Journal of Alloys and Compounds 714 (2017) 1–5

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

White-light manipulation in $Ho^{3+}/Yb^{3+}/Tm^{3+}$-doped $LiNbO_3$ single crystals through transition metal Mn^{2+} ion doping

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A R T I C L E I N F O

Article history:
Received 12 January 2017
Received in revised form
17 April 2017
Accepted 19 April 2017
Available online 19 April 2017

Keywords:
Upconversion
Lithium niobate
Rare-earth-doped material
Mn^{2+} ion
White-light emission

A B S T R A C T

A strategy for ideal upconversion white-light emission in $LiNbO_3:Ho^{3+}/Yb^{3+}/Tm^{3+}$ single crystals is demonstrated simply through transition metal Mn^{2+} doping. The addition of different Mn^{2+} concentrations favors the probability of upconversion red emission transition, and the ratio of red-to-green is enhanced resulting in a purer upconversion white-light emission. It is observed the cross-relaxation of energy between Ho^{3+}, Tm^{3+} and Mn^{2+} ions plays an important role in improving the red emission. The obtained results greatly benefit in the further discovery to design upconversion process and fabricate other ideal upconversion white-light materials.

1. Introduction

In recent years, the development of upconversion white-light materials is a very active research field, driven by the needs for optical bioimaging, multicolor display, optical temperature sensor, solar cell, and so on [1–5]. One of the current academic interests is in pursuing the single white-light phosphors to avoid the intrinsic color balance, device complication, and high cost problems when using multiphosphors or multi-LEDs [6–8]. Among them, doping low-phonon energy materials with rare-earth (RE) ions becomes a promising approach. During the past few years, to realize the upconverted white-light emission, much attentions have been focused on the RE ions concentration, size/shape/phase-controlled synthesis of host material, excitation source, etc [9–12]. However, the chromaticity of white-light is not ideal so far because of the deficiency of red emission under normal circumstances. In general, the intensities of blue and green emissions can be easily enhanced by selecting the appropriate pump power, rare-earth ion or host material [13–15]. Thus, it is of technological and scientific importance to look for an effective and feasible way to enhance the upconversion red emission intensity and obtain a purer white-light emission. As known, the spectroscopic properties of transition metal ions are very sensitive to the surrounding environment due to the exposure of d electrons [16], so it is expected to tune the upconversion processes of RE ions by using transition metal ions as sensitizers. Some efforts are devoted to the studies of selective enhancement of upconversion emissions by doping transition metal ions. Recently, a few reports have been related to the enhancement in red emission, such as Mn^{2+} doped Yb/Er systems [17,18]. In the reported systems, the ratio of red-to-green can be greatly enhanced owing to the energy transfer between Mn^{2+} ion and RE ions [19–21]. However, the realization of such optical manipulation for upconversion materials is still a challenge now. Relative studies are still in their infancy, and need to be further explored to promote their applications in bioimaging and multicolor display.

Oxide single crystal, as a kind of promising alternative host material for upconversion luminescence, has gained much attention due to its high stability and favorable performances. Among them, $LiNbO_3$ single crystal seems particularly attractive due to its excellent piezoelectric, electro-optic, nonlinear optic, and easily-prepared performances. More typically, the highest phonon energy of $LiNbO_3$ is about 880 cm^{-1} [22], which promises a high upconversion efficiency. The advantages of stability and versatility make $LiNbO_3$ single crystal suitable for applications in severe

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http://dx.doi.org/10.1016/j.jallcom.2017.04.200

environment and device integration by means of upconversion white-light property. So far, more promising results on the upconversion luminescence property in RE-doped $LiNbO_3$ single crystals have been obtained [23–26].

In this letter, we represent a facile strategy to manipulate the transition possibilities between the red and green upconversion emissions of Ho^{3+} ions through manganese ions (Mn^{2+}) doping. Moreover, the purer white-light emission in $LiNbO_3$ single crystal has been achieved, and the rational explanation is given.

