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RESEARCH ARTICLE

Investigation of up-conversion luminescence of Er^{3+} and Er^{3+}/Yb^{3+} ions doped in PLZT for active electro-optical applications

Baozeng LI[1], Anting WANG[1], Hai GUO[1], Xuesheng CHEN[2], Hua JIANG[3], Zhiqiang ZHENG[4], Hai MING (✉)[1]

1 Department of Physics, University of Science and Technology of China, Hefei 230026, China
2 Department of Physics and Astronomy, Wheaton College, Norton, MA 02766, USA
3 Boston Applied Technologies, Inc., 150H New Boston Street, Woburn, MA 01801, USA
4 Department of Physics, Fujian Normal University, Fuzhou 350007, China

Abstract The up-conversion luminescence of Er^{3+} and Er^{3+}/Yb^{3+} ions doped in lanthanum-modified lead zirconate titanate (PLZT) under 980 nm excitation at room temperature has been investigated. The green up-conversion luminescence at 540 and 566 nm was observed in Er^{3+}:PLZT; the greater the concentration of Er^{3+} ions, the stronger the intensity. In Er^{3+}–Yb^{3+}:PLZT, other than the green up-conversion luminescence at 540 and 566 nm, a relatively weak red up-conversion luminescence at 668 nm was also observed. Both green and red up-conversion luminescence intensities presented an approximately quadratic dependence on excitation power, which indicated that two excitation photons are involved in the up-conversion process of Er^{3+}:PLZT and Er^{3+}–Yb^{3+}:PLZT. The characteristics of PLZT ceramic material were also studied by Raman spectroscopy. This work shows a promising future for developing multifunctional up-conversion electro-optical devices using Er^{3+} and Er^{3+}/Yb^{3+} ions doped PLZT.

Keywords up-conversion luminescence, Er^{3+} and Er^{3+}/Yb^{3+} doped, lanthanum-modified lead zirconate titanate (PLZT)

1 Introduction

Ceramic laser materials are attractive because they are potentially great candidates for novel microchips or high power laser devices. Erbium-doped and erbium-ytterbium co-doped ceramic laser materials have received much attention in the past few years. Compare to popular single-crystal laser materials such as Nd:YAG, ceramic laser materials have emerged with several advantages such as easy fabrication, lower cost, and fabrication at larger sizes. Another advantage of ceramic laser materials is that it is easy to dope with high rare-earth ion concentrations. It is very easy to fabricate ceramic laser materials into structures that include stripe, rod, disk and tube shapes [1]. PLZT is a transparent ceramic based on the perovskite structure of ABO_3 [2], which is formulated as $(Pb,La)(Zr,Ti)O_3$. Recently, a new electro-optic ceramic material, Er^{3+} and Er^{3+}/Yb^{3+} ion doped PLZT, has been fabricated by means of pressure assisted sintering (PAS). Since PLZT has an exceptionally high electro-optic (EO) effect [3], it has been successfully used for a variety of optical devices in telecommunications [4,5]. PLZT ceramic materials can be used to make electro-optical integrated multifunctional laser devices.

Up-conversion promises a whole range of potential applications that cover infrared laser detection, three-dimensional volumetric display, visible lasers, and optical data storage. Since the 1960s, up-conversion luminescence have been investigated extensively for rare-earth ions such as Er^{3+}, Tm^{3+}, Nd^{3+}, Pr^{3+}, and Eu^{3+} in various host materials, including fluoride and phosphate glasses, crystal and ceramic materials [6–16]. In this paper, experimental investigation for up-conversion luminescence of Er^{3+}:PLZT and Er^{3+}–Yb^{3+}:PLZT was presented for different doping concentrations. The materials used in this study were 2%Er^{3+}:PLZT, 5%Er^{3+}:PLZT, and 0.5%Er^{3+}–2.5%Yb^{3+}:PLZT. The characteristics of PLZT ceramic materials were also studied by Raman spectroscopy.

