Journal of Luminescence 131 (2011) 2574–2578

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Investigation on upconversion photoluminescence of $Bi_3TiNbO_9:Er^{3+}:Yb^{3+}$ thin films

Hengzhi Chen [a], Bin Yang [a,*], Yan Sun [a], Mingfu Zhang [b], Yu Sui [a], Zhiguo Zhang [a], Wenwu Cao [a,c]

[a] Center for Condensed Matter Science and Technology, Department of Physics, Harbin Institute of Technology, Harbin 150001, China
[b] Center for Composite Materials, Harbin Institute of Technology, Harbin 150001, China
[c] Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 18 March 2011
Received in revised form
4 June 2011
Accepted 7 June 2011
Available online 28 June 2011

Keywords:
Pulsed laser deposition
Upconversion photoluminescence
Rare-earth ions

ABSTRACT

$Bi_3TiNbO_9:Er^{3+}:Yb^{3+}$ (BTNEY) thin films were fabricated on fused silica by pulsed laser deposition. It was demonstrated that different laser fluence and substrate temperature during growth of BTNEY upconversion photoluminescence (UC-PL) samples control the film's grain size and hence influences the UC-PL properties. The average grain size of BTNEY thin films deposited on fused silica substrates with laser fluence 4, 5, 6, and 7 J/cm^2 are 30.8, 35.9, 40.6, and 43.4 nm, respectively. The 525 nm emission intensities increase with the deposition laser fluence and the emission intensities of BTNEY thin film deposited under 700 and 600 °C are almost 24 and 4 times, respectively, as strong as those of samples under 500 °C. The grain size of BTNEY thin film increases with the increasing temperature. UC-PL of BTNEY films is enhanced by increasing grain size of the films.

1. Introduction

Recently, there has been an intense interest in the investigation of Er^{3+}-doped materials, which have strong upconversion photoluminescence (UC-PL). The interest was triggered by need for all-solid short wavelength compact laser devices, which can be used for optical data storage and color display [1–3]. Active optical thin films for integrated gain devices play an important role in device miniaturization. Doping high refractive index dielectric materials with rare-earth (RE) ions is one of the most promising approaches. Bi_3TiNbO_9 thin film has good nonlinear optical properties and excellent optical waveguide properties [4, 5]. Compared with other optical materials, Bi_3TiNbO_9 has superior qualities, such as broad transparency range (0.2–2.5 μm), high refractive index (>2.2), large band gap (3.4 eV), and excellent physical and chemical stability [4]. The Stokes Raman spectra of Bi_3TiNbO_9 in Ref. [6] have proven that the highest phonon fluence of Bi_3TiNbO_9 is about 800 cm^{-1}. According to the Miyakawa–Dexter theory, multiphonon relaxation rates become steeply small in the phonon energy region below 1000 cm^{-1} [7]. Therefore, Bi_3TiNbO_9 is an excellent host material for rare earth ions doping and a potential host for integrated optics.

Er^{3+} ion is an excellent candidate for upconversion as its metastable levels $^4I_{11/2}$ can be conveniently populated by commercial low-cost high-power near-infrared laser diodes [8–10]. Due to local symmetry restriction around rare-earth ions, only a relative weak UC-PL emitted from a host doped only with Er^{3+}. Fortunately, UC-PL intensity can be enhanced when Er^{3+} and Yb^{3+} ions are co-doped into the host, because Yb^{3+} ion has a much greater absorption cross section and a broader absorption band in comparison with the Er^{3+} ion under the excitation of 976 nm near infrared (NIR) photons. There is a very high Yb→Er energy transfer efficiency [11].

The biggest hindrance of using UC-PL materials in thin film form is their low luminescent efficiency in comparison with those in bulk and powder counterparts. So there have been enormous efforts to improve luminescent efficiency in oxide-based UC-PL system. This letter reports an enhancement of green UC-PL of $Bi_3TiNbO_9:Er^{3+}:Yb^{3+}$ (BTNEY) thin films by a pulsed laser deposition (PLD) through increase in the grain size of the film.