2. Experimental section

2.1. Sample preparation

The $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} (0.025/2.0/0.2 mol%) single crystals doped with xMn^{2+} ion concentrations (x mol% = 0.0, 0.2, 0.5 and 1.0) were grown by the Czochralski method. In this article, the $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} (0.025/2.0/0.2 mol%) single crystal without Mn^{2+} ion doping is used as a reference sample, which has been fully studied in our previous research work [27]. The raw materials were Li_2CO_3, Nb_2O_5, Ho_2O_3, Yb_2O_3, Tm_2O_3 and MnO with 4 N purity. Firstly, the raw materials were precisely weighed and thoroughly mixed for 48 h, underwent the heat treatment of 750 °C for 2 h to complete the decomposition reaction of Li_2CO_3, and then sintered at 1150 °C for 10 h to obtain the doped $LiNbO_3$ polycrystals. Secondly, the doped $LiNbO_3$ single crystals were grown along the [0 0 1] direction using a diameter controlled Czochralski apparatus from corresponding polycrystals. In order to grow the single crystals with good quality, the following optimum growth conditions were selected: the temperature gradient above the melt was 25 °C/mm, the pulling rate was 0.3 mm/h, and the seed rotation rate was 30 rpm. After growth, the crystals were cooled down to room temperature at a speed of 40 °C/h. Finally, Y-cut plates of the samples were cut and polished for the optical tests. The tested samples are transparent and their colors are uniform.

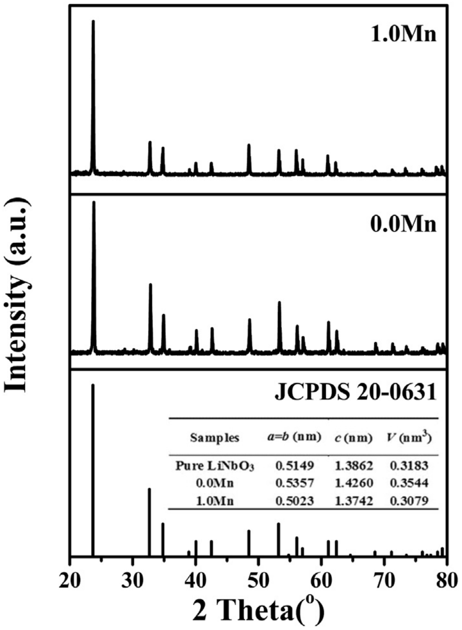
2.2. Characterization

To identify the crystallization phase, the X-ray diffraction spectra of samples were measured by an XRD-6000 diffractometer using a copper Kα radiation source. The upconversion luminescence spectra were recorded by Zolix-SBP300 grating spectrometer equipped with CR131 photomultiplier. Multi-point measurements for spectra are performed to guarantee the accuracy of experimental results. The results show that the upconversion emission spectrum has very good reproducibility. A 980 nm diode laser was used as the pump source with an excitation power density of about 60 W cm^{-2}. All the spectra were measured using the same optical path, and all the measurements were performed at room temperature. CIE chromaticity coordinate of the upconversion fluorescence was calculated based on the 1931 CIE chromaticity theory [28].

3. Results and discussion

3.1. X-ray diffraction study

Fig. 1 shows the XRD patterns of Mn^{2+} ion doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystals. The results show that all the diffraction peak positions of single crystals can be well indexed to the standard XRD pattern of $LiNbO_3$ phase with or without Mn^{2+} ion doping, and no extra diffraction peaks were detected even the Mn^{2+} ion concentration is increased to 1.0 mol%. It means that no impurity phases are formed in these doped $LiNbO_3$ single crystals. In addition, it is suggested that the Mn^{2+} and RE^{3+} dopants are inclined to occupy the chemical substitutional sites (Li and Nb sites), resulting in the variations of diffraction peak intensities. Moreover, the lattice parameters of $LiNbO_3$ single crystals doped with RE^{3+} ions and Mn^{2+} ion are shown in the inset of Fig. 1. Compared with pure $LiNbO_3$ crystal, it is found that the lattice parameters of $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystals are increased, while the lattice parameters of Mn^{2+} ion doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystals are decreased. As known, the ionic radius has the following relation: Mn^{2+} ion < Li^+ or Nb^{5+} ion < RE^{3+} ion. We believe that the ionic radius differences of dopants result in the changes of lattice parameters.



