

Transparent Green-Emitting  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  Suspensions

Young-Sik Cho and Young-Duk Huh\*

Department of Chemistry, Institute of Nanosensor and Biotechnology, Dankook University, Gyeonggi-Do 448-701, Korea

\*E-mail: ydhuh@dankook.ac.kr

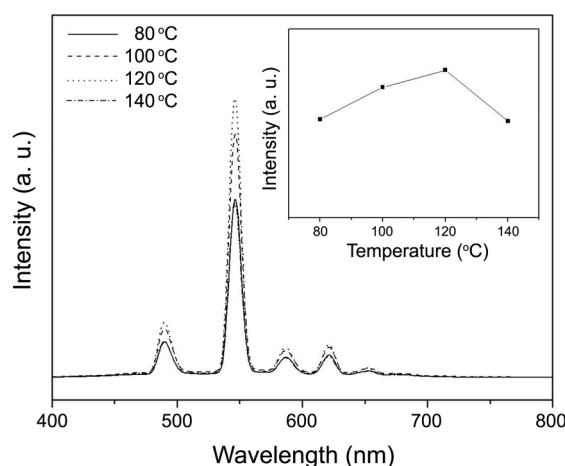
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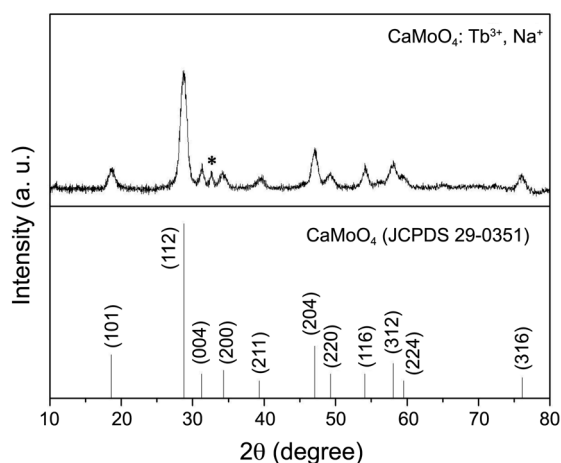
Transparent displays have attracted considerable interest for their applications in lighting and flexible display devices.<sup>1-3</sup> Nontransparent displays prevent the viewing of some objectives through them. They also reflect a large proportion visible light and reduce the contrast ratio of the displays. Inorganic nanoparticles do not have any scattering effect in the visible region, and nanophosphors are useful for the fabrication of transparent displays.<sup>4-7</sup> However, nanophosphors agglomerate easily in solvents. Relatively little is known about the preparation of suspensions of mono-dispersed inorganic nanophosphors in solvents. Therefore, a method for the preparation of transparent suspensions of nanophosphors is needed for applications to transparent displays.

Over the past few decades, trivalent rare earth molybdate phosphors, such as  $\text{Y}_2(\text{MoO}_4)_3:\text{Eu}^{3+}$  and  $\text{Gd}_2(\text{MoO}_4)_3:\text{Dy}^{3+}$ , have been investigated because they are good candidates for red- and green- emitting phosphors for solid-state lighting based on InGaN diodes.<sup>8-14</sup> Most activators in inorganic phosphors are trivalent ions ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , or  $\text{Ce}^{3+}$ ) that easily substitute at the host site of the trivalent rare earth ions in trivalent rare earth molybdate phosphors. On the other hand, there are few reports on divalent alkali earth metal molybdate phosphors.<sup>15-19</sup> Recently, the emission intensity of  $\text{CaMoO}_4:\text{Eu}^{3+},\text{Na}^+$  phosphor was reported to be higher than that of well-known bright red-emitting  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  phosphor.<sup>20,21</sup> This suggests that divalent alkali earth metal molybdate may be also a good host for the inorganic phosphors with trivalent activator ions. For the charge compensation of divalent alkali earth metal, trivalent activator ions and alkali metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$ ) must be substituted. Normally,  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphors are prepared by a solid-state reaction and sol-gel reaction.<sup>15-17</sup> This paper reports a simple hydrothermal method for preparing the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  nanophosphors. To the best of our knowledge, this is the first report of transparent suspensions of  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  nanophosphors in organic solvents.