2. Experiments

Bi_3TiNbO_9 ceramics doped with 2 mol% Er^{3+} and 5 mol% Yb^{3+} were prepared by the conventional solid-state reaction technique. Firstly, materials BiO_2, TiO_2, Nb_2O_5, Er_2O_3, and Yb_2O_3 in powder form were mixed in stoichiometric ratio by ball milling for 12 h, then the mixture was preheated at 700 °C for 3 h. Excess 10 mol% BiO_2 was added to compensate for the Bi evaporation. The calcined uniform mixture of powders was pressed into pellets. Finally, the pellets were sintered at 1000 °C for 2 h in a conventional box furnace.

* Corresponding author. Tel./fax: +86 451 86402771.
E-mail address: zerodistance7@163.com (B. Yang).

0022-2313/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2011.06.045

The PLD experiments were performed using a KrF excimer pulsed laser (LPX205i, Lambda Physik, 248 nm wavelength, 30 ns pulse width and 5 Hz frequency). Bi_3TiNbO_9: 2 mol% Er^{3+}, 5 mol% Yb^{3+} thin films were deposited on double-sided polished fused silica substrates. The deposition of thin films was performed in the chamber under 100 mTorr oxygen atmosphere and the substrate temperature was 600 °C. Four different laser fluences 4, 5, 6, and 7 J/cm^2 were used. These films will be referred to as sample A, B, C, and D in the rest of this paper. The other three films were deposited in the chamber under 100 mTorr oxygen atmosphere and the laser fluence was 7 J/cm^2. Three different substrate temperatures 500, 600, and 700 °C were used. These films will be referred to as sample E, F, and G in the rest of this paper. The annealing following the deposition was *in situ* at the same temperature for 10 min with 0.5 atm oxygen pressure.

The microstructure and the morphology of the as grown films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM, Nanoscope IIIa), and scanning electron microscopy (SEM, FEI SIRISON 200, Philips). The BTNEY thin films were irradiated by a 976 nm diode laser at with full width at half maximum of 5 nm. The UC-PL collected with a lens was coupled to a monochromator with a spectral resolution of 1 nm attached to a photomultiplier at room temperature. In order to compare different samples, all spectra were measured under the same experimental condition.

3. Results and discussion

The BTNEY thin films fabricated on fused silica substrates by PLD were studied by X-ray diffraction (XRD). Fig. 1 shows the XRD patterns of sample A, B, C and D. All peaks can be indexed by the BTN tetragonal phase. Although there is 10 mol% excess Bi_2O_3 in the target, no Bi_2O_3 peaks were observed, which means that the excess bismuth ions in starting materials compensated the Bi evaporation during the preparation of BTNEY targets and the thin films. Because the XRD patterns do not contain Er_2O_3 and Yb_2O_3 crystalline phase, Er^{3+} and Yb^{3+} were doped into the crystal structure and substituted for Bi^{3+} ions. Even though fused silica has no lattice parameter relation with the aurivillius BTNEY unit cell, a highly (0 0 *l*) oriented texture had been obtained. This means that the intrinsic properties of BTNEY films, such as differences in surface energy for different planes of the unit cell and strong interaction between the octahedrons, could lead to preferred orientation [12]. The full width at half maximum (FWHM) of (0 0 8) peak for the film grown at 4, 5, 6, and 7 J/cm^2 is 0.264°, 0.226°, 0.200°, and 0.187°, respectively. The average grain size of the thin films can be obtained by the Scherrer equation [13]. The average grain sizes for the film grown at 4, 5, 6, and 7 J/cm^2 are 30.8, 35.9, 40.6, and 43.4 nm, respectively. It indicates that film produced by the higher laser fluence has a better crystallinity and a bigger grain size than that produced by the lower laser fluence.