Samples	a=b (nm)	c (nm)	V (nm³)
Pure $LiNbO_3$	0.5149	1.3862	0.3183
0.0Mn	0.5357	1.4260	0.3544
1.0Mn	0.5023	1.3742	0.3079

Fig. 1. XRD patterns of Mn^{2+} doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystals. The inset is the lattice parameters of $LiNbO_3$ single crystals doped with RE^{3+} ions and Mn^{2+} ion.

3.2. Upconversion luminescence spectra

Fig. 2 shows the upconversion emission spectra of $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystals doped with 0.0, 0.2, 0.5, 1.0 mol% Mn^{2+} ion concentrations under 980 nm excitation at room temperature. The blue, green, and red upconversion emissions centered at 476 nm, 550 nm, and 651/664 nm can be easily assigned to Tm^{3+}: $^1G_4 \rightarrow {}^3H_6$ transition, Ho^{3+}: $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ transition, and Tm^{3+}: $^1G_4 \rightarrow {}^3F_4$/$Ho^{3+}$: $^5F_5 \rightarrow {}^5I_8$ transitions, respectively [27]. From Fig. 2, it can be observed that the peak positions of emission bands are hardly changed while the relative emission intensities are changed differently with increasing the Mn^{2+} ion concentrations. As known, the optical properties of $LiNbO_3$ crystal are closely related to its intrinsic defects [29–31]. The dopants preferentially occupy the Li sites. With the increase of dopant concentration, the dopants begin to occupy the Nb sites, which can shorten the distance between the doped ions effectively [32,33]. As a result, the energy transfer processes among Mn^{2+} ions and RE^{3+} ions are enhanced, and the intensity ratios of blue, green and red emissions are adjusted. Furthermore, it should be noted that the upconversion emission of Mn^{2+} ion is not observed, which implies the Mn^{2+} ion is not the luminescent active ion in our research system.

In order to reflect the true colors of the luminescence, the CIE 1931 color coordinates for upconversion emissions of $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystals with different Mn^{2+} ion concentrations

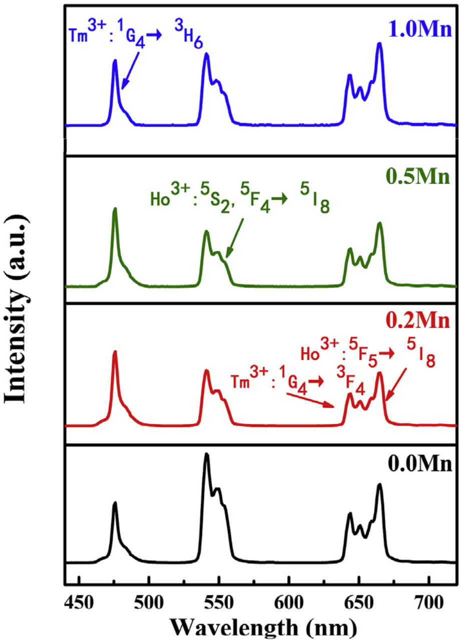


Fig. 2. Upconversion emission spectra of xMn^{2+} doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystals (x = 0.0, 0.2, 0.5, 1.0 mol%) under 980 nm excitation at room temperature.

are calculated and marked in CIE diagram, as shown in Fig. 3. It can be seen that all the color coordinates fall within the white-light region of 1931 CIE diagram when the Mn^{2+} ion concentrations are below 1.0 mol%. Besides, the color coordinates have the trend of shift towards red region with the increase of Mn^{2+} ion concentration. So, it is concluded that the Mn^{2+} ion can improve the probability of the red emission transition relative to blue and green emissions. Compared with some other similar works [34–36], the white-light manipulation of Mn^{2+} ion achieved in our work is significant and convenient in respect of color coordinate and excitation source. When the Mn^{2+} ion concentration reaches 1.0 mol%, the upconversion emission is very close to the standard white-light (0.33, 0.33).

