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Tunable luminescence properties of $NaLa(MoO_4)_2:Ce^{3+},Tb^{3+}$ phosphors for near UV-excited white light-emitting-diodes

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The $NaLa(MoO_4)_2:Ce^{3+},Tb^{3+}$ phosphors were synthesized by a high temperature solid-state reaction. Co-doping of Ce^{3+} enhances the emission intensity of Tb^{3+} greatly by transferring its excitation energy to Tb^{3+}. Through an efficient energy transfer process, the obtained phosphors exhibit both a indigo emission of Ce^{3+} and a yellowish green emission of Tb^{3+} with considerable intensity under near-ultraviolet excitation (339 nm). The energy transfer mechanism from Ce^{3+} to Tb^{3+} in $NaLa(MoO_4)_2$ host was demonstrated to be dipole–quadrupole interaction. The varied emitted color of the phosphors from indigo to yellow-greenish can be achieved by properly tuning the relative ratio of Ce^{3+} and Tb^{3+} through the energy transfer from the Ce^{3+} to Tb^{3+} ions. These results indicate that the $NaLa(MoO_4)_2:Ce^{3+},Tb^{3+}$ phosphors have potential applications as an UV-convertible phosphor for white light emitting diodes because of its effective excitation in the near ultraviolet range.

1. Introduction

The white light emitting diodes (LEDs) have many excellent properties such as low power consumption, long operating time, and environmental benefit [1–4]. Therefore, white LEDs are expected to be new light sources in the illumination field and have attracted increasing attention in recent years. There are several ways to gain white light [5–7]. Among these, the most common and simple method to realize white-light LEDs is to combine an InGaN-based blue LED with a yellow phosphor material, such as YAG:Ce (YAG denotes yttrium aluminum garnet). The blue chip/YAG:Ce system has many advantages. However, because YAG:Ce emits a yellow-greenish light, the emission from an InGaN-based blue LED coated with YAG:Ce is deficient in the red spectral region and its color rendering property is poor. White LEDs can also be made by coating a near ultraviolet (n-UV) emitting LED with a mixture of high efficient red, green and blue emitting phosphors [8]. This method yields light with better spectral characteristics, which render color better. Therefore, more and more attention has been paid to the development of new phosphors that can be excited in the range of near-UV due to the necessity of increasing the efficiency of white light-emitting solid-state devices [9–12].

In recent years, much research effort has been directed towards the synthesis of rare-earth compounds since they can be used as highly efficient phosphors, catalysts, and other functional materials by virtue of their novel optical, electronic, and chemical properties [13–16]. In particular, rare-earth molybdate comprise a large class of inorganic compounds that exhibit interesting physical properties and thus have technological applications in the fields of catalysis and optics [17,18]. Therefore, much effort has been made towards the development of synthetic methodologies for fabricating rare-earth molybdate. $NaLa(MoO_4)_2$ possesses the tetragonal scheelitelike structure and belongs to the family of double molybdate (DM) compounds with the general formula $NaT(MoO_4)_2$, where T is a trivalent cation (such as Y^{3+}, La^{3+}, or Gd^{3+}). The distribution of T^{3+} induces the inhomogeneous broadening of optical spectra when rare-earth ions are doped in the crystals and occupy the positions of T^{3+} ions. The spectroscopic and laser properties of rare-earth ion doped $NaT(MoO_4)_2$ have been investigated in recent years due to their attractive potential for diode pumped tunable solid-state laser and ultrashort pulse laser [19,20]. However, to the best of our knowledge, little attention has been paid to the down-conversion luminescence properties of rare-earth doped $NaLa(MoO_4)_2$ phosphors [21]. Among the lanthanide ions, Ce^{3+} and Tb^{3+} ions are two of the most important luminescent centers [22–25]. However, the optical properties of $NaLa(MoO_4)_2:Ce^{3+},Tb^{3+}$ phosphors have not been reported before.

In this paper, we report the luminescence property and the energy transfer of $NaLa(MoO_4)_2:Ce^{3+},Tb^{3+}$ phosphors. We suggest