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E-mail: minghai@ustc.edu.cn

2 Experiments

Three samples, 2%Er^{3+}:PLZT, 5%Er^{3+}:PLZT, and 0.5%Er^{3+}–2.5%Yb^{3+}:PLZT, were used in this study. These ceramic materials were fabricated by Boston Applied Technologies, Inc. They show polycrystalline structures with the average grain size in the micrometer range and grain boundary width in the nanometer range. Each sample was well-polished and measured 3.04 mm × 3.04 mm × 2 mm. For the up-conversion luminescence measurement, the sample was excited by a diode laser at a wavelength of 980 nm. The luminescence from the sample was modulated before transmitting through the entrance slit of a J-Y double-grating monochromator. The light from the monochromator was detected by a Hamamatsu R456 photomultiplier and then amplified by a lock-in-amplifier EG&G 7265 DSP. Up-conversion luminescence spectra were taken in the 500 – 700 nm range. Pump intensity-dependent up-conversion luminescence was also measured for analyzing the up-conversion excitation mechanisms. All measurements were performed at room temperature.

3 Results and discussion

Figure 1 shows the up-conversion luminescence spectra of 2%Er^{3+}:PLZT, 5%Er^{3+}:PLZT, and 0.5%Er^{3+}–2.5%Yb^{3+}:PLZT in the wavelength range from 500 to 700 nm with 980 nm laser under the same pumping power of 51.7 mW. In the case of 2%Er^{3+}:PLZT and 5%Er^{3+}:PLZT, the up-conversion luminescence had four peaks at 527, 540, 553.5, and 566 nm in the green band. The emission band with two peaks at 527 and 540 nm is attributed to the $^2H_{11/2}\rightarrow{}^4I_{15/2}$ transition, and another emission band with two peaks at 553.5 and 566 nm is attributed to the Er^{3+}:$^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition. Each band with two peaks is due to the energy level Stark splitting of Er^{3+}:$^2H_{11/2}$ and $^4S_{3/2}$. The 5%Er^{3+}:PLZT sample produces much stronger up-conversion luminescence than 2%Er^{3+}:PLZT.

As shown in Fig. 1, the general feature of an up-conversion luminescence spectrum in the green band for 0.5%Er^{3+}–2.5%Yb^{3+}:PLZT is similar to that of Er^{3+}:PLZT. We also observed red up-conversion luminescence at about 668 nm correspond to the Er^{3+}:$^4F_{9/2}\rightarrow{}^4I_{15/2}$ transition. The measurements in Fig. 1 revealed the up-conversion luminescence at about 560 nm, for Er^{3+}–Yb^{3+}:PLZT is much stronger than that obtained for Er^{3+}:PLZT. The up-conversion efficiency at about 560 nm in the 0.5%Er^{3+}–2.5%Yb^{3+}:PLZT is about 5 times stronger than in the 5%Er^{3+}:PLZT. This indicates the importance of the energy transfer (ET) process between Yb^{3+} and Er^{3+} ions in the excitation mechanism. Yb^{3+} ion is doped in PLZT as a sensitizer to improve pumping efficiency, since it exhibits an intense broad absorption cross section between 850 and 1080 nm, while Er^{3+} has weak absorption at this band range.

