

Luminescent properties of Tb³⁺ doped CaMoO₄ nanophosphor for fluorescent lamp application.

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Abstract: A green-emitting CaMoO₄ co-doped by Tb³⁺ nanophosphor was fabricated by solid-state metathesis reaction route for the first time. X-ray powder diffraction (XRD) analysis revealed that pure CaMoO₄ was obtained. Under excitation of UV light, these CaMoO₄:x Tb³⁺ phosphors showed a strong emission band centered at 547 nm (green) which corresponds to ⁵D₄→⁷F₅ transition of Tb³⁺. Analysis of the emission spectra with different Tb³⁺ concentrations revealed that the optimum dopant concentration for CaMoO₄: x Tb³⁺ phosphors are about 8 mol% of Tb³⁺. All properties show that CaMoO₄: x Tb³⁺ is a very appropriate green-emitting phosphor for fluorescent lamp applications.

Keywords: rare earth ions, phosphors, solid-state metathesis reaction, green emission.

Introduction

Because rare earth ions retain a great deal of energy levels and may transfer between 4f electrons, its fluorescence wavelength ordinarily extends from UV to IR range. Thus, the addition of trivalent rare earth ions as luminescent center to matrices is thought-out as an exemplary method for synthesising excellent luminescent material [1–2]. Tb³⁺-doped materials have been extensively employed as the green emitting phosphors by virtue of their strong ⁵D₄→⁷F₅ emission in the green spectral region. Earlier investigations have demonstrated that Tb³⁺-doped aluminates and phosphates displayed almost intense absorption in the UV region and illustrate strong green emission with satisfying color purity. However, the conventional aluminate, borate and phosphate phosphor have their defects respectively [3–4]. CaMoO₄ is an illustrative scheelite compound, and its central Mo metal ion is organized by four O²⁻ ions in tetrahedral symmetry (*Td*). For CaMoO₄ phosphor, green emission arises under UV-light excitation (250–310 nm), but the orange emission at 580nm is observable only if the excitation wavelength is longer than 320nm [5]. However, the introduction of Tb³⁺ influences upon the luminescence of the host material.

In continuation to our previous work on the red luminescent CaMoO₄:Eu³⁺ [13], in the present work we have undertaken the green luminescent Tb³⁺ in CaMoO₄ powder phosphor for its systematic optical characterization.

Experimental Method

Preparation of Phosphors

The green phosphors of CaMoO₄: x Tb³⁺ (x= 0.02, 0.04, 0.06, 0.08 and 0.10 mol) were prepared by mechanochemically assisted solid state metathesis reaction route at room temperature. The chemical equation in this method is as follows:



The beginning chemicals were logical in evaluation, for example, CaCl_2 , Na_2MoO_4 and TbCl_3 (99.9%). Stoichiometric measures of the starting materials were blended and were processed for a time of two hours in a planetary ball mill Pulverisette- 7 (FRITSCH). Processing was fulfilled in two granulating vials of 15 cm volume comprising of balls with a measurement of 12 mm. Both the compartment and balls were made of tungsten carbide material. The quantity of processing balls and the revolution rate of the planetary arrangement of processing gadget were kept consistent. The resultant powder was washed a few times with refined water to uproot sodium chloride that was the by-result of the response and afterward dried at 80°C for 3h in a furnace in air and sieved. At long last, the productive green phosphor material was gotten.

Measurements

X – ray powder diffraction (XRD) analysis was carried out using Pan Analytical X'pert pro x- ray diffractometer with Cu K-alpha radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of 0.02° per second. The morphology of the powder samples were inspected by using scanning electronic microscope (SEM Philips XL30). The measurements of PL and photoluminescence excitation (PLE) spectra were performed by a Jobin Yvon Fluorolog-3-11 Spectrofluorometer with 450W xenon lamp was used as the excitation source (200-700 nm). All spectroscopic measurements of the phosphors were carried out at room temperature.

