3$ (BTO) is selected as ferroelectric host because it has been regarded as a model system for investigating crystal structure transformation under mechanical stress, electric field, and temperature.[17] Lanthanide Er^{3+} ion is composed of an incompletely filled 4f inner shell and two closed outer shells. Actually, Er^{3+} ion in doped hosts has been a spectroscopic probe for many applications,[18–20] including ferroelectric domain imaging.[21] Very recently, we have observed the effects of Er doping and measuring temperature on the upconversion emission in BTO:Er powders.[22] Therefore, it is interesting to observe the influence of electric field on the upconversion spectra of Er doping ions. Herein, we present a new approach to enhance and modulate upconversion emission through applying a relatively low bias voltage to the lanthanide-doped BTO thin films.



Scheme 1. The setup used to measure the upconversion emission of a BTO:Yb/Er thin film when an external electric field is switched "off" (left) and "on" (right). A 980 nm diode laser is used as an excitation source. See text for details.

The method used for the modification of upconversion from BTO:Yb/Er thin film under control of electric field is shown in Scheme 1. The light excitation and emission as well as applied electric field are denoted. For the typical parallel-plate capacitor structure, BTO:Yb/Er film was deposited on conductive $SrRuO_3$ (SRO)-coated $SrTiO_3$ (STO) substrates. A transparent electrode of 200 nm-thick indium tin oxide (ITO) was deposited on top at about 250 °C, the excitation and emission light can pass through the ITO layer. The

---

[*] Prof. J. H. Hao, Y. Zhang, Dr. X. H. Wei
Department of Applied Physics and Materials Research Centre
The Hong Kong Polytechnic University
Hong Kong (China)
Fax: (+852) 2333-7629
E-mail: apjhhao@inet.polyu.edu.hk

[**] This work was supported in part by RGC GRF grant (PolyU500910) and Hong Kong Polytechnic University Grant (J-BB9R). Helpful discussion with Prof. Peter Tanner in CityU is gratefully acknowledged.

utilization of the BTO:Yb/Er thin film described herein facilitates the application of higher electric field on the sample under a low bias voltage than required for the bulk material.

The X-ray diffraction (XRD) patterns of the BTO:Yb/Er thin film on the SRO-coated STO (001) substrate are shown in Figure 1. In the θ–2θ scan, only the (00l) peaks of BTO are present along with those of the STO substrate and SRO buffer layers (Figure 1 a). This result shows that the BTO:Yb/Er film grows with its c-axis normal to the substrate surface. The full widths at half-maximum (FWHM) of the BTO (001) and (002) peaks are approximately 0.2° and 0.3°, respectively. These small FWHMs indicate good crystallinity of the BTO:Yb/Er thin film along the out-of-plane orientation. The ϕ scans for the BTO:Yb/Er film and the STO substrate/SRO buffer layer are shown in Figure 1 b. The (101) diffraction peaks for the BTO:Yb/Er film and the substrate/buffer layer are used. Only four peaks, 90° apart, are observed for the BTO:Yb/Er film, which are at the same angles with those of substrate/buffer layer. This indicates that the BTO:Yb/Er film is in-plane aligned with the substrate/buffer layer. Thus, XRD measurements reveal that the BTO:Yb/Er film was epitaxially grown on the (001) surface of SRO with an in-plane relationship of [100]BTO//[100]SRO//[100]STO.