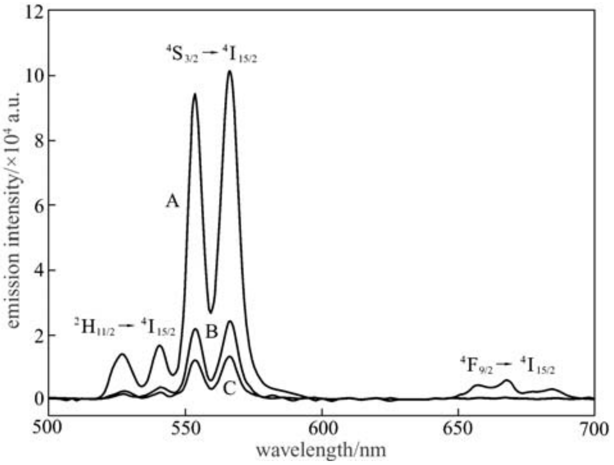

Fig. 1 Excited by 980 nm laser under the same power of 51.7 mW, the up-conversion luminescence spectra in PLZT doped with (A) 0.5%Er^{3+}–2.5%Yb^{3+}, (B) 5%Er^{3+}, (C) 2%Er^{3+}

The dependence of the visible up-conversion luminescence intensities upon excitation power at 980 nm was examined. Figure 2 shows the log-log dependences of the green up-conversion luminescence (541 and 556.5 nm) intensities on the excitation power for 5%Er^{3+}:PLZT. The dependences of the green (527 and 556.5 nm) and red (668 nm) up-conversion luminescence intensities on the excitation power for 0.5%Er^{3+}–2.5%Yb^{3+}:PLZT are presented in the log-log plot of Fig. 3. In a frequency up-conversion process, the up-conversion luminescence intensity I_{up} increases in proportion to the power of excitation intensity I_{ex}, i.e., $I_{\mathrm{up}}\propto I_{\mathrm{ex}}^n$ [17–19], where n is the number of excitation photons absorbed per visible photon emitted. The plots of $\log I_{\mathrm{up}}$ vs $\log I_{\mathrm{ex}}$ yield a straight line with slope n. It was observed that all visible up-conversion luminescence intensities presented an

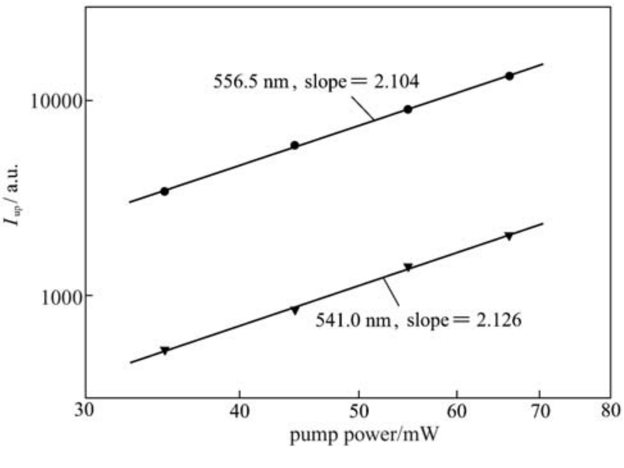

Fig. 2 Log-log plot of up-conversion luminescence intensities as a function of excitation power for 5%Er^{3+}:PLZT

approximately quadratic dependence on excitation power. This quadratic dependence indicates that two excitation photons are involved in the up-conversion process of Er^{3+}:PLZT and Er^{3+}–Yb^{3+}:PLZT.

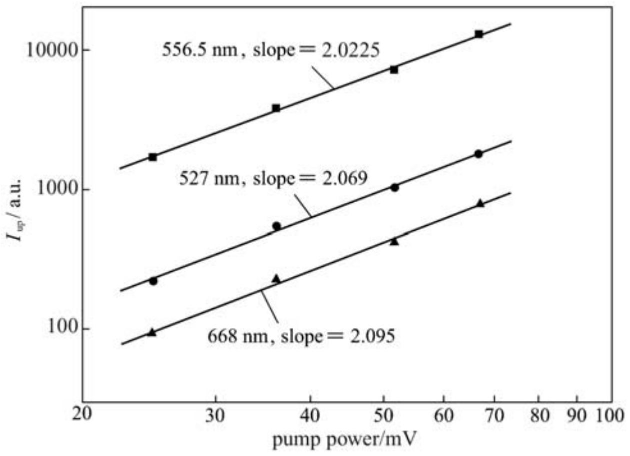

Fig. 3 Log-log plot of up-conversion luminescence intensities as a function of excitation power for 0.5%Er^{3+}–2.5%Yb^{3+}: PLZT

