



Upconversion photoluminescence properties of $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped YNbO_4 powder



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ABSTRACT

Upconversion luminescence characteristic about YNbO_4 powder material doped with Ho^{3+} and Yb^{3+} ions is reported. $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped YNbO_4 powder material is prepared through solid-state reaction, absorption spectrum of prepared sample is measured and spectral characteristic is calculated through Judd-Ofelt (J-O) theory. Emission spectrum of prepared sample excited under 980 nm laser diode (LD) is obtained, and results indicate that there are three groups of upconversion emission peaks located at 540 nm and 548 nm, 642 nm and 663 nm, 758 nm, respectively, which correspond to level transitions from ${}^5\text{F}_4$ to ${}^5\text{I}_8$, from ${}^5\text{F}_5$ to ${}^5\text{I}_8$, from ${}^5\text{F}_5$ to ${}^5\text{I}_7$ of Ho^{3+} ions. Curve fitting of relationship between upconversion luminescence intensity and working current of exciting LD is done, and the fitting results prove that this up-conversion luminescence are all two-photon absorption procedure.

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1. Introduction

Rare earth niobates have many advantages such as good chemical and electrochemical stability [1–3], photon-electron activity [4], ionic conductivity [5] and luminescence characteristic [6], etc., and can also be used as fluorescent powder in solid-state lighting field [7,8] and photo-catalyst field [4].

Yttrium orthoniobate YNbO_4 has been received considerable attention in recent years because of its excellent phosphor properties [9]. The pure YNbO_4 emits a broad emission band centered at 405 nm excited at wavelength 260 nm, which is associated with $[\text{NbO}_4]^{3-}$ groups from the crystalline lattice in YNbO_4 [10,11]. YNbO_4 has two crystalline forms: the high temperature tetragonal phase corresponding to the scheelite structure and the low temperature monoclinic phase (M-fergusonite) [12,13]. The reversible phase transition between the two phases has been observed in the temperature range 500–800 °C depending on the rare earth (RE) ion [14,15].

The compounds with ABO_4 composition are suggested to be excellent hosts for luminescent materials [16–20]. YNbO_4 belongs to this family of compounds. Introducing different rare-earth ions to YNbO_4 matrix will induce different photoluminescence phenomenon, depending on the type of the RE dopant. Loiko et al. [21]

have fabricated transparent glass-ceramics of $\text{Eu}^{3+}/\text{Yb}^{3+}$ doped YNbO_4 and investigated its optical spectroscopy and cooperative upconversion phenomenon. Dacanin et al. [22] have investigated temperature quenching of luminescence emission in $\text{Eu}^{3+}/\text{Sm}^{3+}$ doped YNbO_4 powders. Xiao et al. [23] have studied luminescent properties of micro-crystalline phosphors YNbO_4 doped with Eu^{3+} and Tb^{3+} . Chen et al. [24] has reported the excellent near-infrared quantum cutting luminescence of Tm^{3+} doped YNbO_4 powder phosphor. The photoluminescence properties of YNbO_4 doped with other RE ions (Dy^{3+} , Er^{3+} and Nd^{3+}) have also been reported [25–27].

Due to special energy level structure and richer absorption peaks, Ho^{3+} ions can be excited by photons or sensitized by other rare-earth ions easily to realize particle population of higher energy levels and obtain stronger blue or green luminescence. There are many researchers have studied upconversion luminescence properties of Ho^{3+} ions [28–31].

However, to the best of our knowledge, luminescence properties of Ho^{3+} ions in the host of YNbO_4 has not been investigated, and no investigation about optical absorption spectra of RE doped YNbO_4 and its Judd-Ofelt analysis is reported. The optical absorption spectra of rare earth ions helped for understanding their radiative properties. The sharp absorption lines arise from the 4f-4f electronic transition, which is electric dipole or magnetic dipole in character. The qualitative calculations of the intensities of these transitions can be implemented using Judd-Ofelt theory [32,33].

In this article, upconversion luminescence characteristic about

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YNbO₄ powder material doped with Ho³⁺ and Yb³⁺ ions is reported. Firstly, sample of Ho³⁺/Yb³⁺ co-doped YNbO₄ powder material is prepared through solid-state reaction and its phase composition is analyzed through X-ray diffraction (XRD) pattern. Secondly, absorption spectrum of sample is measured and spectral characteristic is calculated through Judd-Ofelt theory. Finally, upconversion emission spectrum excited under 980 nm laser diode is measured, and luminescence mechanism of sample is analyzed and elaborated. Moreover, curve of up-conversion luminescence power varying from exciting laser power is fitting, which proved that this upconversion luminescence all belong to two-photon absorption procedure.

2. Experiment

2.1. Material preparation

Weighing a share of raw material with mass of 10 g in accordance with mole ratio as Nb₂O₅:Y₂O₃:Ho₂O₃:Yb₂O₃ = 50:45.5:0.5:4. In raw material, rare earth oxide is spectroscopic reagent and others is analytical reagent.

Weighed raw material is grinded and mixed thoroughly in an agate mortar, then placed in a ceramic crucible. The ceramic crucible filled with raw material is put into a muffle furnace made up of silicon carbide rod and calcined at 1300 °C for two hours, then is taken out and cooled to room temperature naturally. Cooled sample is grinded again and prepared for measurement.