Results and discussion

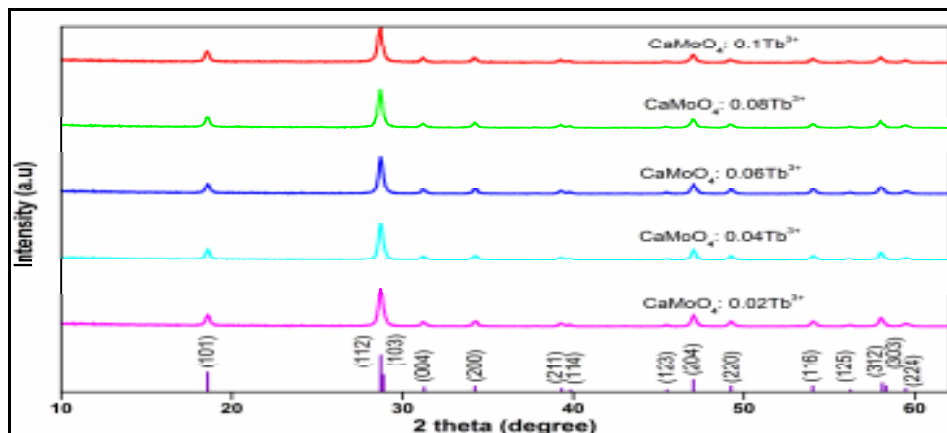


Fig. 1 XRD patterns of $\text{Ca}_{1-x}\text{MoO}_4: x \text{Tb}^{3+}$ ($x = 0.02, 0.04, 0.06, 0.08$ and 0.1 mol)

Fig. 1 displays the XRD patterns of $\text{Ca}_{1-x}\text{MoO}_4: x \text{Tb}^{3+}$ ($x = 0.02, 0.04, 0.06, 0.08$ and 0.1 mol) phosphor samples prepared by mechanochemically assisted solid state metathesis reaction route at room temperature. It can be seen that all diffraction peaks are consistent well with JCPDS 851267 standard data of CaMoO_4 . The peaks in the XRD spectra are sharp and intense proving that a highly crystalline single-phase of tetragonal scheelite structure of CaMoO_4 had been successfully synthesized by mechanochemically assisted solid state metathesis reaction route at room temperature. No impurity peak was found in the XRD patterns, distinctly indicating the incorporation of Tb^{3+} ions into the compounds.

Raman spectra of the as synthesized $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ phosphor material exhibits several peaks referring to the Raman-active internal mode vibrations in the tetrahedral $[\text{MoO}_4]^{2-}$ units as shown in figure 2(a). Those at around $871, 843, 793, 393, 322$ and 210 cm^{-1} which correspond to $\nu_1(\text{A}_g), \nu_3(\text{B}_g), \nu_3(\text{E}_g), \nu_4(\text{B}_g), \nu_2(\text{A}_g)$ and $\nu_{\text{free rotation}}(\text{A}_g)$ vibrations for $\text{Ca}_{1-x}\text{MoO}_4: x \text{Tb}^{3+}$ [6-7].

The FTIR spectra of $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ phosphor is shown in Fig.2 (b) and it displays a very weak absorption band around 429 cm^{-1} which is associated with the bending modes of vibration of Mo-O. A very broad strong absorption band around 801 cm^{-1} is due to anti- symmetric stretching vibrations of O-Mo-O in MoO_4^{2-} tetrahedron [14]. The weak absorption band around 3418 cm^{-1} is due to O-H stretching vibration and the bands around 1630 cm^{-1} are due to H-O-H bending vibration of water absorbed from air [8].

The morphology of the crystalline $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ nano particles are obviously exhibited by SEM image, as indicated in Fig.2(c). The powder particles give off an impression of being profoundly crystalline and are slightly agglomerated. However, no significant differences were monitored in the SEM images for the powder samples with different Tb^{3+} concentrations. The average grain size of the near rounded nano particles is about 65 nm which is in full agreement with the data from the XRD patterns.

The particle size distribution of $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ phosphor sample prepared by this method is shown in Fig. 2(d). The particles show a narrow size distribution, with the average diameter of particles at 64 nm, indicating that the particles are fit for the fabrication of solid state lighting devices. [9]