Figure 1 shows the photoluminescence spectra ( $\lambda_{\text{ex}} = 296$  nm) of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphors prepared by hydrothermal synthesis at temperatures between 80 °C and 140 °C. The photoluminescence peaks at 489, 547, 586 and 621 nm correspond to the characteristic emission of  $\text{Tb}^{3+}$ . The emission intensity at 547 nm increased gradually with increasing temperature up to 120 °C, and then decreased at 140 °C. As shown in the inset in Figure 1, the brightest

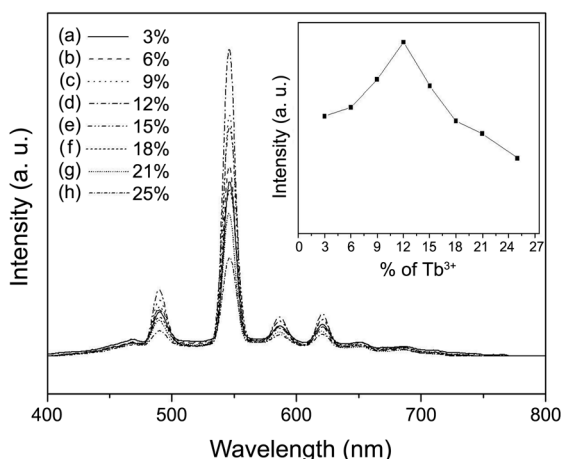


**Figure 1.** Photoluminescence spectra ( $\lambda_{\text{ex}} = 296$  nm) of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphors prepared by hydrothermal synthesis at temperatures between 80 °C and 140 °C. The inset shows the relative intensity at 547 nm as a function of the hydrothermal temperature.



**Figure 2.** XRD patterns of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphor prepared by hydrothermal process at 120 °C.

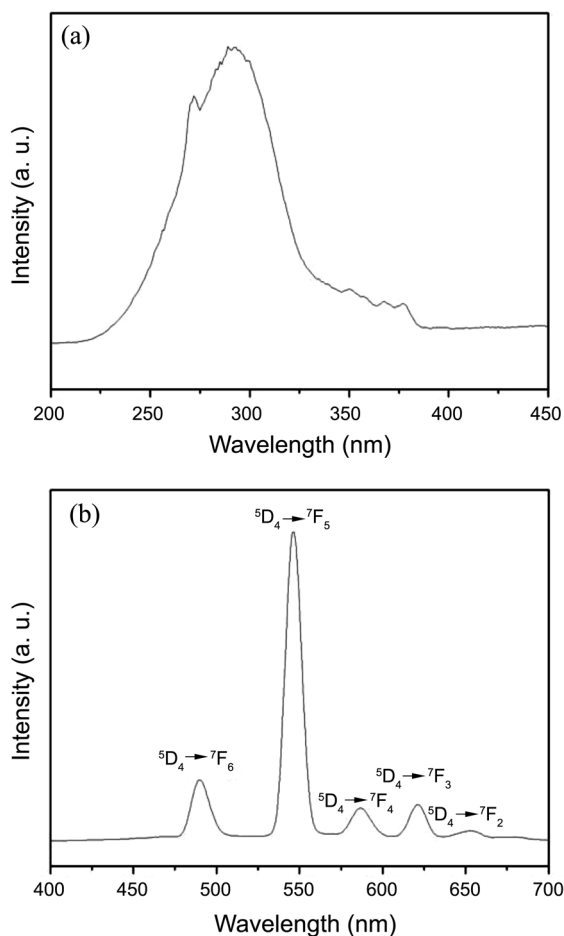
$\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphor was obtained by the hydrothermal process at 120 °C. Figure 2 shows the powder X-ray diffraction (XRD) patterns of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphor prepared by a hydrothermal process at 120 °C. The XRD pattern of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphor matched the tetragonal  $\text{CaMoO}_4$  (JCPDS 29-0351,  $a = 0.5226$  nm,  $c =$