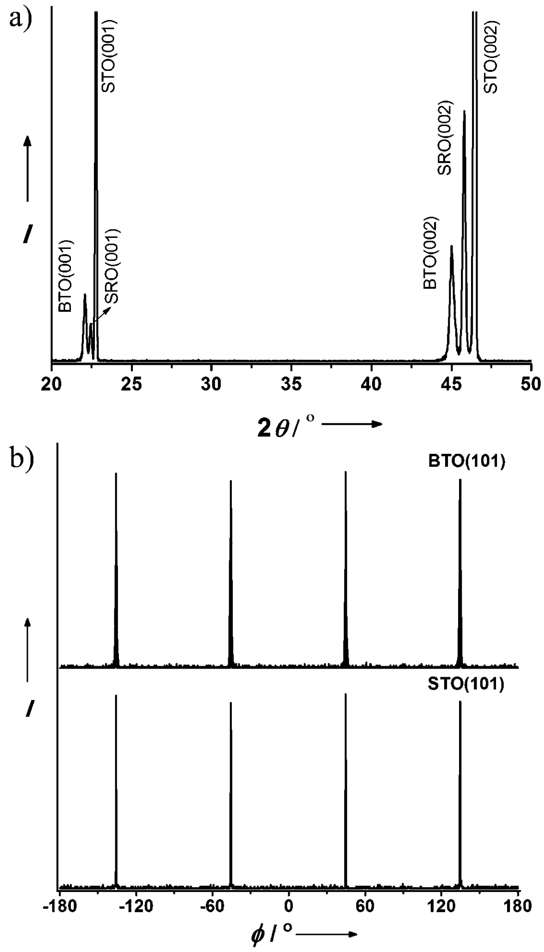


Figure 1. XRD patterns of a BTO:Yb/Er film grown on a conductive SRO buffered STO substrate: a) θ–2θ scan and b) ϕ scans using the (101) peaks for the BTO:Yb/Er film and the STO substrate/SRO buffer layer.

The two-photon upconversion mechanism is described in Figure 2 a. Owing to the weak ground-state absorption of Er^{3+} ions pumped by 980 nm, Yb^{3+} ions as sensitizers are often preferred for increasing the pumping efficiency because of the efficient energy transfer from Yb^{3+} to Er^{3+} ions. Figure 2 b

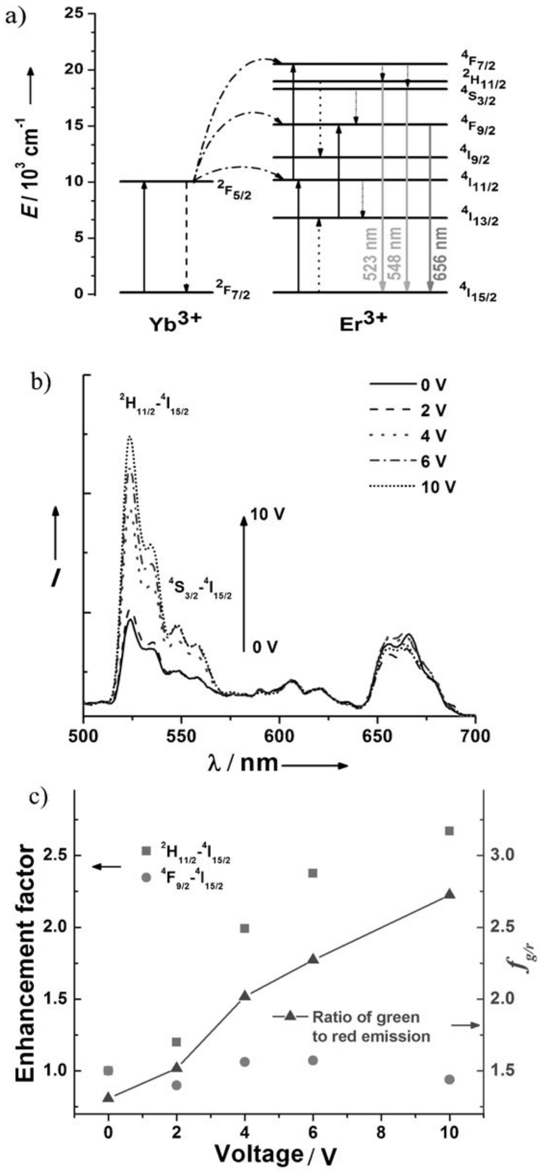


Figure 2. a) Energy scheme with the relevant upconversion process in Yb^{3+}/Er^{3+} co-doped BTO. The dashed-dotted, dashed, and dotted lines represent energy transfer, multiphonon relaxation, and cross-relaxation, respectively. b) The upconversion emission spectra of the BTO:Yb/Er film under dc bias voltage ranging from 0 to 10 V. c) The enhancement factors (left axis) for green and red emission bands as a function of the applied dc voltage. The PL intensity ratio of green to red emission ($f_{g/r}$) (right axis) as a function of the applied bias voltages is also shown. The thin film sample is excited by a 980 nm diode laser.