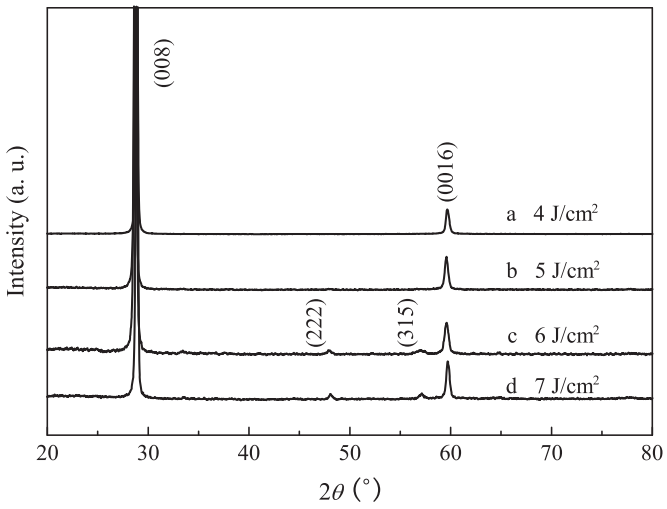

Fig. 1. XRD patterns of BTNEY thin films with deposition laser fluences of 4, 5, 6, and 7 J/cm^2.

The crystallinity of UC-PL films is an important factor for determining luminescent properties [14]. The surface morphology of the BTNEY films was characterized by AFM. Fig. 2 shows the AFM image of BTNEY thin films deposited on fused silica substrates with laser fluence 4, 5, 6, and 7 J/cm^2, respectively. The root mean square roughness of samples A, B, C, and D in an area of 1 μm × 1 μm is 3.43, 3.88, 5.11, and 5.51 nm, respectively. The root mean square roughness increases with the increase of deposition laser fluence, which is attributed to larger grain size.

Fig. 3 shows the SEM image of cross section of BTNEY thin films with deposition laser fluences 4, 5, 6, and 7 J/cm^2. The interface of substrate and the films is quite sharp and we can find that the thickneses of sample A, B, C, and D are about 300, 340, 380, and 430 nm, respectively. It means that the film deposition rate increases with the laser fluence.

Fig. 4 shows the UC-PL spectra of BTNEY thin films with deposition laser fluences 4, 5, 6, and 7 J/cm^2. In order to eliminate the effect of thickness on the UC-PL intensity of the thin films, all spectra were normalized to the thickness of the thin films. The green emissions located at 525 and 545 nm are assigned to $^2H_{11/2}/^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions. The weak red emission located at 655 nm arises from the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. We note that the 525 and 545 nm emission intensities increase with the deposition laser fluence. First, surface area of the thin films and the number of quenching particle reduces with the increasing of grain size, and then the upconversion photoluminescence of the thin films can be enhanced. Second, the enhancement of upconversion photoluminescence emission in large particle size films may be brought about by the reduction of internal reflections due to the substantial decrease of domain wall density [15].

In order to prove that the enhancement of upconversion photoluminescence in Bi_3TiNbO_9: 2 mol% Er^{3+}, 5 mol% Yb^{3+} films due to increasing grain size, three thin films with different substrate temperature were produced by PLD. Fig. 5 shows the XRD patterns of samples E, F, and G, respectively. All peaks can be indexed by the BTN tetragonal phase. As we all know, with the increase in temperature, grain size increases. The surface morphology of the BTNEY films was characterized by atomic force microscopy. Fig. 6 shows the AFM image of BTNEY thin films deposited with different substrate temperatures 500, 600, and 700 °C, respectively. The root mean square roughness of samples C, D, and E in an area of 5 μm × 5 μm is 2.95, 4.38, and 21.20 nm, respectively. The root mean square roughness increases with the increase in substrate temperature, which is attributed to larger grain size.

The UC-PL spectra of BTNEY thin films with different substrate temperature were measured. Fig. 7 shows the UC-PL spectra of the three kinds of BTNEY thin films. We note that the 525 nm emission intensities of sample G and F are almost 24 and 4 times, respectively, as strong as those of sample E. Due to the larger grain size, the density of grain boundaries in sample G is lower, which produced less scattering and dissipation of light, causing the enhancement in UC-PL intensity [15].

