Available online at www.sciencedirect.com

ScienceDirect

JOURNAL OF RARE EARTHS

ELSEVIER

*JOURNAL OF RARE EARTHS, Vol. 33, No. 5, May 2015, P. 475*

www.re-journal.com/en/

# Blue upconversion of $Tm^{3+}$ using $Yb^{3+}$ as energy transfer bridge under 1532 nm excitation in $Er^{3+}$, $Yb^{3+}$, $Tm^{3+}$ tri-doped $CaMoO_4$

LI Xinyue (李心悦)[1], ZHOU Shaoshuai (周少帅)[1], JIANG Guicheng (姜桂铖)[2], WEI Xiantao (韦先涛)[1], CHEN Yonghu (陈永虎)[1], YIN Min (尹 民)[1,*]

*(1. Department of Physics, University of Science and Technology of China, Hefei 230026, China; 2. Condensed Matter Science and Technology Institute, Harbin Institute of Technology, Harbin 150001, China)*

Received 2 December 2014; revised 2 March 2015

---

**Abstract:** Nano-sized $CaMoO_4$ phosphors tri-doped with $Er^{3+}$, $Yb^{3+}$ and $Tm^{3+}$ ions were successfully synthesized by sol-gel method. Intense blue emission from $Tm^{3+}$ ions was observed upon excitation of 1532 nm infrared light in Er-Yb-Tm system, while this blue upconversion could not be achieved with the absence of $Yb^{3+}$ ions in Er-Tm co-doped sample. In order to understand this upconversion process, the upconversion spectra in these samples were investigated, and the possible mechanism was proposed based on experimental results. It showed that two different energy transfer from $Er^{3+}$ to $Tm^{3+}$ existed simultaneously in Er-Yb-Tm system, the one-step direct energy transfer from $Er^{3+}$ to $Tm^{3+}$, and the two-step $Er^{3+}\rightarrow Yb^{3+}\rightarrow Tm^{3+}$ energy transfer. In particular, the $^1G_4$ state of $Tm^{3+}$ could only be populated from the $^3H_4$ state by cross-relaxation with an excited $Yb^{3+}$ ion, producing blue emission of $Tm^{3+}$. In this upconversion process, $Yb^{3+}$ ions acted as an energy transfer bridge between $Er^{3+}$ and $Tm^{3+}$, which also meant that the upconversion of other rare-earth ions under the excitation of 1532 nm was possible with the presence of $Er^{3+}$ and $Yb^{3+}$.

**Keywords:** upconversion luminescence; $CaMoO_4$ nanograins; energy transfer; rare earths

---

Over the past decades, growing attention has been paid on lanthanide doped luminescent materials for their upconversion from near infrared radiation to visible light, offering very large anti-Stokes shifts, sharp f–f emission peaks, long lived excited states and high photostability[1–5]. Superior to organic fluorescent dyes and quantum dots, lanthanide doped upconversion materials have exhibited various potential applications in temperature sensors[6–8], solid state lasers, photovoltaic solar cells[9], three-dimensional displays, high density optical data storage, scintillators, and fluorescent bio-imaging[10]. Considerable efforts have been devoted to tuning upconversion emissions, typically involving manipulating dopant/host combinations and dopant concentrations.

Trivalent erbium ($Er^{3+}$), in particular, is an outstanding candidate for upconversion luminescence and can be used as both a sensitizer and/or an activator, for its ladder-like energy level structure over a broad spectral range, providing opportunities to produce intense visible and infrared upconversion emission. In particular, $Er^{3+}$ ions have strong absorption at ~1532 nm, corresponding to the $^4I_{13/2}$ state. Furthermore, excited $Er^{3+}$ ions can also transfer energy to other rare earth ions such as $Yb^{3+}$, $Gd^{3+}$ [11] and $Eu^{3+}$ [12], then sensitize them to realize their upconversion luminescence. However, only a few reports focused on upconversion luminescence using $Er^{3+}$ ions as sensitizers under the excitation of 1532 nm laser[13,14]. Recently many studies have been done on the metal molybdate families, especially for calcium molybdate ($CaMoO_4$) phosphor. It has been proved to be an excellent luminescent material with high upconversion efficiency for potential application[15,16], owing to its remarkable optical, thermal, chemical properties, superior photostability, high density and reflection coefficient, as well as a low phonon threshold energy. Moreover, the $Mo^{6+}$ ions in $CaMoO_4$ matrices have strong polarization induced by large electric charge and small radius, accounting for the decreased symmetries, and enhanced stark energy split in the crystal field[17].