**Figure 3.** Photoluminescence spectral intensity of the  $\text{Ca}_{(1-2x)}\text{MoO}_4:x\text{Tb}^{3+},x\text{Na}^+$  phosphors with different  $x$  values; (a) 0.03, (b) 0.06, (c) 0.09, (d) 0.12, (e) 0.15, (f) 0.18, (g) 0.21, and (h) 0.25. The inset shows the relative intensity at 547 nm of the  $\text{Ca}_{(1-2x)}\text{MoO}_4:x\text{Tb}^{3+},x\text{Na}^+$  phosphors as a function of  $x$ .

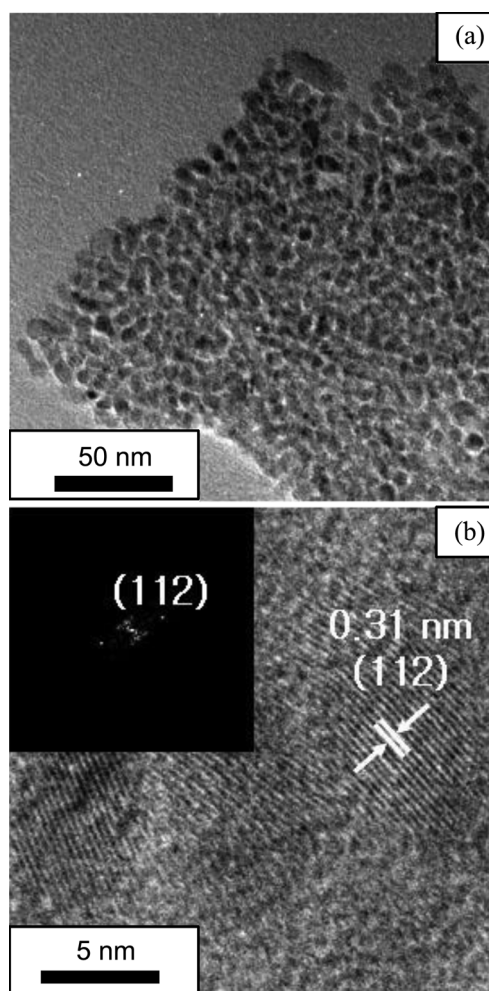
1.143 nm) except one unknown peak marked by the asterisk.  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  was synthesized successfully from the XRD patterns and photoluminescence spectra of  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$ .

In general, the photoluminescence intensity depends strong-

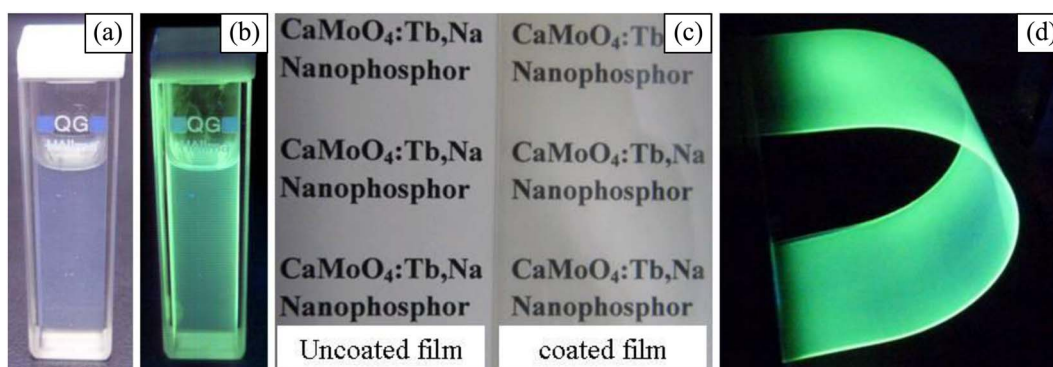


**Figure 4.** Photoluminescence (a) excitation ( $\lambda_{\text{em}} = 547$  nm) and (b) emission ( $\lambda_{\text{ex}} = 296$  nm) spectra of the  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  phosphor.