To understand the UC-PL mechanism, the pump power dependence of the radiative intensity was investigated. For an unsaturated UC-PL process, the number of photons that are necessary to populate the upper emitting state can be obtained by the

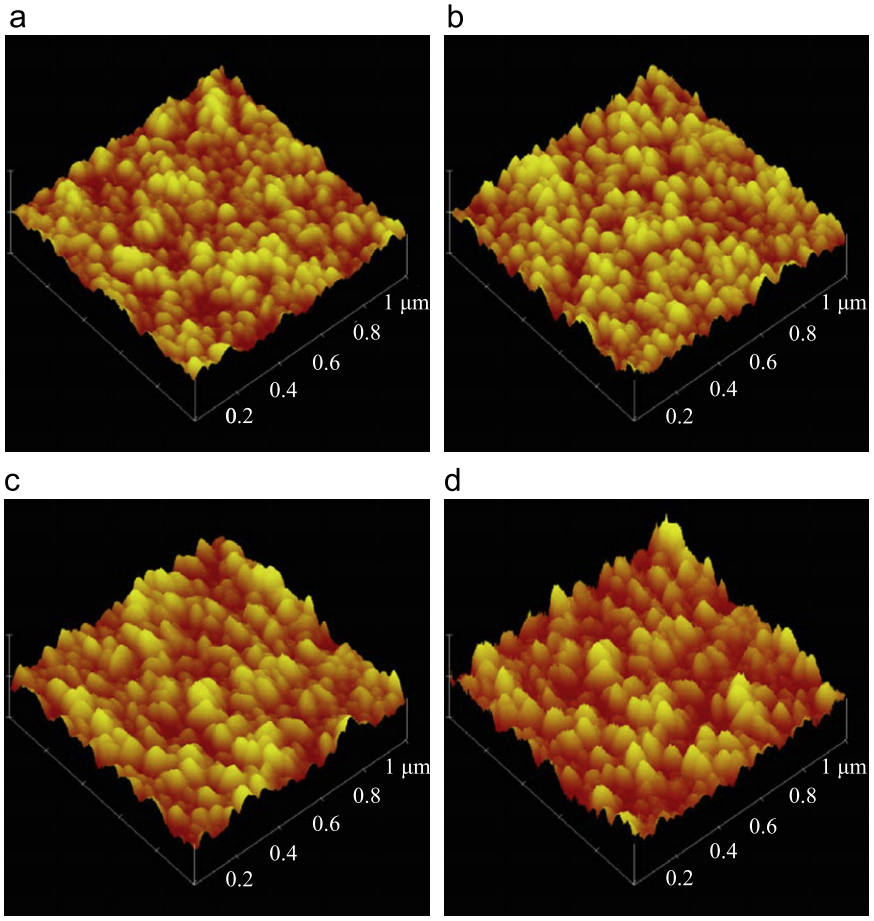

Fig. 2. AFM image of BTNEY thin films with deposition laser fluences of (a) 4, (b) 5, (c) 6, and (d) 7 J/cm^2.

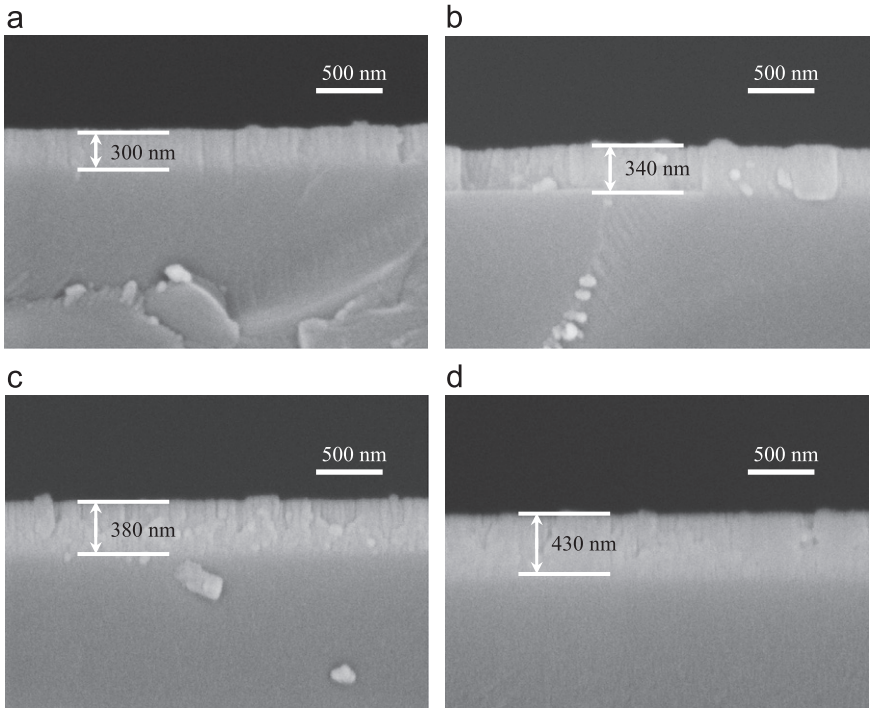

Fig. 3. SEM image of cross section of BTNEY thin films with deposition laser fluences of (a) 4, (b) 5, (c) 6, and (d) 7 J/cm^2.