shows the upconversion spectra of BTO:Yb/Er under a bias voltage up to 10 V limited by the breakdown voltage. Great attention was paid to ensure that the BTO:Yb/Er film was kept to be an insulator during measurements by monitoring leakage current. Green emission bands centered at 523/548 nm correspond to $^2H_{11/2}/^4S_{3/2}\rightarrow^4I_{15/2}$ transitions of Er^{3+} ion. Generally, the PL intensity of thin films which can be measured is usually much lower than that of the corresponding bulks or powders. Therefore, the relatively high power density of incident light was used in our measurements in order to enhance the ratio of signal to noise. Since the upper $^2H_{11/2}$ level is thermally populated at the expense of $^4S_{3/2}$ level owing to Boltzmann's distribution,[23] the emission from $^2H_{11/2}$ level is more intense than that from $^4S_{3/2}$ state (Figure 2b), owing to the thermal effect caused by the laser. Obviously, the upconversion can be strongly enhanced when increasing the dc bias voltage. An enhancement factor of main green band can reach up to 2.7. On the other hand, the red emission centered at 656 nm corresponding to $^4F_{9/2}\rightarrow^4I_{15/2}$ transition almost remains unchanged with an increase of voltage. It indicates that the emission enhancement is highly wavelength-dependent. As the enhancement factors located in the green band are much higher than those in the red band (Figure 2c), the PL intensity ratio of green to red emission ($f_{g/r}$) is significantly enhanced with increasing dc bias voltage up to 10 V, which is equivalent to an electric field of 125 kV cm^{-1}. The result rules out a potential piezoelectric effect that causes a misalignment of the sample.

Figure 2 demonstrates a novel approach to modify PL. A large number of previous studies have indicated that the PL of dopant ions could be influenced by the crystal symmetry of the host materials.[24–26] However, approaches to vary the symmetry of the host materials have been limited to the use of chemical routes to date.[1,6,7] In Figure 2b, the external electric field is applied to a ferroelectric BTO host to modify PL instead of conventional chemical methods. The observed results are largely ascribed to the unique crystal structure of ferroelectric host, which can provide an opportunity to couple variables including electric field to crystal symmetry. In a sense, the consequence for the variable-symmetry in a single ferroelectric host controlled by an external electric field in this work is in analogy to that for the variation of symmetry in different hosts made by conventional chemical route. To provide an in-depth explanation of our measured results, schematic diagrams of the lattice of Er doped BTO are illustrated in Figure 3. The prototypical perovskite BTO used in this work is non-centrosymmetric in tetragonal phase with the point group 4*mm* (C_{4v}) at room temperature, and Ti is shifted related to the negatively charged oxygen atoms, producing a polarization. Our previous study showed that the doping Er^{3+} ions can substitute Ti^{4+} ions in BTO,[22] hence Er^{3+} ions in the lattice are non-centrosymmetric even when no electric field is applied (Figure 3a). Therefore, the perturbation caused by the odd-order term of crystal-field forces the parity forbidden 4f–4f electric dipole (ED) transitions allowed, leading to the observed PL emission with zero bias as shown in Figure 2b. When applying an electric field along the direction of spontaneous polarization, the *c*-axis of the lattice elongates (Figure 3b) and promotes the structure asymmetry of the BTO host,[27] approaching lower symmetry around Er^{3+} ions. In principle, the lower symmetry at the site of lanthanide ions means that the more uneven crystal-field components can mix opposite-parity into 4f configurational levels and subsequently increase the ED transition probabilities of the dopant ions. Herein, the increase in the radiative transition probabilities relating to the displacement of Ti^{4+} and O^{2-} ions by the external electric field is responsible for the enhancement of PL emission with bias as shown in Figure 2b, while nonradiative transition probabilities are not dependent on the site symmetry.

