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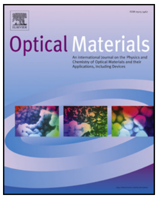

Impact of crystal defect on upconverted white-light emission in lanthanide-doped $LiNbO_3$ single crystal

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ABSTRACT

Efficient and stable upconversion white-light is critical for optical applications. Herein, $LiNbO_3$:Ho/Yb/Tm single crystals with different [Li]/[Nb] ratios were grown by Czochralski method. It is found that the crystal structures are not changed with [Li]/[Nb] ratios which varied from 0.946 to 0.991 in the single crystals. The RE ion concentrations are reduced faintly and crystal structures approach perfect with increasing the [Li]/[Nb] ratios. More ideal upconversion white-light is obtained when the [Li]/[Nb] ratio is close to 1. The integrated effects of intrinsic defect concentrations and RE ion concentrations affect the upconversion emission intensity of the single crystal. The lower crystal defect in the bulk single crystal has a positive impact on the enhancement of upconversion emission intensity. In addition, all the CIE coordinates are hardly changed with [Li]/[Nb] ratios and located in the white-light region. The upconversion mechanism analysis indicates the longer lifetimes of intermediate energy levels and the shorter lifetimes of luminous energy levels are beneficial to the upconversion process, and the larger intensity variation of upconversion emission arises from its greater lifetime variations of energy levels. The near-stoichiometric $LiNbO_3$:Ho/Yb/Tm single crystal demonstrates potential applications in stable white-light devices and photoelectric instruments.

1. Introduction

Lanthanide-doped upconversion white-light materials with unique optical properties have attracted much attentions due to their potential applications in multicolor display, bio-label, solar cell, optical temperature sensor, and so on [1–5]. As known, upconversion is an anti-stokes process which can convert two or more low-energy photons into a high-energy photon directly. Under near-infrared excitation, lanthanide-doped materials will exhibit desirable visible emissions. Currently, the single white-light materials are pursed in order to avoid the matching and cost problems when using multiphosphors [6–9]. On account of this, various lanthanide ions codoped in one host material has been considered as the most efficient approach to achieve white-light emission. Many researches focus on the Yb^{3+}, Ho^{3+} and Tm^{3+} tri-doped systems, where the Yb^{3+} ions act as sensitizers to efficiently absorb the near-infrared photons and transfer their energy to luminous ions Tm^{3+} and Ho^{3+} [10–12]. As a result, the blue, green and red emissions are generated simultaneously in one host material, and the white-light emission is produced under appropriate regulations. For practical applications, the top priority is to enhance the upconversion emission intensity and maintain the color stability. During the past few years, great endeavors have been paid to perfect the upconversion white-light properties, for example, modulation of rear earth (RE) ion concentration, controlled synthesis of host material, suitable selection of excitation source, the optimization of external temperature, and some other affecting factors, etc [13–16]. However, the adverse effects exist in the above approaches. In general, too high RE ion concentrations may induce the quenching of upconversion luminescence, while manipulations of host material structure and affecting factors are detrimental for application to some extent. Right now, the obtained upconversion white-light are not satisfying, it is of technological and scientific importance to look for a more effective way to improve the properties of upconversion white-light emission.

Worthy of notice, the local environment around the emitters plays an important role in improving luminescence behavior. It is assumed that the crystal field symmetry and crystal defect are the main forms of local environment. At present, a few reports have focused on the enhancement of upconversion emission intensity by codoping some non-luminous ions (Li^+, Na^+, etc.) in lanthanides doped upconverting materials [17–21]. The results show that these encouraging achievements derived from the distortion of crystal field symmetry, which is a promising way to increase the upconversion emission intensity recently. Furthermore, some researchers certified the reduction of crystal defect could dramatically enhance the upconversion emission intensity in

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Table 1
The optimum crystal growth conditions of $LiNbO_3$:Ho/Yb/Tm single crystals with different [Li]/[Nb] ratios.

Samples	[Li]/[Nb] ratio in melt	Temperature gradient above melt (°C/mm)	Pulling rate (mm/h)	Seed rotation rate (rpm)
1	0.946	25	0.3	30
2	1.000	25	0.2	28
3	1.250	25	0.2	25

nanocrystals [22,23]. In fact, we argue that it is equal importance to investigate the influence of crystal defect on upconversion properties in bulk single crystals, but the relative studies are still in their infancy. Herein, $LiNbO_3$ single crystal was chosen as the material to host RE ions, its lower phonon energy (about 880 cm^{-1}) [24] guarantees the higher upconversion efficiency [25]. Besides, the growth of bulk $LiNbO_3$ single crystal is realized with mature technology, and more remarkable, the [Li]/[Nb] ratio of $LiNbO_3$ single crystal can be easily tuned through Li^+ ion doping. In brief, $LiNbO_3$ single crystal can provide favorable conditions to explore the effect of crystal defect on luminescence properties by simply changing the [Li]/[Nb] ratio.

In this article, $LiNbO_3$:Ho/Yb/Tm single crystals with different [Li]/[Nb] ratios were grown to illuminate the impact of crystal defect on upconversion luminescence behavior. Under 980 nm excitation, the influences of [Li]/[Nb] ratios for $LiNbO_3$:Ho/Yb/Tm single crystals on the intensity and chromaticity of upconversion white-light emission were demonstrated, and the rational explanation was given based on crystal defect theory. Preferably, the multi-function of $LiNbO_3$ single crystal will create sufficient conditions for opening up new perspectives to the studies of integration and tiny devices.