following relation [16]:

$$I_f \propto P^n, \quad (1)$$

where I_f is the integrated radiative intensity, P is the pump laser power, and n is the number of required laser photons. Fig. 8(a) is the pump power dependence of the radiative intensity of sample A. n can be evaluated from the slope of $\ln(I_f)$ versus $\ln(P)$. It shows that for these three transitions n may be approximated by 2, which suggests that the UC-PL processes are two-photon processes. Fig. 8(b) shows energy level scheme of Er^{3+} and Yb^{3+} as well as proposed UC mechanism. Two energy transfer processes (ET1 and ET2) from Yb^{3+} to Er^{3+} ion populate the $^4F_{7/2}$ (Er^{3+}) state. Then the $^4F_{7/2}$ level depopulates through a rapid multiphonon relaxation down to the $^2H_{11/2}$ and $^4S_{3/2}$. Finally, it will decay to the $^4I_{15/2}$ level with green light emission. The $^4F_{9/2}$ is the red emission state. The cross relaxation (CR) process ($^4F_{7/2}+{}^4I_{11/2}\rightarrow 2\ {}^4F_{9/2}$) is important for the direct population of the $^4F_{9/2}$ state [17]. However, the CR efficiency is very low, because the energy gaps among the $^4F_{9/2}$, $^2H_{11/2}$, and $^4S_{3/2}$ are very small, which cause the depopulation of the $^4F_{7/2}$ level. This is the reason why the red emission is very weak.

For all-solid compact laser devices UC-PL thin film must exhibit strong UC-PL intensity. The BTNEY thin films deposited on fused silica substrate with large deposition laser fluence satisfy these criteria. Our results demonstrated that BTNEY is a promising material for all-solid compact laser device applications.

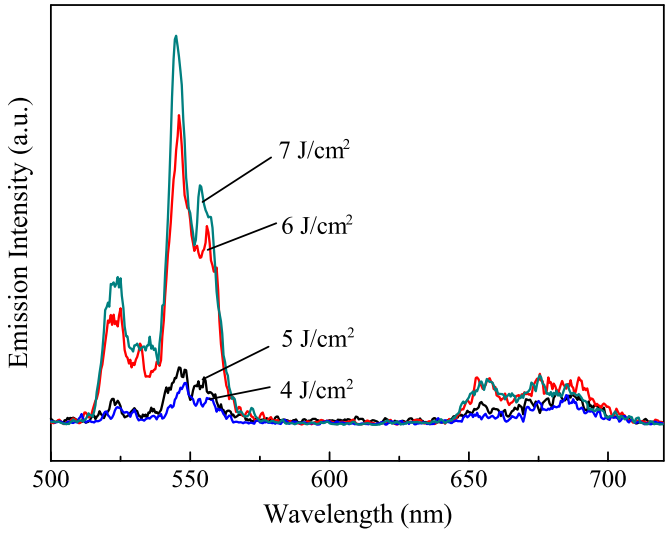

Fig. 4. UC-PL spectra of BTNEY thin films with deposition laser fluences of 4, 5, 6, and 7 J/cm^2. The spectra were normalized to the thickness of the thin films.

