Up-conversion Properties of Er3+/Yb3+ Co-doped Li3Ba2Gd3(MoO4)8 Phosphors (Post-print)

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Abstract

Er3+/Yb3+ co-doped Li3Ba2Gd3(MoO4)8 phosphors were synthesized by conventional solid state reaction method, and their structure and spectral properties were investigated. The diffuse reflectance spectra showed that the 4I15/2 → 4I11/2 transition of Er3+ and the 2F7/2 → 2F5/2 transition of Yb3+ ions were highly overlapped. Under the excitation of 980 nm, three up-conversion (UC) luminescence bands around 530, 555 and 660 nm were observed, corresponding to the 2H11/2 → 4I15/2, 4S3/2 → 4I15/2 and 4F9/2 → 4I15/2 transitions of Er3+ ions, respectively. The effects of the concentration and pumping power on the UC intensities of Li3Ba2Gd3(MoO4)8:Er3+/Yb3+ phosphors were investigated, and the possible UC mechanism was proposed based on the results.

Full Text

Preamble

Up-conversion Properties of Er³ /Yb³ Co-doped Li Ba Gd (MoO) Phosphors

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ABSTRACT

Er³ /Yb³ co-doped Li Ba Gd (MoO) phosphors were synthesized by conventional solid-state reaction method, and their structure and spectral properties were investigated. The diffuse reflectance spectra showed that the I / → I / transition of Er³ and the ²F / → ²F / transition of Yb³ ions were highly overlapped. Under 980 nm excitation, three up-conversion (UC) luminescence bands around 530, 555, and 660 nm were observed, corresponding to the ²H / → I / , S / → I / , and F / → I / transitions of Er³ ions, respectively. The effects of concentration and pumping power on the UC intensities of Li Ba Gd (MoO) :Er³ /Yb³ phosphors were investigated, and the possible UC mechanism was proposed based on the results.

Keywords: up-conversion; molybdate compounds; phosphors; energy transfer

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1. INTRODUCTION

As is well known, the up-conversion (UC) process provides a means to convert infrared pumping sources into visible radiation, which has potential applications in solid-state lasers, multicolor displays, solar cells, temperature sensing, and other fields [1-5]. Consequently, with the rapid development of diode lasers in the infrared region over recent decades, considerable attention has been devoted to infrared-to-visible UC luminescence materials. Among rare earth ions, Er³ is perhaps the most frequently investigated activator for UC processes, since its complex energy level scheme with numerous metastable excited states enables multi-step energy transfer and excited-state absorption processes. However, the primary disadvantage of Er³ is its low absorption cross-section in the laser diode emission range (0.8–1.5 μm), which severely limits pump efficiency. One effective solution is to add a second ion as a sensitizer, with Yb³ commonly serving this role due to its large absorption cross-section at 980 nm. Furthermore, the energy gap between the ²F / and ²F / levels of Yb³ is very close to those of the I / → I / and I / → F / transitions of Er³ , enabling efficient resonant energy transfer from Yb³ to Er³ .

The properties of host materials—including phonon energy, mechanical robustness, and thermal stability—also exert significant influence on UC performance. For achieving high UC efficiency, one critical requirement is that host materials should possess low phonon energy. Consequently, current candidate host materials for UC primarily focus on chlorides, fluorides, and sulfides. These materials are characterized by low phonon energy that yields high UC efficiency [6-8], but their applications are restricted by chemical instability and poor mechanical robustness [9]. Additionally, fluorides and sulfides inevitably cause environmental pollution due to their high fluorine and sulfur content. In recent years, molybdate-based materials have been intensively studied as promising hosts for solid-state lasers and luminescent phosphors owing to their excellent chemical stability, moderate synthesis conditions, and pollution-free

characteristics. Moreover, since they also possess relatively low lattice phonon energy, many molybdate compounds have been reported as UC hosts, such as CaMoO :Er³ /Yb³ [1], ALn(MoO) :Er³ /Yb³ (A = Li, Na, and K; Ln = La, Gd, and Y) [9], BaGd (MoO) :Er³ /Yb³ [10], Gd (MoO) :Er³ /Yb³ [11], and others.