ly on the concentration of activators. To examine the photoluminescence intensity dependence of the activator concentration, several  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphors were prepared with various concentrations of  $\text{Tb}^{3+}$  and  $\text{Na}^+$  with the formula,  $\text{Ca}_{(1-2x)}\text{MoO}_4:x\text{Tb}^{3+},x\text{Na}^+$ . Because  $\text{Tb}^{3+}$  and  $\text{Na}^+$  substitute the  $\text{Ca}^{2+}$  site, the concentrations of  $\text{Tb}^{3+}$  and  $\text{Na}^+$  were the same to compensate for the charge of  $\text{Ca}^{2+}$ . Figure 3 shows the relative emission intensity of  $\text{Ca}_{(1-2x)}\text{MoO}_4:x\text{Tb}^{3+},x\text{Na}^+$  phosphors with  $x = 0.03, 0.06, 0.09, 0.12, 0.15, 0.18, 0.21,$  and  $0.25$ . The photoluminescence intensity of the  $\text{Ca}_{(1-2x)}\text{MoO}_4:x\text{Tb}^{3+},x\text{Na}^+$  phosphor increased with increasing  $\text{Tb}^{3+}$  concentration up to 12 mol %. However, photoluminescence intensity decreased gradually with further increases in the  $\text{Tb}^{3+}$  concentration above 12 mol %. This concentration quenching can be generally explained in terms of the  $\text{Tb}^{3+}-\text{Tb}^{3+}$  interactions. Figure 4(a) and 4(b) shows the photoluminescence excitation and emission spectra of the  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  phosphor, respectively.  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  phosphor shows strong absorption in the ultraviolet region at  $\sim 296$  nm, which is due to the  $\text{O} \rightarrow \text{Mo}$  charge transfer transition.<sup>16</sup> The emission spectrum consisted of a series of emission lines between 470 and 650



**Figure 5.** (a) TEM and (b) HRTEM images of the  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  nanophosphor. The inset in (b) shows FFT patterns of the individual  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  nanophosphor.



**Figure 6.** Transparent suspensions of  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  nanophosphors in toluene (a) in daylight and (b) under a 254 nm hand-held UV light excitation. (c) Photograph of the transparent  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension coated layer on an overhead transparency film. (d) Photograph of the flexible  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension coated layer on overhead film under UV excitation.

nm, which correspond to transitions from the  $^5\text{D}_4$  state to the  $^7\text{F}_J$  ( $J = 6, 5, 4, 3, 2$ ) states of  $\text{Tb}^{3+}$ . The strongest emission line at 547 nm was assigned to the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition.<sup>16</sup> The emission at 547 nm is suitable for the green-emitting region of the displays. Therefore,  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  can be used as a bright green-emitting phosphor excited by UV irradiation with high green color purity.

Figure 5(a) shows a transmission electron microscopy (TEM) image of the  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  nanophosphor. Monodispersed nanoparticles, 10 nm in diameter, were obtained. Because the oleic acid and oleylamine were used as surfactants, monodispersed nanoparticles were possibly obtained by forming the external nonpolar surfaces of the nanoparticles. The fringe pattern of an individual  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  nanoparticle in the high-resolution TEM (HRTEM) image showed a spacing of 0.31 nm, which corresponds to the (112) plane of a tetragonal  $\text{CaMoO}_4$  nanoparticle, as shown in Figure 5(b). The inset in Figure 5(b) shows the fast Fourier transform (FFT) patterns of the  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  nanoparticle corresponding to the lattice fringe, which revealed its highly crystalline nature.

A highly transparent  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension was prepared by dispersing the  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  nanophosphor in toluene, as shown in Figure 6(a). This suspension was quite stable without sedimentation after being left to stand for one week. Intense green light emission was observed under a 254 nm hand-held UV light, as shown in Figure 6(b). Because oleic acid and oleylamine were used as capping agents, the surfactants made the surface of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  nanophosphors hydrophobic, and a highly transparent suspension was formed without agglomeration. Therefore, oleic acid and oleylamine play an important role in the preparation of transparent  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspensions.