4. Conclusion

We found that the grain size of BTNEY films can be manipulated by the deposition laser fluence and substrate temperature. The 525 and 545 nm emission intensities of BTNEY films increase with the deposition laser fluence. In order to prove our viewpoint, three BTNEY thin films with different substrate temperatures

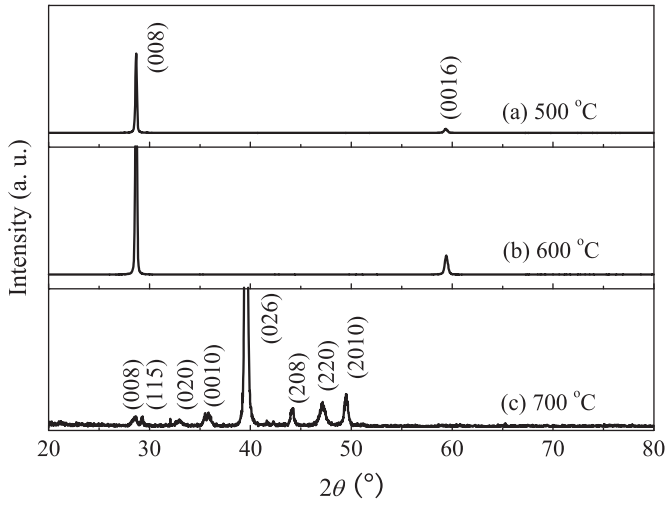

Fig. 5. XRD patterns of BTNEY thin films with substrate temperatures of 500 °C (a), 600 °C (b), and 700 °C (c).

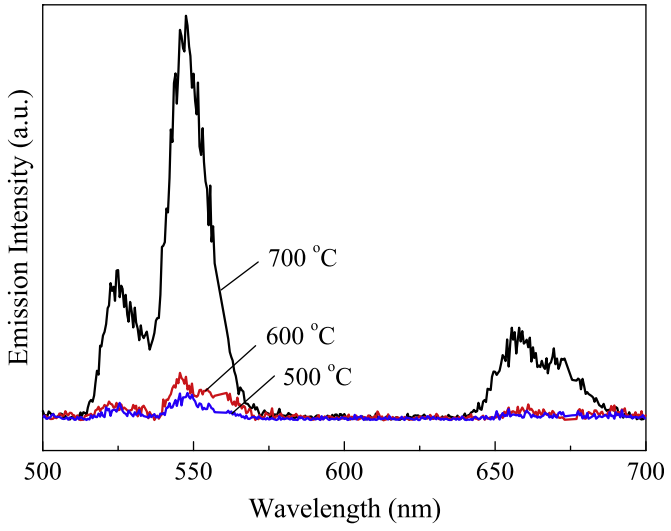

Fig. 7. UC-PL spectra of BTNEY thin films deposited with substrate temperatures of 500 °C , 600 °C , and 700 °C.

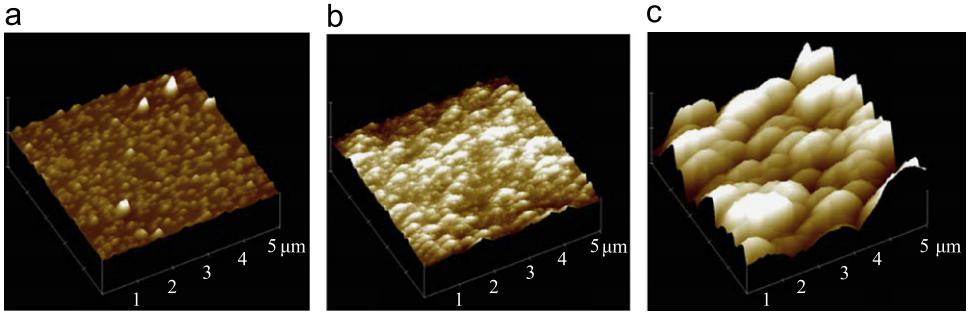

Fig. 6. AFM image of BTNEY thin films with substrate temperatures of 500 °C (a), 600 °C (b), and 700 °C (c).