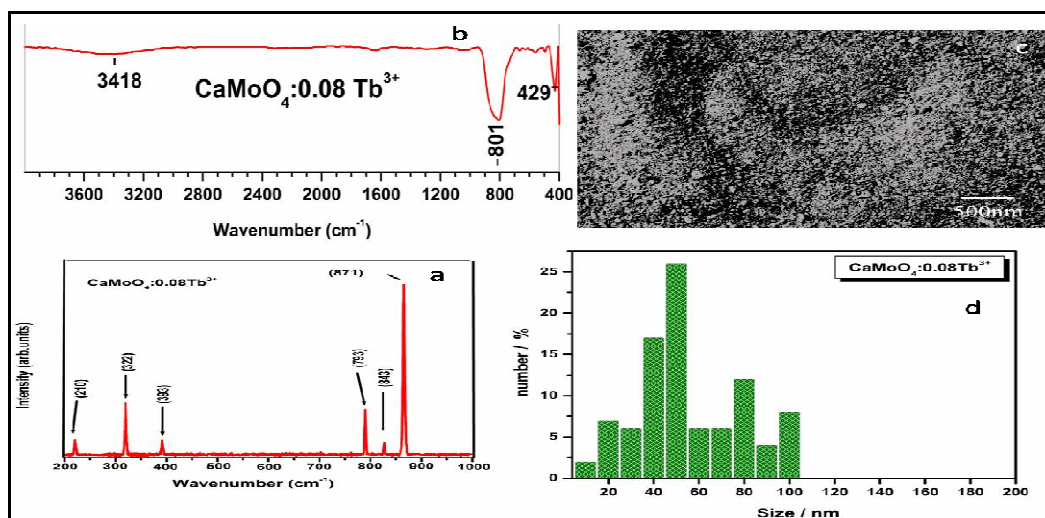


Fig. 2 (a) Raman spectra of the as prepared $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ (b) FTIR spectra of the as prepared $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ phosphor (c) SEM image of the as prepared $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ phosphor (d) Particle size distribution of as prepared $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ phosphor

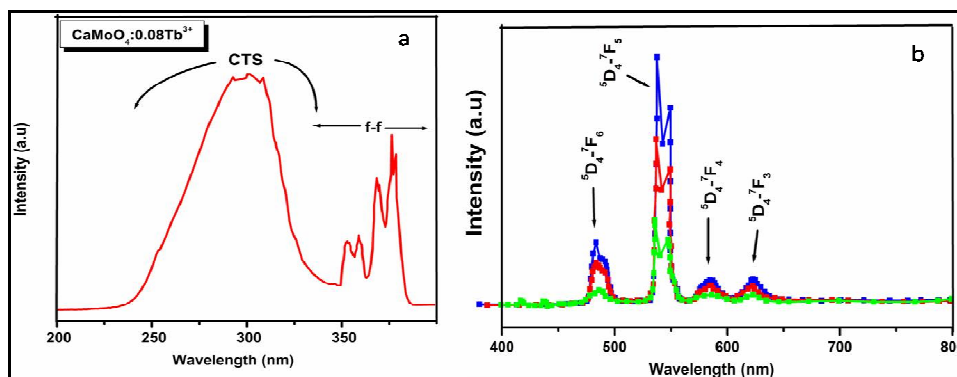


Fig. 3 (a) The excitation spectrum of $\text{CaMoO}_4: 0.08 \text{Tb}^{3+}$ at the emission wavelength of 545 nm (b) The emission spectrum of $\text{Ca}_{1-x}\text{MoO}_4: x \text{Tb}^{3+}$ ($x = 0.02, 0.08$ and 0.1 mol)

The excitation and emission spectra of $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ phosphors prepared by solid state metathesis reaction route at room temperature is shown in Fig. 3(a). The excitation spectrum is monitored at the emission wavelength of 547 nm. It can be seen clearly that the excitation spectrum consists of a strong and broad band from 230 to 330 nm with a maximum at about 299 nm assigned as the charge-transfer band (CTB) originated from oxygen to molybenum within the MoO_4^{2-} groups. The other sharp lines including the peaks from 350 nm to 500 nm are attributed to the intra-configurational f-f transition absorption of Tb^{3+} ions in the host lattice. [10]

When the CTB is excited, the energy absorbed from charge-transfer state is efficiently transferred to Tb^{3+} ion by a non-radiative mechanism, and generate green-light emission of the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transition of Tb^{3+} ions in the $\text{CaMoO}_4: 0.08\text{Tb}^{3+}$ nanophosphors. [11]

Upon excitation at 299 nm, the obtained emission spectrum exhibits four major emission bands at 487, 547, 590 and 623 nm, corresponding to the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$ typical transitions of Tb^{3+} , as shown in Fig 3(b) respectively. The strongest peak appears at 547 nm is the characteristic emission of Tb^{3+} with $^5D_4 \rightarrow ^7F_5$ green emission 547 nm. Compared with the emission of Tb^{3+} , the intrinsic emission from MoO_4^{2-} groups is very weak, suggesting that an efficient energy transfer from MoO_4^{2-} to Tb^{3+} has occurred in the $CaMoO_4: x Tb^{3+}$ ($x = 0.02, 0.08$ and 0.10 mol) phosphors. Only the transitions from 5D_4 to lower lying 7F_J levels are observed at room temperature upon excitation in the UV range.