The room-temperature Raman spectrum of the PLZT ceramic is shown in Fig. 4. The band at 264 cm^{-1} is assigned to Zr–O torsional vibration coming out from F_{2u} mode of cubic symmetry, and the bands at 568 and 797 cm^{-1} are due to vibrations involving Zr–O stretching motions coming out from a triply degenerate F_{1u} [20,21]. Compared to the energy difference (3600 cm^{-1}) between the energy levels $^4I_{11/2}$ and $^4I_{13/2}$, the phonon energy of PLZT ceramic material, viz. Raman shift 797 cm^{-1} corresponding to the right Raman intensity peak, is very small. The lower phonon energy in PLZT, the lower the probability for non-radiation relaxation between the energy levels of Er^{3+} ion. Owing to low non-radiation relaxation probability, it was inferred that PLZT laser materials are potentially great candidates for frequency up-conversion applications.

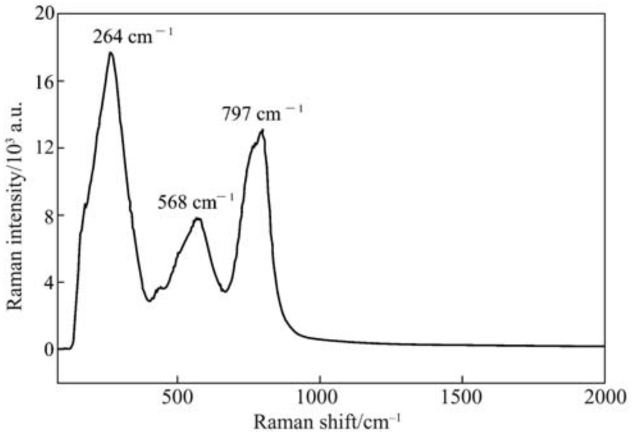

Fig. 4 Raman spectrum of PLZT at room temperature

Figure 5 shows the schematic diagram of the energy levels of Er^{3+} and Yb^{3+} ions as well as some possible up-conversion mechanisms presented in the process of up-conversion. Upward arrows indicate the excitation photons, downward arrows indicate emission photons, and broken downward arrows stand for non-radiation relaxation. For the Er^{3+}:PLZT sample, the $^4I_{11/2}$ is excited by 980 nm pumping light. Since the $^4I_{11/2}$ has a much longer lifetime, the same Er^{3+} ion absorbs a second pump photon by means of excited state absorption (ESA), provoking its excitation from the $^4I_{11/2}$ level to the $^4F_{7/2}$ level. The $^4F_{7/2}$ level of Er^{3+} ion will then decay non-radiation to the $^2H_{11/2}$ level, undergo the radiation transition $^2H_{11/2} \rightarrow {}^4I_{15/2}$, then produce the green luminescence at 527 and 540.5 nm. Some Er^{3+} ions in $^4F_{7/2}$ level will also decay non-radiation to $^4S_{3/2}$, thus resulting in green up-conversion luminescence at 553.5 and 566 nm due to the radiation transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$. It is considered that the $^2H_{11/2}$ level is populated from the $^4S_{3/2}$ level via a fast thermal equilibrium between the levels [22]. Thus, the green up-conversion luminescence from $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition is much stronger than that from $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition.