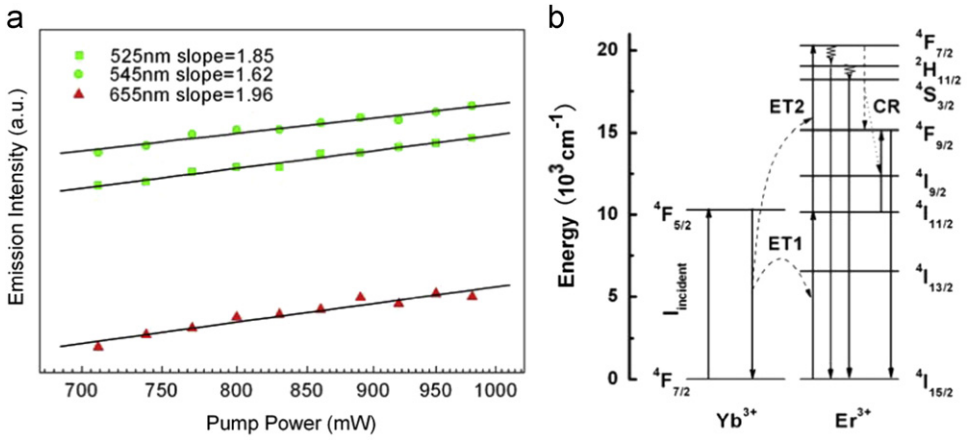

Fig. 8. Pump power dependence of UC-PL intensities for the sample D (a) and energy level scheme of Er^{3+} and Yb^{3+} as well as proposed UC mechanism (b).

were produced by PLD. With the increase in the substrate temperature, the grain size and the UC-PL of BTNEY thin films increase. We believe that the enhancement of UC-PL emission in large particle size films may be brought about by the reduction of internal reflections due to the substantial decrease of domain wall density. These BTNEY thin films are very promising to be used for all-solid compact laser devices.

Acknowledgment

This work was supported by the National Nature Science Foundation of China (Grant no. 10704021) and the Project (2009055) supported by Natural Scientific Research Innovation Foundation in Harbin Institute of Technology.

References

[1] M. Shojiya, M. Takahashi, R. Kanno, K. Kadono, Appl. Phys. Lett. 65 (1994) 1874.
[2] C.B. de Araujo, L.S. Menezes, G.S. Maciel, L.H. Acioli, A.S.L. Gomes, Y. Messaddeq, A. Florez, M.A. Aegerter, Appl. Phys. Lett. 68 (1996) 602.
[3] H.X. Zhang, C.H. Kam, Y. Zhou, X.Q. Han, S. Buddhudu, Q. Xiang, Y.L. Lam, Y.C. Chan, Appl. Phys. Lett. 77 (2000) 609.
[4] B. Yang, H.Z. Chen, M.F. Zhang., F.Y. Wang., K. Cheah, W.W. Cao, Appl. Phys. A 96 (2009) 1017.
[5] B. Yang, Y.P. Wang, F. Wang, Y.F. Chen, S.N. Zhu, Z.G. Liu, W.W. Cao, Appl. Phys. A 81 (2005) 183.
[6] Z.Y. Zhou, X.L. Dong, H.X. Yan, Scr. Mater. 55 (2006) 791.
[7] T. Miyakawa, D.L. Dexter, Phys. Rev. B 1 (1970) 2961.
[8] T. Aisaka, M. Fujii, S. Hayashi, Appl. Phys. Lett. 92 (2008) 132105.
[9] G.Y. Chen, H.C. Liu, G. Somesfalean, Y.Q. Sheng, H.J. Liang, Z.G. Zhang, Q. Sun, F.P. Wang, Appl. Phys. Lett. 92 (2008) 113114.
[10] J.A. Capobianco, F. Vetrone, J.C. Boyer, J. Phys. Chem. B 106 (2002) 1181.
[11] M.P. Hehlen, N.J. Cockroft, T.R. Gosnell, A.J. Bruce, Phys. Rev. B 56 (1997) 9302.
[12] M. Blomqvist, S. Khartsev, A. Grishin, Appl. Phys. Lett. 82 (2003) 439.
[13] B. Pejova, I. Grozdanov, Thin Solid Films 515 (2007) 5203.
[14] S.S. Yi, J.S. Bae, K.S. Shim, B.K. Moon, H.J. Seo, J.H. Jeong, J.H. Kim, Appl. Phys. A 80 (2005) 727.
[15] J.H. Jeong, J.S. Bae, S.S. Yi, J.C. Park, Y.S. Kim, J. Phys.: Condens. Matter 15 (2003) 567.
[16] M. Pollnau, D.R. Gamelin, S.R. Luthi, H.U. Gudel, Phys. Rev. B 61 (2000) 3337.
[17] F. Vetrone, J.C. Boyer, J.A. Capobianc, A. Speghini, M. Bettinelli, J. Appl. Phys. 96 (2004) 661.