Therefore, in this work, we employed $CaMoO_4$ as a suitable matrix, and $Er^{3+}$ as a sensitizer, $Yb^{3+}$ as an efficient energy transfer bridge, and $Tm^{3+}$ as a activator, and the upconversion luminescence from $Er^{3+}$ and $Tm^{3+}$ ions was investigated in $Er^{3+}$, $Yb^{3+}$, $Tm^{3+}$ tri-doped $CaMoO_4$ nanograins. Under the excitation of 1532 nm laser, $Er^{3+}$ ions could absorb photons efficiently through ground state absorption and excited state absorption, and directly transfer energy to $Tm^{3+}$ ions by populating them to excited $^3H_4$ state, resulting in the near-infrared emission of $Tm^{3+}$. On the other hand, the $^3H_4$ state could also be

---

**Foundation item:** Project supported by the National Natural Science Foundation of China (11204292, 11274299, 11311120047, 11374291, 11404321), and Anhui Provincial Natural Science Foundation (1308085QE75)

* **Corresponding author:** YIN Min (**E-mail:** yinmin@ustc.edu.cn; **Tel.:** +86-551-63606912)

**DOI:** 10.1016/S1002-0721(14)60443-9

populated through two-step energy transfer process from $Er^{3+}$ to $Yb^{3+}$ to $Tm^{3+}$. But the excited $^1G_4$ state could only be reached from $^3H_4$ state by cross-relaxation with excited $Yb^{3+}$ ions, then producing blue emission. The possible mechanism for these upconversion emissions was discussed based on our experimental results.

## 1 Experimental

The powder phosphors of $CaMoO_4$ were synthesized by the sol-gel method[18,19]. All of the chemicals were of analytical-grade reagents and used without further purification. The $RE(NO_3)_3$ standard solutions were prepared by dissolving the respective rare earth oxide (99.99%) in dilute nitric acid at elevated temperature. The starting materials, including $Ca(NO_3)_2{\cdot}4H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $RE(NO_3)_3$, $LiNO_3$ and citric acid monohydrate which served as the chelating agent for metal ions, were mixed with the desired stoichiometric ratio. Under vigorous stirring for 30 min, the mixtures were heated in an 80 ºC water bath to form a yellow transparent gel. After sintering the precursor gel at 700 ºC for 4 h, the samples could be obtained.

The phase identification of the $CaMoO_4$ phosphors was characterized by an X-ray diffractometer (MAC Science Co., Ltd., MXP18AHF) using nickel-filtered Cu Kα radiation ($\lambda$=0.15418 nm) in the $2\theta$ range from 10º to 70º. The size and morphology were obtained by a field emission scanning electron microscope (FESEM, Model FEI, Sirion 200). The upconversion emission spectra, using a 1532 nm diode laser as the excitation source, were measured with a Jobin-Yvon HRD-1 double monochromator and a Hamamatsu R928 photomultiplier. The signal was analyzed by an EG&G 7265 DSP lock-in amplifier and stored into computer memories. All the measurements were performed at room temperature.

## 2 Results and discussion

The XRD pattern for the $CaMoO_4$ sample is shown in Fig. 1. All diffraction peaks could be assigned to a scheelite-type structure of $CaMoO_4$ with space group $I4_1/a$ (No. 88), which are indexed by the standard powder diffraction file card JCPDS No. 77-2239, and no second phase is detected, suggesting that the sample was successfully synthesized via the sol-gel method. The fairly narrow full width at half maximum and intense diffraction peaks indicate the fine crystallization of the phosphors. The morphology and size of the $CaMoO_4$ phosphors were confirmed in the SEM graph as is depicted in Fig. 2, revealing a fine and grain-shaped morphology with nano-sized particles.