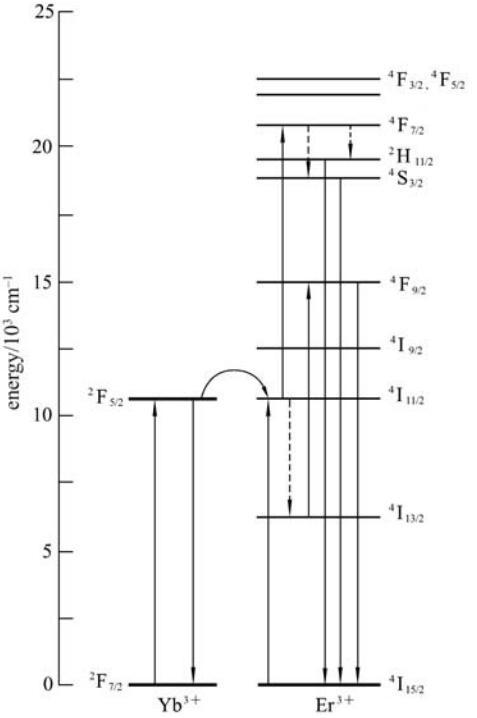

Fig. 5 Energy levels diagram of Yb^{3+} and Er^{3+} ions

For the Er^{3+}–Yb^{3+}:PLZT sampler, the green emissions also correspond to the transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$, respectively. Since the absorption cross section of Yb^{3+} at 980 nm is much larger than that of Er^{3+}, the ET is dominant in the excitation of the $^4I_{11/2}$ level of Er^{3+} ion. An Yb^{3+} at the ground state $^2F_{7/2}$ absorbs a

980 nm photon and promotes it to the excited $^2F_{5/2}$ level. The $^4I_{11/2}$ level of Er^{3+} ion is excited by the ET process from the $^2F_{5/2}$ level of Yb^{3+} to Er^{3+} ion. The long-lived $^4I_{11/2}$ level undoubtedly stimulated other ET processes. Either the same or a nearby Yb^{3+} ion absorbs a second pump photon and transfers the energy to the same Er^{3+} ion, provoking its excitation from the $^4I_{11/2}$ level to the $^4F_{7/2}$ level. The $^4F_{7/2}$ level of Er^{3+} ions will then decay non-radiation to the lower $^4I_{11/2}$ and $^4S_{3/2}$ levels due to their small energy gap. The green emission band at 527 and 540.5 nm is attributed to the transition $^2H_{11/2}\rightarrow{}^4I_{15/2}$, and another green emission band at 553.5 and 566 nm is attributed to the transition $^4S_{3/2}\rightarrow{}^4I_{15/2}$.

For the red up-conversion luminescence at 668 nm due to the transition $^4F_{9/2}\rightarrow{}^4I_{15/2}$, the mechanism involves the excitation of the population at the $^4I_{13/2}$ through the ET process from the $^2F_{5/2}$ level of Yb^{3+} to the Er^{3+} ion [23]. The $^4I_{13/2}$ level is populated due to non-radiation from the upper $^4I_{11/2}$ level. This excitation mechanism depends on the energy transfer rates between Er^{3+}, Yb^{3+} ions and the Yb^{3+} concentration. The 663 nm red up-conversion luminescence increases with Yb^{3+} concentration.

4 Conclusions

The experimental investigation of infrared-to-visible up-conversion luminescence in Er^{3+}:PLZT and Er^{3+}–Yb^{3+}:PLZT has been presented. The green up-conversion luminescence (540 and 566 nm) was observed in Er^{3+}:PLZT under 980 nm excitation, and the luminescence increased with the concentration of Er^{3+} ions. In Er^{3+}–Yb^{3+}:PLZT, relatively weak red up-conversion luminescence at 668 nm was also observed. All visible up-conversion luminescence intensities presented an approximately quadratic (slope $n\sim2$) dependence on excitation power. The quadratic dependence indicates that two excitation photons are involved in the up-conversion process of Er^{3+}:PLZT and Er^{3+}–Yb^{3+}:PLZT. The characteristics of PLZT ceramic materials was also studied by Raman spectroscopy. This work shows that Er^{3+}:PLZT and Er^{3+}–Yb^{3+}:PLZT are promising candidates for applications in up-conversion based multi-functional electro-optical devices.

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