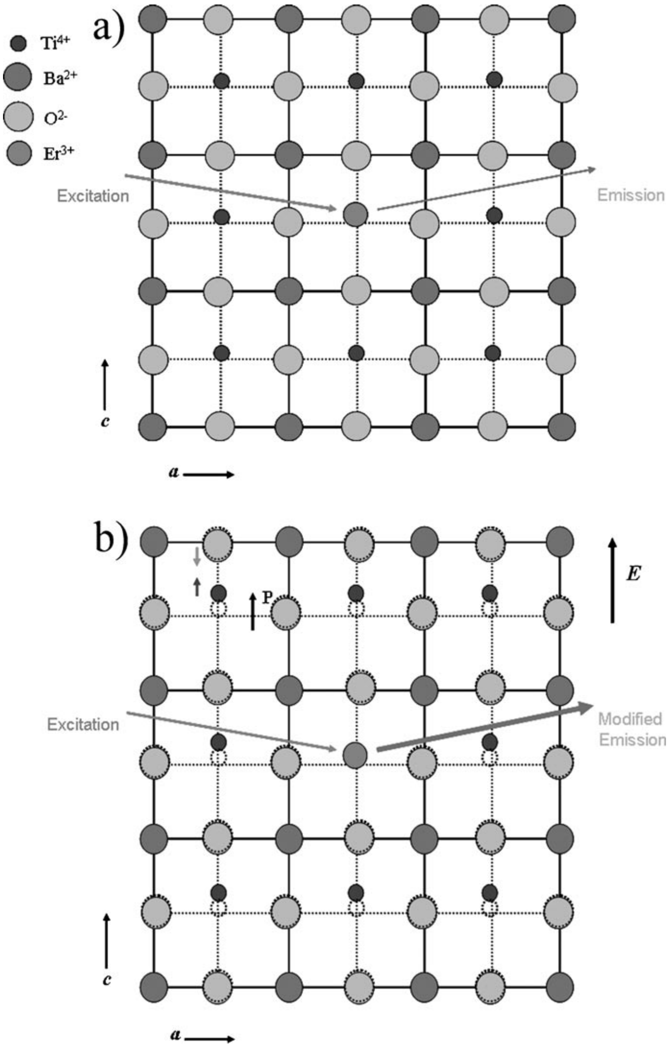


Figure 3. The tetragonal lattice of Er-doped BTO thin films a) without and b) with an external electric field *E*. When applying an electric field, the Ti^{4+} ions are displaced in the direction of the electric field, whereas the O^{2-} ions are shifted in the opposite direction to the electric-field direction (original positions indicated by dotted circles). An increase in the radiative transition probabilities relating to the displacement of Ti^{4+} and O^{2-} ions causes the modification of PL emission. P: polarization.

The difference in the enhancement factors of green and red emission bands shown in Figure 2c could be considered that the extent of the local symmetry influence on the different emission bands may vary greatly, depending on the corresponding intra-4f transitions. According to the Judd–Ofelt (J–O) theory,[28,29] the spontaneous emission probability A_{ed} for an ED transition between initial J manifold $|[S,L]J\rangle$ and a final J manifold $|[S',L']J'\rangle$ is given by Equation (1)

$$A_{ed} = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3}\left[\frac{n(n^2+2)^2}{9}\right]S_{ed} \tag{1}$$

where e is the electron charge, λ is the mean wavelength of the transition, n is the refractive index at the wavelength of the transition and h is plank constant. The ED line strength S_{ed} is given by Equation (2)

$$S_{ed} = \sum_{t=2,4,6} \Omega_t \left|\langle 4f^n[S,L]J \| U^{(t)} \| 4f^n[S',L']J'\rangle\right|^2 \tag{2}$$