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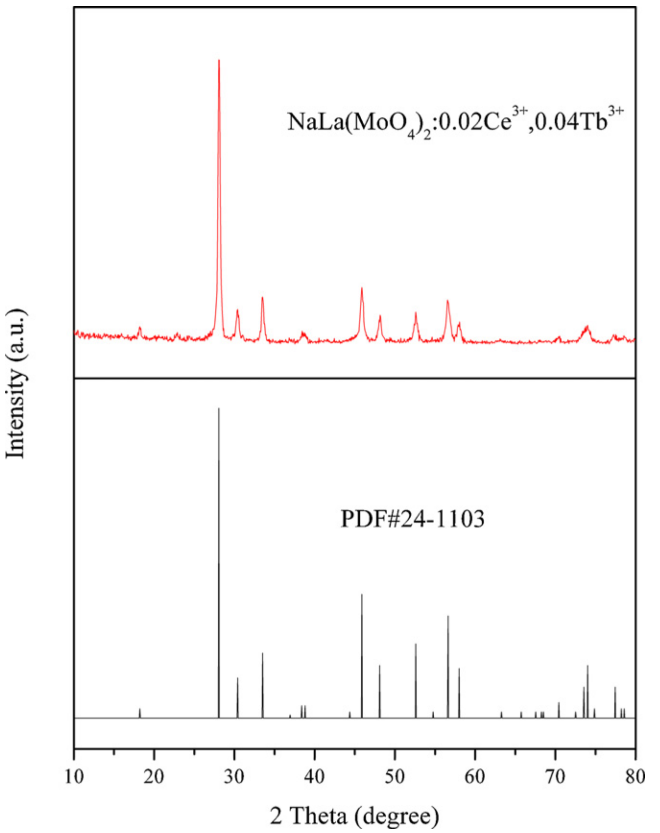

Fig. 1. XRD patterns of NaLa(MoO$_4$)$_2$:0.02Ce^{3+},0.04Tb^{3+} along with the standard data for NaLa(MoO$_4$)$_2$ (JCPDS card no. 24-1103) as a reference.

that there exists efficient energy transfer from Ce^{3+} to Tb^{3+} on the base of large overlap between the emission spectrum of indigo NaLa(MoO$_4$)$_2$:Ce^{3+} and the excitation spectrum of green NaLa(MoO$_4$)$_2$:Tb^{3+}. The developed phosphors can generate lights from indigo to green region. They can be effectively excited by near-UV (about 339 nm) and suitable for use in white LEDs.

2. Experimental

The samples were synthesized through the solid-state reaction technique. NaLa$_{1-x-y}$(MoO$_4$)$_2$:xCe^{3+},yTb^{3+} were initially prepared by mixing stoichiometric amounts of Na$_2$CO$_3$ (99.8%), MoO$_3$ (99.9%), La$_2$O$_3$ (99.99%), CeO$_2$ (99.99%) and Tb$_4$O$_7$ (99.99%). These powders were blended and milled thoroughly in an agate mortar for 3 h. Then the mixtures were transferred to alumina crucibles and annealed successively at 1100 °C for 4 h under a reducing atmosphere created by burning activated carbon.

The samples were examined by X-ray diffraction (XRD) measurements performed on a Rigaku D/max-II B X-ray diffractometer with monochromatic Cu K$_\alpha$ radiation. The PL excitation and emission spectra were recorded with a Hitachi F-7000 spectrophotometer equipped with a 150 W Xe lamp as the excitation source at room temperature. All measurements were performed at room temperature.

3. Results and discussion

The XRD patterns of as-prepared NaLa(MoO$_4$)$_2$:0.02Ce^{3+}, 0.04Tb^{3+} are shown in Fig. 1. The diffraction patterns of the products can be indexed with a pure tetragonal phase (space group: I41/a), which is preferably in agreement with the literature (JCPDS card no. 24-1103). The doped Ce^{3+}and Tb^{3+} ions do not induce any significant phase change. The XRD patterns indicate that the NaLa(MoO$_4$)$_2$ structures can be easily obtained under the current synthetic conditions. The calculated lattice constants are $a = b = 0.5343$ nm and $c = 1.1743$ nm. In addition, the XRD patterns of NaLa(MoO$_4$)$_2$ doped with Ce^{3+} and Tb^{3+} of different concentrations are showed in Fig. S1 (see Supplementary Materials). The XRD patterns are consistent with the phase of NaLa(MoO$_4$)$_2$ perfectly (JCPDS card no. 24-1103) and no peaks of other phases or impurities are detected.

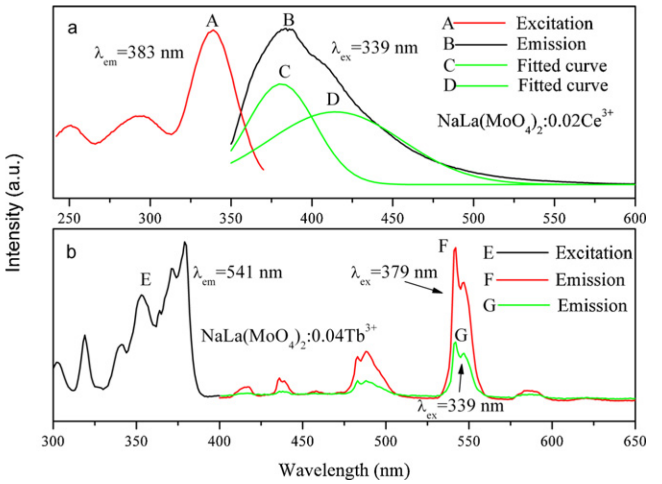

Fig. 2. Excitation and emission spectra of NaLa$_{0.98}$(MoO$_4$)$_2$:0.02Ce^{3+} (a) and NaLa$_{0.96}$(MoO$_4$)$_2$:0.04Tb^{3+} (b).