3.3. Upconversion mechanism investigations

To analyze the possible white-light upconversion mechanism in Mn^{2+} ion doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystal, the dependences of upconversion emission intensities on pump powers for the samples are investigated under 980 nm excitation at the same test conditions (Fig. 4). As shown, when the Mn^{2+} ion concentration is 1.0 mol%, the power law exponents for blue, green, and red emissions in Mn^{2+} ion doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystal are 2.28, 1.65, and 2.17, respectively. When the Mn^{2+} ion concentration is 0.2 mol%, they are 2.36, 1.79, and 2.02, respectively. However, the above values in $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystal are 2.51, 1.93, and 1.80, respectively. It is well known that the slopes deviating from the integer values can be attributed to the competition between the linear decay and the upconversion processes for the depletion of the intermediate excited states and the local thermal effect [37,38]. Undoubtedly, the blue emission is a three-photon process and the green emission is a two-photon process in both Mn^{2+} ion doped and undoped systems. The reductions of needed photons number for upconversion blue and green emissions are induced by Mn^{2+} ion doping. But for the red emission, the photon numbers are extraordinarily large in Mn^{2+} ion doped systems compared with Mn^{2+} ion undoped system, implying the participation of a three-photon process except for a two-photon process.

The schematics of the populating and upconversion luminescence processes for the blue, green, and red emissions in Mn^{2+} doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} system under 980 nm excitation are illustrated visually in Fig. 5. As shown, the Yb^{3+} ions act as sensitizers to absorb laser photons, the excited Yb^{3+} ions in the $^2F_{5/2}$ state may transfer their excitation energy to Ho^{3+} and Tm^{3+} ions. Through two successive energy transfer processes, the $^5F_4$, $^5S_2$ and $^5F_5$ states of Ho^{3+} ions are populated, which generate the 550 nm and 664 nm upconversion emissions. The $^1G_4$ states of Tm^{3+} ions are populated by three successive energy transfer processes, resulting in the 476 nm and 651 nm upconversion emissions. Herein, we emphatically discuss the influence of Mn^{2+} ion on upconversion process. As presented in Fig. 5, the red upconversion emission can also be ascribed to non-radiative energy transfer from the $^3H_6$, $^5G_5$ and $^5F_4$, $^5S_2$ levels of Ho^{3+} ions and $^1G_4$ levels of Tm^{3+} ions to $^4T_1$ levels of Mn^{2+} ions, followed by a back-energy transfer

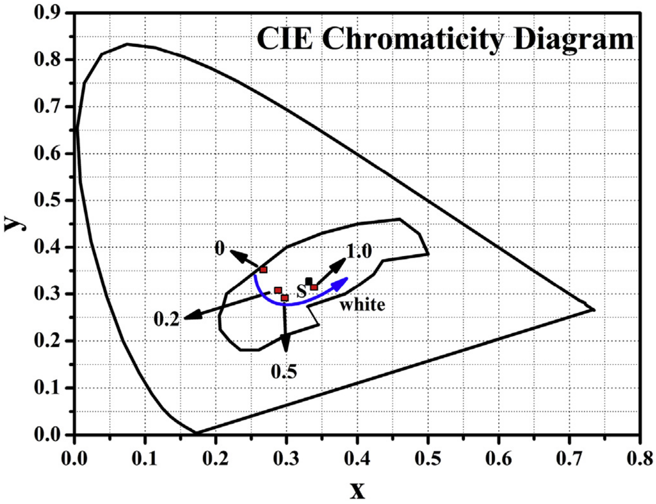


Fig. 3. Calculated color coordinates for the upconversion emissions of xMn^{2+} doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystals (x = 0.0, 0.2, 0.5, 1.0 mol%) under 980 nm excitation. S point is the standard white light coordinate (0.33, 0.33).