where three terms $\langle \| U^{(t)} \| \rangle$ are reduced matrix elements of the unit tensor operators, and three J–O intensity parameters Ω_t ($t=2,4,6$) contain the effect of the crystal-field terms, radial integrals of an electron, and so on. In Figure 2b, the transition producing main green emission band is one of hypersensitive transitions of Er^{3+} ions which could occur in the point group $4mm$ (C_{4v}) of BTO. Such a hypersensitive transition is dominated by Ω_2. Furthermore, the variation of Ω_2 parameter is known to be closely associated with asymmetry of the lanthanide ion sites.[30] The lower symmetry usually contributes to the larger Ω_2. Therefore, the larger enhancement factor of main green band shown in Figure 2b should be due to the increased Ω_2 parameter induced by the lower symmetry of Er^{3+} sites with the application of electric field. On the other hand, the red emission is little affected by Ω_2 and is therefore, relatively insensitive to the variation in local symmetry. Consequently, we consider that the observed modification of PL emission in BTO:Yb/Er is attributed to an increase of distortion of Er^{3+} site symmetry caused by an external electric field strongly coupling on the ferroelectric BTO thin-film host.

Note that the PL intensity at the wavelength of 523 nm from the sample under the bias voltage at 10 V is almost 2.7-times that of the unbiased sample in Figure 2c. Currently, the enhancement of inefficient upconversion still represents a great challenge. Very recently, an enhancement factor of about 3 from plasmon-enhanced upconversion was reached in $NaYF_4$ nanocrystals co-doped with Yb^{3+}/Er^{3+} or Yb^{3+}/Tm^{3+} through very precise manipulation.[10,11] The enhanced upconversion from the gold nanostructures was attributed to the local electric-field enhancement associated with plasmonic resonance. Comparatively, we can simply apply a relatively low voltage to the sample and obtain the upconversion with an enhancement factor comparable to that of plasmon-enhanced upconversion. Definitely, the value of enhancement factor reported herein is not a fundamental limit as the BTO:Yb/Er film was not completely poled in the measurement. There is much room for improvement, for example, applying larger poling fields limited by the breakdown field.

The structural symmetry in ferroelectrics can be switchable, implying that reversible and dynamic tuning of PL emission by external electric field could be realized. To validate the hypothesis, we further study on the modification of PL with the application of ac electric field. It indicates that the specific emission of BTO:Yb/Er can not only be amplified, but also be electrically modulated. Figure 4 shows the kinetics of PL emission at the wavelength of 523 nm in BTO:Yb/Er thin film under a sinusoidal ac bias. It is found that the PL intensity of the BTO:Yb/Er film can be modulated with the same frequency as that of the sinusoidal ac electric voltage. Obviously, the modulation of upconversion PL cannot be realized by conventional chemical and plasmonic methods. To the best of our knowledge, a reversible control of the upconversion by applying low voltages has not yet been reported. It could open up a new avenue for potential device applications, such as electric controlled upconvertors.

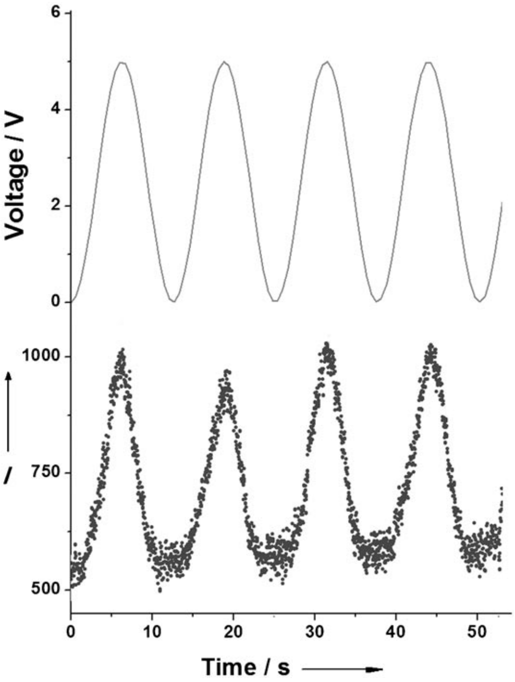


Figure 4. Sinusoidal ac electric voltage applied to the BTO:Yb/Er film (top), and PL emission at a wavelength of 523 nm as a function of time while the sinusoidal ac electric field is applied to the BTO:Yb/Er film (bottom).