The concentration quenching occurs when the Tb^{3+} concentration is beyond 8 mol%. The reason for the concentration quenching is that if the Tb^{3+} concentration continues to increase, the interaction of $Tb^{3+}-Tb^{3+}$ also increases, consequently, the emission intensity becomes lower.[12]

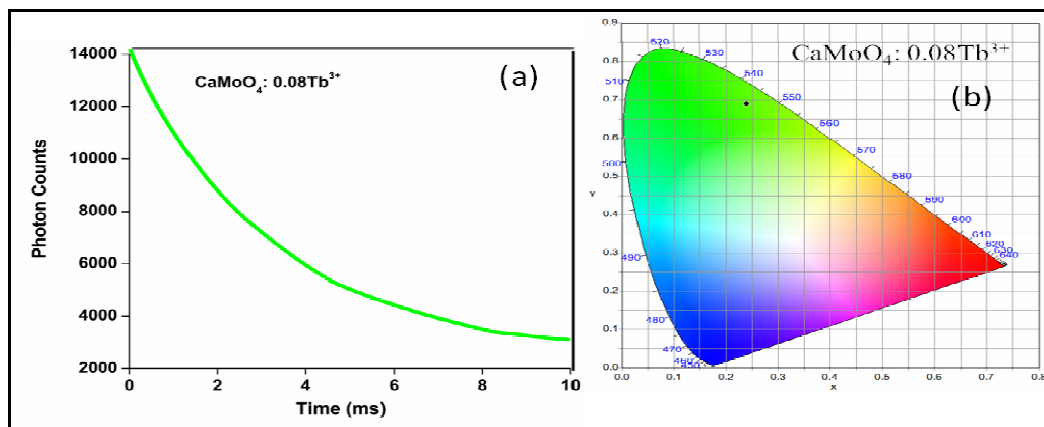


Fig. 4 (a) The luminescence decay of the transition at 546nm of 0.08 mol Tb^{3+} doped $CaMoO_4$ phosphor sample (b) The CIE chromaticity diagram for the as prepared $CaMoO_4:0.08Tb^{3+}$ phosphor

The luminescence decay of the transition at 546nm of 0.08 mol Tb^{3+} doped $CaMoO_4$ phosphor sample has been studied at room temperature and is demonstrated in Fig.4 (a). The measured lifetime (means) for the $^5D_4 \rightarrow ^7F_5$ transition has been resolved from the decay curve which is represented by the $I = I_0 Ae^{-t/\tau}$. Where 'A' is the amplitude and ' τ ' is the fluorescence life time. Decay curve for $CaMoO_4: 0.08Tb^{3+}$ phosphor can be fitted to a single exponential and life time is calculated to be 0.51ms.

Fig.4 (b) shows the CIE chromaticity diagram for the emission spectra of $CaMoO_4: 0.08Tb^{3+}$ 299 nm excitation wavelength. The emission color was analyzed and confirmed with the help of Commission Internationale de l'Eclairage CIE chromaticity coordinates x,y. The calculated CIE coordinates for the $CaMoO_4: 0.08Tb^{3+}$ phosphors are found to be $x = 0.24$, $y = 0.69$, respectively. These coordinates are found to fall in the green region of the CIE chromaticity coordinate diagram, as shown in Figure. This indicates that the $Li_3Ba_2Gd_3 \cdot x(MoO_4)_8: 0.08Tb^{3+}$ phosphor is a promising green emitting component for fluorescent lamp phosphors.

Conclusion

A class of novel green emitting Tb^{3+} doped $CaMoO_4$ nanophosphors were successfully prepared by solid state metathesis reaction at room temperature. These phosphors emit intense green light dominated by 545 nm from $^5D_4 \rightarrow ^7F_5$ transition of Tb^{3+} under excitation of UV light. The CIE coordinates of these phosphors located in the green area and the measured CIE coordinates were observed to be (0.24, 0.69) for $CaMoO_4: 0.08Tb^{3+}$. All these properties indicate that these phosphors could serve as a potential green emitting phosphor for application on short ultraviolet fluorescent lamps.

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