Figure 6(c) shows the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension coated layer on the overhead transparency film with high transparency. The  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension was mixed with PAS ink and applied as a 90  $\mu\text{m}$  thick film to a commercial overhead transparency film using an applicator. The transmittance of the bare overhead transparency

film, coating with only PAS ink, and coating with the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension with PAS ink measured by a UV-vis spectrometer at 500 nm were 72.3, 63.0 and 56.9%, respectively. This suggests that the decrease in transmittance is caused by the overhead transparency film and PAS ink not from the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension. Figure 6(d) presents a flexible  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension coated layer on an overhead film under UV lamp irradiation. Therefore, the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension can be used as a green-emitting material for flexible and transparent thin film devices with little loss of light due to visible light scattering.

In conclusion,  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  nanophosphors were prepared from a hydrothermal reaction of  $\text{Ca}(\text{NO}_3)_2$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ,  $\text{NaNO}_3$ , and  $\text{Tb}(\text{NO}_3)_3$ . Monodispersed  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  nanoparticles, 10 nm in diameter, were obtained by capping of oleic acid and oleylamine surfactants. A highly transparent suspension was obtained by dispersing the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  nanophosphor in toluene without agglomeration. This suspension was found to be suitable for transparent green-emitting phosphors *via* excitation with UV light, and can be also used in flexible and transparent thin film displays.

## Experimental Section

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Aldrich),  $\text{NaNO}_3$  (Aldrich),  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (Aldrich),  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (Aldrich), sodium oleate (TCI), oleic acid (Aldrich) and oleylamine (TCI) were used as received. In a typical synthesis of  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$ , 0.152 M of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 0.0240 M of  $\text{NaNO}_3$  and 0.0240 M of  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were dissolved in 10 mL of water. 1.22 g of sodium oleate, 5 mL of oleic acid, 5 mL of oleylamine and 40 mL of hexane were added to the above solution with vigorous stirring for 1 h. 0.0286 M of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  was dissolved in 10 mL of water. The two optically transparent solutions were mixed, transferred to a 100 mL Teflon-lined autoclave, and heated to temperatures ranging from 80  $^\circ\text{C}$  to 140  $^\circ\text{C}$  for 16 h to prepare the  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  phosphor *via* a hydrothermal reaction. The  $\text{Ca}_{0.76}\text{MoO}_4:0.12\text{Tb}^{3+},0.12\text{Na}^+$  phosphor solution in a hexane layer was separated from the bottom

solution of an aqueous layer by a separating funnel. The hexane solution was centrifuged at 4000 rpm for 15 min, and a clear top solution was obtained by separating the bottom nontransparent solution. The  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  nanoparticles were obtained by adding 40 mL of ethanol to the clear solution through precipitation. The precipitate was centrifuged, washed several times with water and ethanol, and dried at 60 °C for 12 h. 0.1 g of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  nanophosphor was dispersed in 3 mL of toluene in a 10 mL vial for 10 min. 1.0 g of PAS (series 800, Jujo) ink was dispersed into the above mixture and stirred for 15 min. The  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension was coated on commercial overhead transparency film to a thickness of 90  $\mu\text{m}$  using an applicator.

The structures of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphors were analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD) using  $\text{Cu K}\alpha$  radiation. The morphology of the products was examined by transmission electron microscopy (TEM, JEOL JEM-3010). The photoluminescence excitation and emission spectra of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  phosphor was measured using a spectrum analyzer (DARSA, PSI) with a 27.5 cm monochromator, a photomultiplier tube and a 500 W Xe lamp as the excitation source. A hand-held 12 W UV lamp (Uvitec,  $\lambda_{\text{max}} = 254 \text{ nm}$ ) was used for UV excitation of the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension. The transmittance of the overhead transparency coated with the  $\text{CaMoO}_4:\text{Tb}^{3+},\text{Na}^+$  suspension was measured using a UV-vis spectrometer (Perkin Elmer Lambda 25).

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