The triple molybdate compounds Li Ba Re (MoO) (Re = La–Lu, Y) belong to the monoclinic system with space group C2/c. Historically, interest in these compounds focused primarily on bulk crystals to exploit their laser properties, benefiting from their excellent spectral characteristics and straightforward growth techniques. Notably, efficient laser performance has been achieved with Yb³ :Li Ba Gd (MoO) and Tm³ :Li Ba Lu (MoO) crystals [13]. In recent studies, Li Ba Re (MoO) has been further investigated as a potential host for rare earth ions in luminescent materials, with Eu³ -, Tb³ -, and Dy³ -doped Li Ba Re (MoO) phosphors reported for white-light emitting applications [14-16]. However, to our knowledge, these compounds have never been investigated as UC hosts. Therefore, in this work, Er³ /Yb³ co-doped Li Ba Gd (MoO) was synthesized by solid-state reaction, and its UC properties were characterized under 980 nm excitation. Additionally, the effects of Er³ /Yb³ concentration and pump power on UC emission were examined, and the possible UC mechanism is presented.

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2. EXPERIMENTAL

The Li Ba Gd (MoO) :Er³ /Yb³ phosphors were synthesized via solid-state reaction using Li CO (A.R.), BaCO (A.R.), Gd O (99.999%), Er O (99.99%), Yb O (99.99%), and MoO (A.R.) as raw materials. First, a stoichiometric mixture of the raw materials was ball-milled for 10 h using planetary milling with zirconia balls and ethanol as the medium. The dried powders were then placed in alumina crucibles and calcined at 900 °C for 6 h in air. Finally, the synthesized samples were ground into fine powders in an agate mortar for measurement.

The structures of Li Ba Gd (MoO) :Er³ /Yb³ phosphors were analyzed by X-ray powder diffraction (D8 Advance diffractometer, Bruker Corporation, Germany) with Cu K radiation (= 1.54056 Å, 40 kV, 30 mA). Diffuse reflection spectra were measured using a Shimadzu UV-vis-NIR spectrophotometer (UV-3600). UC luminescence spectra and luminescence decay curves were recorded using an Edinburgh Instruments FLS980 spectrophotometer equipped with an external power-controllable 980 nm semiconductor laser as the excitation source. All measurements were performed at room temperature.

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3. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of Li Ba Gd (MoO) :Er³ /Yb³ phosphors are shown in Fig. 1 [Figure 1: see original paper] and compared with that of pure Li Ba Gd (MoO) . All diffraction peaks of the synthesized samples are consistent with those of pure Li Ba Gd (MoO) from the powder standard card, and no additional diffraction peaks were observed, indicating that Er³ and Yb³ ions were completely incorporated into the host matrix, substituting for Gd³ ions. However, as shown in Fig. 1(b), the main diffraction peaks gradually shift to higher 2 angles with increasing Yb³ concentration, which is attributed to the smaller ionic radius of Yb³ compared to Gd³ .

To investigate the energy level structures of Er³ and Yb³ ions in the Li Ba Gd (MoO) host, the absorption spectra of Li Ba Gd (MoO) :Er³ /Yb³ phosphors were recorded. Fig. 2 [Figure 2: see original paper] shows the diffuse reflection spectra of Li Ba Gd (MoO) :20%Yb³ , Li Ba Gd (MoO) :2%Er³ , and Li Ba Gd (MoO) :2%Er³ /20%Yb³ phosphors. All samples exhibit a broad, smooth absorption band around 280 nm, corresponding to the O → Mo charge-transfer transition. Additionally, six prominent absorption bands around 380, 485, 520, 655, 800, and 975 nm are observed for the Li Ba Gd (MoO) :2%Er³ and Li Ba Gd (MoO) :2%Er³ /20%Yb³ phosphors. The first five absorption bands for these two samples are very similar and can be ascribed to intrinsic transitions of Er³ ions from the ground state I / to the excited states G / , F / , ²H / , F / , and I / , respectively. Notably, the absorption band around 975 nm in Li Ba Gd (MoO) :2%Er³ is much weaker than that in Li Ba Gd (MoO) :2%Er³ /20%Yb³ . For Li Ba Gd (MoO) :2%Er³ , the absorption band peaking at 975 nm corresponds to the I / → I / transition of Er³ ions, while for Li Ba Gd (MoO) :2%Er³ /20%Yb³ , the band at 968 nm represents the superposition of the ²F / → ²F / transition of Yb³ ions and the I / → I / transition of Er³ ions. For the Li Ba Gd (MoO) :20%Yb³ sample, only an intense band around 975 nm is observed, arising from the ²F / → ²F / transition of Yb³ ions.