In conclusion, we have demonstrated that the enhancement and modulation of upconversion PL can be realized by applying relatively low voltages to Yb/Er co-doped BTO thin films in an in-situ and real-time manner. The approach for the modification of PL is in contrast to conventional chemical routes, such as changing the composition of host materials and/or doping lanthanide ions. The observed phenomena can be ascribed to the increase in the radiative transition probabilities resulting from the lower symmetry of Er^{3+} sites which arises when an external electric field is applied. These results will aid further investigations of luminescence and the widespread applications of upconversion materials because they provide an additional degree of freedom in the design of luminescent materials and devices.

Experimental Section

The Yb/Er co-doped BTO target was prepared by conventional solid-state reaction methods using analytical grade $BaCO_3$, TiO_2, Yb_2O_3, and Er_2O_3 powders as the starting materials. These powders were weighted according to the molecular formula $BaTi_{0.97}Yb_{0.025}Er_{0.005}O_3$. When Yb^{3+} and Er^{3+} were substituted at the Ti^{4+} site, the negative effective charge could be compensated by oxygen vacancies. The starting powders with designed stoichiometric quantities were ball milled for 24 h, then dried and calcinated at 1100 °C for 8 h. The resulting powders were pressed into disk pellets and sintered at 1350 °C for 4 h. The as-prepared target showed a prominent BTO crystalline phase in the XRD pattern. The BTO:Yb/Er film was grown by pulsed laser deposition (PLD). A 150 nm thick lattice-matched $SrRuO_3$ (SRO) was used as a bottom electrode between BTO:Yb/Er film and $SrTiO_3$ (STO) substrate. The BTO:Yb/Er-SRO bilayers were deposited in situ with the substrate temperature of 700 °C, oxygen pressure of 20 Pa, and laser pulse energy density of 5 $J\,cm^{-2}$. The thickness of the BTO:Yb/Er film was 800 nm. After the deposition, the bilayer films were in-situ post-annealed at the growth temperature in 0.5 atm oxygen pressure for 15 min before they were allowed to cool naturally to room temperature to minimize oxygen deficiency. A 200 nm thick ITO layer as a top transparent electrode was deposited on the BTO:Yb/Er film at 250 °C under 2.5 Pa oxygen ambient by PLD.

Characterization: The crystal structure of the multi-layer structure was examined by a Bruker D8 Discover X-ray diffractometer with $Cu_{K\alpha}$ radiation. The PL spectra were recorded using an Edinburgh FLSP920 spectrophotometer under the excitation of a 980 nm diode laser. All measurements were carried out at room temperature.