2. Experimental

2.1. Single crystal growth

The $LiNbO_3$:Ho/Yb/Tm single crystals with different [Li]/[Nb] ratios were grown by the Czochralski method. The concentrations of Ho^{3+}, Yb^{3+} and Tm^{3+} ions in the melts were fixed to 0.025 mol%, 2.0 mol% and 0.2 mol%, and the [Li]/[Nb] ratios in the melts are 0.946, 1.000 and 1.250, respectively. The raw materials were Li_2CO_3, Nb_2O_5, Ho_2O_3, Yb_2O_3 and Tm_2O_3 with 4 N purity. Firstly, the RE-doped $LiNbO_3$ polycrystals were prepared by high temperature solid state method. The raw materials were weighed and thoroughly mixed for 24 h, underwent a heat treatment of 800 °C for 2 h to resolve Li_2CO_3 into Li_2O and CO_2, and then sintered at 1150 °C for 10 h to form polycrystals. Secondly, the RE-doped $LiNbO_3$ single crystals were grown along the [0 0 1] direction using a diametercontrolled Czochralski apparatus. To grow single crystals with good quality, the optimum growth conditions were selected, as shown in Table 1. After growth, the single crystal was cooled down to room temperature at a speed of 30 °C/h to release its thermal stress. It should be noted that single crystal growth becomes more difficult with increasing the [Li]/[Nb] ratio in the melt. So under the same temperature gradient above melt, the lower pulling rate and seed rotation rate were chosen to ensure the quality of bulk single crystal. For phase structure analyses, the samples were grinded into powder using an agate mortar. And for optical tests, Y-cut plates of the single crystals were cut and polished.

2.2. Measurements and characterization

The Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Optima-7500 type was used to measure the mass fractions of cations in the single crystals. To identify the crystallization phase, power X-ray diffraction spectra of $LiNbO_3$:Ho/Yb/Tm crystals with different [Li]/[Nb] ratios were measured by an XRD-6000 diffractometer using a copper Kα radiation source. The infrared absorption spectra and UV–visible absorption spectra were test by a infrared spectrometer with Nicolet iS10 type and UV–visible spectrophotometer with CARY type, respectively. And the upconversion luminescence spectra were recorded by Zolix-SBP300 grating spectrometer equipped with CR131 photomultiplier under 980 nm excitation at room temperature. In the measurement of luminescence decay dynamics, the continuous wave from 980 nm laser diode was tuned into pulsing by a signal generator, and the luminescence decay curves were measured by a digital phosphor oscilloscope (Tektronix DPO 4140). The CIE chromaticity coordinate for the upconversion fluorescence was calculated based on the 1931 CIE standard.

3. Results and discussion

3.1. Phase and structure analysis

It is well known that the crystal growth from melt exists in the segregation phenomenon. Based on the ICP-MS measurement, the molar compositions of cations in $LiNbO_3$:Ho/Yb/Tm single crystals with different [Li]/[Nb] ratios are obtained, which are list in Table 2. It can be concluded that the [Li]/[Nb] ratios in the single crystals are approximate to 1 with the increase of [Li]/[Nb] ratios in the melts. It means that the crystal structures are approaching perfect and crystal intrinsic defects are vanishing. Besides, the segregation coefficients of RE ions are decreased with increasing the [Li]/[Nb] ratios, resulting in the faint reductions of total molar concentrations for RE ions in the single crystals. It is also validated the doping of RE ions becomes difficult with the crystal structure perfecting.

In addition, in the single crystal growth process, the water-vapor was expect to cause H^+ ion to enter into $LiNbO_3$ crystal constantly in the form of OH^-. The stretching vibration of OH^- is sensitive to the local environment, and the variation of structure defect in $LiNbO_3$ crystal will induce the shift of infrared peak position for OH^- group, so this specialty can be used to detect the crystal defect forms [26–28]. From the classic lithium vacancy model, two types of intrinsic defects exist in the $LiNbO_3$ crystal, namely Li vacancy (vi_{Li}^-) and anti-site Nb (Nb_{Li}^{4+}), to form $3vi_{Li}^-$- Nb_{Li}^{4+}-OH^- defect center, the infrared absorption peak positions of OH^- group are located near 3483 cm^{-1}. But when the RE ions enter into crystal, in general, they occupy Nb_{Li}^{4+} sites firstly and then normal Li sites followed by normal Nb sites. When the RE ions begin to occupy normal Li sites, it forms RE_{Li}^{2+}-OH^- defect center, corresponding to the infrared absorption peak positions of OH^- at 3490 cm^{-1}. Similarly, with increasing the RE ion concentrations, the RE ions occupy both the normal Li sites and Nb sites to form RE_{Li}^{2+}-OH^--RE_{Li}^{2+} and RE_{Li}^{2+}-OH^- defect centers, resulting in the continuous violet shift of infrared absorption peak for OH^- group. Fig. 1(a) shows

Table 2
Molar compositions of cations in the melts or single crystals of $LiNbO_3$:Ho/Yb/Tm with different [Li]/[Nb] ratios.

Samples	[Li]/[Nb] ratio in melt	[Li]/[Nb] ratio in single crystal	$C_{RE}{}^{3+}$ in melt (mol%)			$C_{RE}{}^{3+}$ in single crystal (mol%)		
			Ho^{3+} (mol%)	Yb^{3+} (mol%)	Tm^{3+} (mol%)	Ho^{3+} (mol%)	Yb^{3+} (mol%)	Tm^{3+} (mol%)
1	0.946	0.946	0.025	2.0	0.2	0.016	3.04	0.298
2	1.000	0.979	0.025	2.0	0.2	0.015	3.02	0.298
3	1.250	0.991	0.025	2.0	0.2	0.011	2.99	0.295