Based on Fig. 2, the energy transfer process between Yb³ and Er³ ions in Li Ba Gd (MoO) should be highly effective due to the significant overlap between the I / → I / transition of Er³ and the ²F / → ²F / transition of Yb³ ions.

Under 980 nm excitation, the UC luminescence spectra of Li Ba Gd (MoO) :2%Er³ /xYb³ (x = 8%, 12%, 16%, 20%, 24%, 28%) phosphors were recorded in the wavelength range of 500–700 nm, as shown in Fig. 3 [Figure 3: see original paper]. All spectra display similar profiles consisting of three emission bands around 530, 555, and 660 nm. The green emission bands at 530 and 555 nm can be ascribed to the ²H / → I / and S / → I / transitions of Er³ ions, respectively. The multiple peaks in these green bands are caused by crystal-field Stark splitting. The red emission band at 660 nm corresponds to the F / → I / transition of Er³ ions. In our previous research, a weak

emission band at 490 nm originating from the F / → I / transition of Er³ ions was observed in Er³ :Li Ba Gd (MoO) single crystals under 980 nm excitation [17]. However, this emission band is not observed in the present study, likely because polycrystalline Li Ba Gd (MoO) contains significantly more defects than single-crystal material. These defects act as non-radiative recombination centers and substantially depopulate the F / state. The inset of Fig. 3 shows the integrated intensities of the green and red emission bands as a function of Yb³ concentration. Both green and red emission intensities increase significantly with Yb³ concentration, indicating efficient Yb³ → Er³ energy transfer. However, when the Yb³ concentration exceeds 20 mol%, both intensities decrease due to concentration quenching. This quenching effect arises from energy transfer between neighboring Er³ and Yb³ ions. As the Er³ and Yb³ concentrations increase, the interionic distance decreases, and non-radiative energy transfer becomes more pronounced [9], leading to reduced emission intensities from Er³ ions.

To understand the UC mechanism in Li Ba Gd (MoO) :Er³ /Yb³ , the UC luminescence spectra of Li Ba Gd (MoO) :2%Er³ /20%Yb³ phosphors were measured at various pumping powers (Fig. 4 [Figure 4: see original paper]). While the spectral profiles show little variation, emission intensities increase with pumping power. The relationship between UC luminescence intensity and pumping power can be described by the following equation [18]:

$$I_{em} \propto P_{pump}^{n}$$

where I_{em} is the UC luminescence intensity, P_{pump} is the pumping power, and n represents the number of photons involved in the UC process. Plots of $\ln(I_{em})$ versus $\ln(P_{pump})$ for the three emission bands yield straight lines, as shown in the inset of Fig. 4. Linear fitting gives slope values n of 2.03, 1.85, and 1.80 for the 530, 555, and 660 nm emissions, respectively, which are close to 2. This indicates that a two-photon process is involved in the UC mechanism for the Li Ba Gd (MoO) :Er³ /Yb³ system.

The UC mechanism in Er³ /Yb³ co-doped systems has been extensively investigated in numerous studies [1-6] and can be described by the energy level diagram shown in Fig. 5 [Figure 5: see original paper]. Under 980 nm excitation, Yb³ ions are excited to the ²F / state. Meanwhile, Er³ ions can also be excited to the I / state through ground-state absorption (GSA) and energy transfer (ET) processes:

GSA: I / (Er³) + a photon (980 nm) → I / (Er³)
ET: I / (Er³) + ²F / (Yb³) → I / (Er³) + ²F / (Yb³)

Since the lifetime of the I / state of Er³ is very long [19], the population in this excited state can be further promoted to the upper F / state through excited-state absorption (ESA) and energy transfer processes:

ESA: I / (Er^3) + a photon (980 nm) → F / (Er^3)
ET: I / (Er^3) + ^{2}F / (Yb^3) → F / (Er^3) + ^{2}F / (Yb^3)

Some population in the F / state relaxes non-radiatively to the ^{2}H / and S / states, producing the green emissions at 530 and 555 nm, respectively. Simultaneously, some population in the F / state relaxes non-radiatively to the F / state, from which the red emission at 660 nm originates.