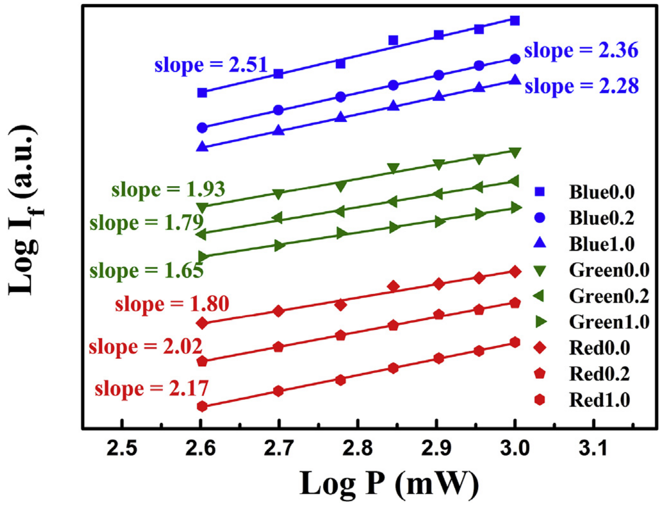


Fig. 4. The dependences of upconversion emission intensities on pump powers for 0.0 mol%, 0.2 mol% and 1.0 mol% Mn^{2+} doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} single crystals under 980 nm excitation.

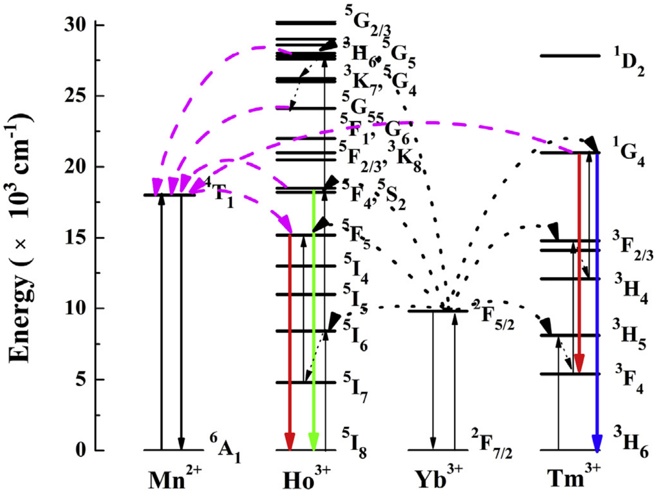


Fig. 5. Schematics of the populating and upconversion luminescence processes for the blue, green, and red emissions in the Mn^{2+} doped $LiNbO_3$:Ho^{3+}/Yb^{3+}/Tm^{3+} system under 980 nm excitation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to $^5F_5$ levels of Ho^{3+} ions. The trapping level ($^4T_1$ level) of Mn^{2+} ion can convert parts blue and green emissions of Tm^{3+} and Ho^{3+} ions into red emissions of Ho^{3+} ions. So it can be concluded that with the increase of Mn^{2+} ion concentration, the probability of the red emission transition is improved. As a result, the higher ratio of red-to-green can be achieved, which is beneficial to the purer white-light emission. Such standard white-light emission in this article should arise from the cross-relaxation of energy between Ho^{3+}, Tm^{3+} and Mn^{2+} ions.

4. Conclusions

we have reported a facile and straightforward strategy for controlling the upconversion white-light emission through Mn^{2+} ions doping. Based on the doping effect, the probability of the upconversion red emission transition is improved and the ratio of red-to-green is enhanced, which is induced by the cross-relaxation of energy between Ho^{3+}, Tm^{3+} and Mn^{2+} ions. As a result, the upconversion color coordinates have the trend of shift towards red region with increasing Mn^{2+} ion concentration. It is found that the upconversion emission is comparable with the standard white-light when the Mn^{2+} ion concentration is 1.0 mol%. Such ideal upconversion white-light in $LiNbO_3$ single crystal makes it have potential applications in photoelectric devices and instrument integration. Furthermore, this mechanism would stimulate further discovery to design upconversion process and fabricate other ideal white-light materials.

Acknowledgements

The authors gratefully acknowledge the financial support from National Natural Science Foundation of China (11504438, 51605499, 11374080 and 81601347), Natural Science Foundation of Guangdong Province (2015A030310348).

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