2.2. Measure equipment and setup of material characteristic

Diffuse reflection spectrum can be measured by using set-up shown in Fig. 1, white optical emitted from halogen tungsten lamp is guided into integrating sphere through an optical fiber, a part of incident white light is absorbed by measured powder sample placed above a standard reflection whiteboard, other incident white light is scattered in all directions. The scattered light will be scattered secondly or repeatedly when collided with wall of integrating sphere, so after many times of collision, remaining scattered light will has spatially uniform distribution in an integrating sphere. A fiber connector is used to guide remaining part of scattered light into a fiber spectrometer for measuring diffuse reflection spectrum.

In order to quantitatively measure diffuse reflection spectrum of the prepared sample, a measuring method is adopted as follows: at first, a share of pure YNbO₄ powder without RE ions dopant is placed at outlet of the integrating sphere and a diffuse reflection

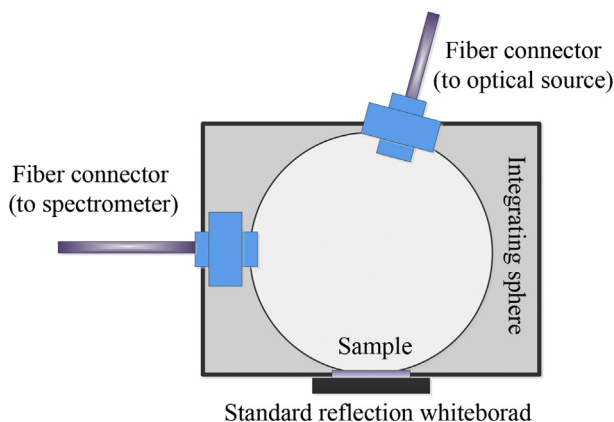


Fig. 1. Set-up diagram for measuring diffuse reflection spectrum.

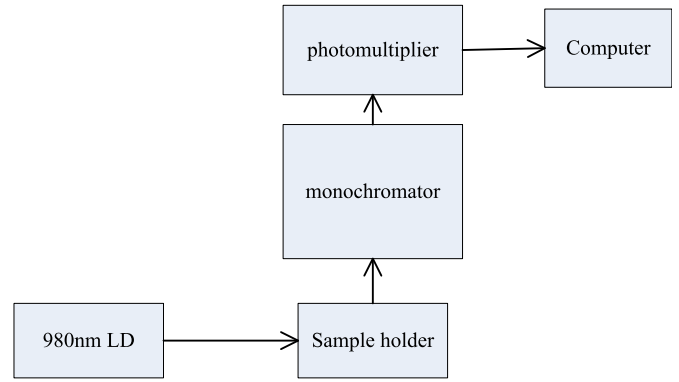


Fig. 2. Set-up diagram for measuring upconversion emission spectrum.

spectrum $I_0(\lambda)$ is measured; then prepared YNbO₄ powder sample doped with Ho³⁺ and Yb³⁺ ions is putted on standard diffuse reflection whiteboard and diffuse reflection spectrum $I(\lambda)$ is obtained by using integrating sphere and fiber spectrometer; at last, relative diffuse reflection spectrum can be obtained through: $R(\lambda) = I(\lambda)/I_0(\lambda)$, absorption spectrum of powder material can be obtained as follows:

$$\alpha(\lambda) = -\text{Ln}[R(\lambda)], \quad (1)$$

here, $\text{Ln}(f)$ means natural logarithm of function f .

Phase composition of prepared sample is measured by using Hitachi DMAX-3A X-ray diffraction (XRD) equipment, which has scanning scope from 10° to 80°.

Upconversion emission spectrum is obtain by adopting Zolix Omi-λ150 mono-chromator and PMTH-S1-CR131 photomultiplier, whose measuring setup is shown as Fig. 2. 980 nm laser emitted by laser diode (LD) is illuminated into measured samples fixed on a sample holder, and stimulated emission light from measured sample is collected into entrance slit of mono-chromator, and upconversion light with different wavelength is split into different exit angle by the mono-chromator and is incident on a photomultiplier selectively through exit slit of mono-chromator. Electrical signal converted by the photomultiplier is put into a computer and is recorded, so upconversion emission spectrum can be obtained.

3. J-O calculation method of spectral characteristic

The optical absorption spectra of rare earth ions helped for understanding their radiative properties. The sharp absorption lines arising from the 4f-4f electronic transitions can be electric dipole or magnetic dipole in character. The qualitative calculations of the intensities of these transitions have been developed independently by Judd [32] and Ofelt [33], called J-O theory.

In J-O theory, intensities of electric dipole transition can be expressed by:

$$S_{ed} = \sum \Omega_t \left| \langle 4f^N \psi_J \parallel U^+ \parallel 4f^N \psi'_J \rangle \right|^2 \quad (t = 2, 4, 6), \quad (2)$$

here, $\parallel U^+ \parallel$ are unit tensor operators and $|\langle 4f^N \psi_J \parallel U^+ \parallel 4f^N \psi'_J \rangle|^2$ are reduced matrix elements, which are related to category and transition levels of rare earth ions but independent of host medium, Ω_t represent spectrum line intensity parameters and are related to coordination property of rare-earth ions in host medium.

Spectrum line oscillator intensity of electric dipole transition can be expressed as:

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