Received: February 24, 2011
Revised: April 21, 2011

Keywords: doping · lanthanides · photoluminescence · thin films · upconversion

---

[1] F. Wang, Y. Han, C. S. Lim, Y. H. Lu, J. Wang, J. Xu, H. Y. Chen, C. Zhang, M. H. Hong, X. G. Liu, *Nature* **2010**, *463*, 1061.
[2] J. C. Boyer, L. A. Cuccia, J. A. Capobianco, *Nano. Lett.* **2007**, *7*, 847.
[3] J. Yang, C. M. Zhang, C. Peng, C. X. Li, L. L. Wang, R. T. Chai, J. Lin, *Chem. Eur. J.* **2009**, *15*, 4649.
[4] H. T. Wong, H. L. W. Chan, J. H. Hao, *Opt. Express* **2010**, *18*, 6123.
[5] Z. L. Wang, J. H. Hao, H. L. W. Chan, *J. Mater. Chem.* **2010**, *20*, 3178.
[6] F. Wang, X. G. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 5642.
[7] S. Heer, O. Lehmann, M. Haase, H. U. Güdel, *Angew. Chem.* **2003**, *115*, 3288; *Angew. Chem. Int. Ed.* **2003**, *42*, 3179.
[8] J. H. Hao, J. Gao, M. Cocivera, *Appl. Phys. Lett.* **2003**, *82*, 2778.
[9] F. Wang, X. G. Liu, *Chem. Soc. Rev.* **2009**, *38*, 976.
[10] S. Schietinger, T. Aichele, H. Q. Wang, T. Nann, Q. Benson, *Nano. Lett.* **2010**, *10*, 134.
[11] H. Zhang, Y. Li, I. A. Ivanov, Y. Qu, Y. Huang, X. Duan, *Angew. Chem.* **2010**, *122*, 2927; *Angew. Chem. Int. Ed.* **2010**, *49*, 2865.
[12] I. Stolichnov, S. W. E. Riester, H. J. Trodahl, N. Setter, A. W. Rushforth, K. W. Edmonds, P. R. Campion, C. T. Foxon, B. L. Gallagher, T. Jungwirth, *Nat. Mater.* **2008**, *7*, 464.
[13] T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin, S. W. Cheong, *Science* **2009**, *324*, 63.
[14] V. Garcia, M. Bibes, L. Bocher, S. Valencia, F. Kronast, A. Crassous, X. Moya, S. Enouzvedrenne, A. Gloter, D. Imhoff, C. Deranlot, N. D. Mathur, S. Fusil, K. Bouzehouane, A. Barthelemy, *Science* **2010**, *327*, 1106.
[15] S. Y. Yang, J. Seidel, S. J. Byrner, P. Shafer, C. H. Yang, M. D. Rossell, P. Yu, Y. H. Chu, J. F. Scott, J. W. Ager, L. W. Martin, R. Ramesh, *Nat. Nanotechnol.* **2010**, *5*, 143.
[16] S. M. Wu, S. A. Cybart, P. Yu, M. D. Rossell, J. X. Zhang, R. Ramesh, R. C. Dynes, *Nat. Mater.* **2010**, *9*, 756.
[17] C. H. Ahn, K. M. Rabe, J. M. Triscone, *Science* **2004**, *303*, 488.
[18] A. Polman, *Physica B* **2001**, *300*, 78.
[19] C. H. Wen, Y. S. Chu, C. K. Wen, *Integr. Ferroelectr.* **2005**, *69*, 267.
[20] J. Schlaghecken, J. Gottman, E. W. Kreutz, R. Poprawe, *Appl. Phys. A* **2004**, *79*, 1255.
[21] V. Dierolf, C. Sandmann, S. Kim, V. Gopalan, K. Polgar, *J. Appl. Phys.* **2003**, *93*, 2295.
[22] Y. Zhang, J. H. Hao, C. L. Mak, X. H. Wei, *Opt. Express* **2011**, *19*, 1824.
[23] F. Vetrone, R. Naccache, A. Zamarrón, A. Fuente, F. S. Rodriguez, L. M. Maestro, E. M. Rodriguez, D. Jaque, J. G Solé, J. A. Capobianco, *ACS Nano* **2010**, *4*, 3254.
[24] T. C. Huang, W. F. Hsieh, *J. Fluoresc.* **2009**, *19*, 511.
[25] S. Y. Kuo, W. F. Hsieh, *J. Vac. Sci. Technol. A* **2005**, *23*, 768.
[26] S. Heer, K. Kömpe, H. U. Güdel, M. Haase, *Adv. Mater.* **2004**, *16*, 2102.
[27] R. Tazaki, D. Fu, M. Itoh, M. Daimon, S. Koshihara, *J. Phys. Condens. Matter* **2009**, *21*, 215903.
[28] B. R. Judd, *Phys. Rev.* **1962**, *127*, 750.
[29] M. J. Weber, *Phys. Rev.* **1967**, *157*, 262.
[30] S. Tanabe, T. Ohyagi, N. Soga, T. Hanada, *Phys. Rev. B* **1992**, *46*, 3305.