The decay curves of the ^{2}H / → I / (530 nm), S / → I / (555 nm), and F / → I / (660 nm) transitions of Er^3 ions in Li Ba Gd (MoO) :2%Er^3 and Li Ba Gd (MoO) :2%Er^3 /20%Yb^3 samples were measured under 980 nm excitation. As shown in Fig. 6 [Figure 6: see original paper], the decay curves for the three transitions in Li Ba Gd (MoO) :2%Er^3 exhibit typical single-exponential behavior, with lifetimes calculated to be 21.6, 20.7, and 22.4 μs through linear fitting. In contrast, the decay curves for the Li Ba Gd (MoO) :2%Er^3 /20%Yb^3 sample are non-single-exponential and can be fitted with a second-order exponential model:

$$I = A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2)$$

where I is the UC luminescence intensity, A_1 and A_2 are constants, and t_1 and t_2 are the lifetimes of the exponential components. The values of A_1, A_2, t_1, and t_2 are presented in Table 1 . The mean lifetimes for the three transitions in the Li Ba Gd (MoO) :2%Er^3 /20%Yb^3 sample can be calculated using the following equation [20]:

$$\tau_{mean} = \frac{A_1 t_1^2 + A_2 t_2^2}{A_1 t_1 + A_2 t_2}$$

The mean lifetimes for Li Ba Gd (MoO) :2%Er^3 /20%Yb^3 are also listed in Table 1. These lifetimes are significantly longer than those in the Li Ba Gd (MoO) :2%Er^3 sample, which can be attributed to energy transfer from Yb^3 to Er^3 ions.

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4. CONCLUSION

A series of Li Ba Gd (MoO) :Er^3 /Yb^3 phosphors were synthesized by conventional solid-state reaction, and their structures were confirmed by X-ray diffraction. Under 980 nm excitation, the samples exhibited a weak red UC emission at 660 nm and two strong green UC emissions at 530 and 555 nm. With a fixed Er^3 concentration of 2 mol%, the effects of Yb^3 concentration on UC luminescence properties were investigated, and the optimal Yb^3 concentration was determined to be 20 mol%. The relationship between UC emission intensities and pumping powers was examined, revealing that a two-photon process is responsible for all three observed UC emissions. The lifetimes of both

Li Ba Gd (MoO) :2%Er³ and Li Ba Gd (MoO) :2%Er³ /20%Yb³ samples were measured, demonstrating that Yb³ introduction significantly enhances the lifetimes of Er³ ions.

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Table 1. Lifetimes of the ^{2}H / , S / , and F / States of Er^3 Ions in Li Ba Gd (MoO) :2%Er^3 and Li Ba Gd (MoO) :2%Er^3 /20%Yb^3 Samples

Samples	Transitions	Lifetime (μs)
Li Ba Gd (MoO) :2%Er^3/	→ I /	21.6
	S / → I /	20.7

Samples	Transitions	Lifetime (μs)
Li Ba Gd (MoO) :2%Er³ //20%Yb³	F / → I /	22.4
		A = 1211.6, t = 117.8; A = 11.2, t = 537.2; = 134.7
	S / → I /	A = 510.6, t = 162.7; A = 1025.3, t = 66.4; = 119.3
	F / → I /	A = 874.9, t = 83.8; A = 311.1, t = 238.4; = 161.5

Fig. 1. XRD patterns of Li Ba Gd (MoO) :2%Er³ /xYb³ with different Yb³ concentrations.

Fig. 2. Diffuse reflectance spectra of Li Ba Gd (MoO) :2%Er³ , Li Ba Gd (MoO) :20%Yb³ , and Li Ba Gd (MoO) :2%Er³ /20%Yb³ .

Fig. 3. UC luminescence spectra of Li Ba Gd (MoO) :2%Er³ /xYb³ with different Yb³ concentrations. The inset shows the dependence of green and red UC emission intensity on Yb³ concentration.

Fig. 4. UC luminescence spectra of Li Ba Gd (MoO) :2%Er³ /20%Yb³ at different pumping powers. The inset shows the power dependence of UC emission intensity at 530, 555, and 660 nm.

Fig. 5. Energy level scheme of Er³ and Yb³ in Li Ba Gd (MoO) and the possible UC mechanisms under 980 nm excitation.

Fig. 6. Decay curves of the ²H / , S / , and F / states for Li Ba Gd (MoO) :2%Er³ (black) and Li Ba Gd (MoO) :2%Er³ /20%Yb³ (red) samples.

Note: Figure translations are in progress. See original paper for figures.