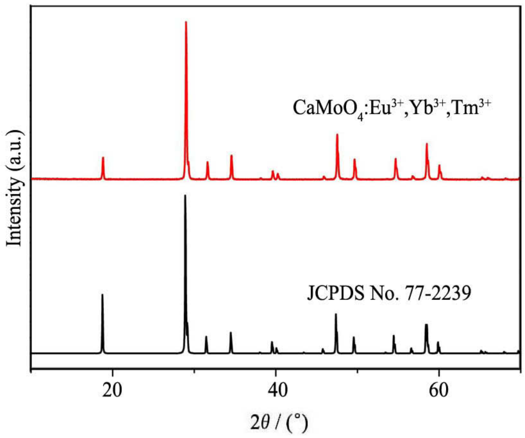

Fig. 1 XRD pattern of $CaMoO_4:Er^{3+},Yb^{3+},Tm^{3+}$ sample (The standard data for $CaMoO_4$ (JCPDS No. 77-2239) is also presented in the figure)

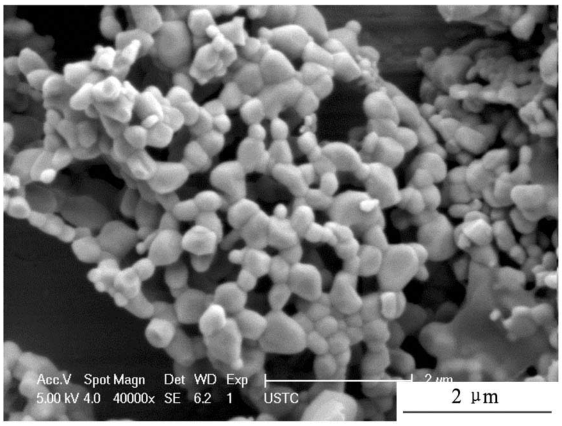

Fig. 2 SEM image for $CaMoO_4$ phosphor

Under the excitation of a 1532 nm diode laser, the upconversion emissions were observed in $CaMoO_4$:2 mol.% $Er^{3+}$,16 mol.%$Yb^{3+}$,0.5 mol.%$Tm^{3+}$ nanograins, as is presented in Fig. 3. In the range of visible light, several characteristic emission bands could be clearly resolved. The emission that centered at 475 nm originates from the $^1G_4{\to}^3H_6$ transition of $Tm^{3+}$ ions, while the remaining emission bands are centered at 521, 545, and 653 nm, which correspond to the transitions from the $^2H_{11/2}$, $^4S_{3/2}$,

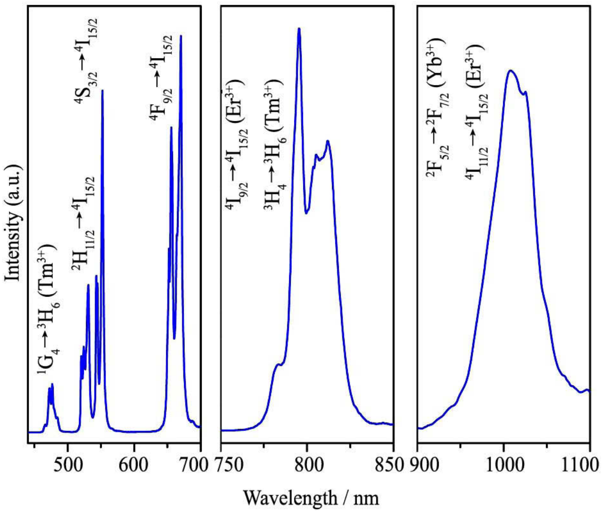

Fig. 3 Upconversion emission spectra of $CaMoO_4:Er^{3+},Yb^{3+},Tm^{3+}$ nanograins under the excitation of 1532 nm at room temperature (The intensity scale is different)