The excitation and emission spectra of the NaLa(MoO$_4$)$_2$: 0.02Ce^{3+} and NaLa(MoO$_4$)$_2$:0.04Tb^{3+} are represented in Fig. 2. In Fig. 2(a), the excitation spectra of the NaLa(MoO$_4$)$_2$:Ce^{3+} monitored at 383 nm show three excitation bands centered at 250, 293 and 339 nm due to the 4f^1–5d^1 transition of the Ce^{3+} ions. When excited under 339 nm, the photoluminescence emission of NaLa(MoO$_4$)$_2$:Ce^{3+} shows an asymmetric band extending from 350 to 580 nm with a maximum at about 383 nm, indicating a single type of luminescent center or strong spectral overlap between spectra belonging to different luminescent centers. The characteristic doublet of Ce^{3+} ion is not clearly observed in the emission spectrum, but it can be resolved by a Gaussian fit into two emission bands with the peaks at 381 nm (26,247 cm^{-1}) and 414 nm (24,155 cm^{-1}), corresponding to the transitions of 5d states to $^2F_{5/2}$ and $^2F_{7/2}$ of Ce^{3+} ion, respectively. The energy difference between the two fitted emission peaks is about 2092 cm^{-1}, which is consistent with the theoretically calculated energy difference between $^2F_{5/2}$ and $^2F_{7/2}$ levels (~2000 cm^{-1}) [26,27]. Fig. 2(b) shows the excitation and emission spectra of NaLa(MoO$_4$)$_2$:Tb^{3+}. The excitation spectrum exhibits a series of sharp peaks between 300 and 400 nm. The sharp bands between 300 and 400 nm are assigned to the intra 4f^8 transitions between the $^7F_6$ and $^5F_{5,4}$, $^5H_{7-4}$, $^5D_{1,0}$, $^5L_{10-6}$, $^5G_{6-2}$ and $^5D_{2-4}$ levels [28]. More details of Tb^{3+} excitation can be referred to references elsewhere [29]. The emission spectra of NaLa(MoO$_4$)$_2$:Tb^{3+} phosphors excited by 379 nm exhibit four peaks at around 488, 541, 587 and 619 nm due to the characteristic green luminescence originated from the transitions between the excited $^5D_4$ level and ^7F_J ($J = 6, 5, 4, 3$) level of the Tb^{3+} ion, respectively. The strongest emission peaks is located at 541 nm corresponding to the typical transition $^5D_4$–$^7F_5$ of Tb^{3+} ion. The emission spectra of NaLa(MoO$_4$)$_2$:Tb^{3+} excited at 339 nm are also showed in Fig. 2(b). The positions of emission peaks are similar to the positions excited at 379 nm. There are four peaks at around 488, 541, 587 and 619 nm, but the emission intensity is lower than the intensity of NaLa(MoO$_4$)$_2$:Tb^{3+} excited at 379 nm.

For the samples, the optimum concentrations of Ce are discussed and the results are shown in Fig. 3. As shown in Fig. 3, the emission intensities increase with increasing Ce^{3+} concentrations, and then decreases. When the value of x is about 0.02, the maximum emission intensity occurs. The optimum concentrations of the other dopant ions (Tb) are shown in Fig. 4, the increase in the emission intensity is observed up to 0.04. Further increase in Tb ions leads to

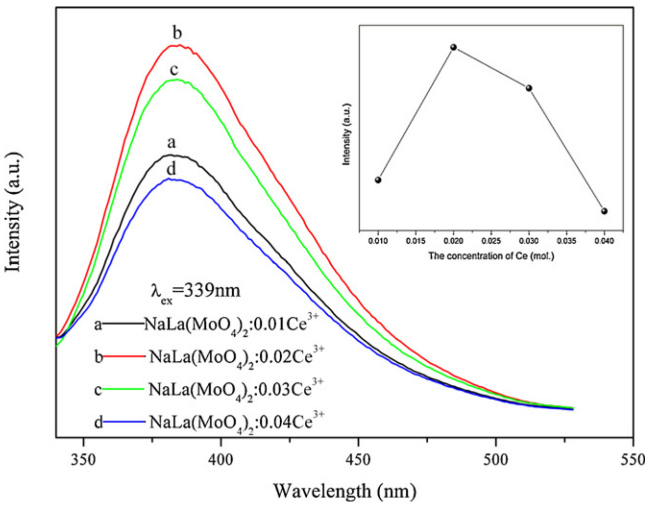

Fig. 3. Emission spectra of $NaLa_{1-x}(MoO_4)_2$:xCe^{3+} phosphors with various Ce concentrations.

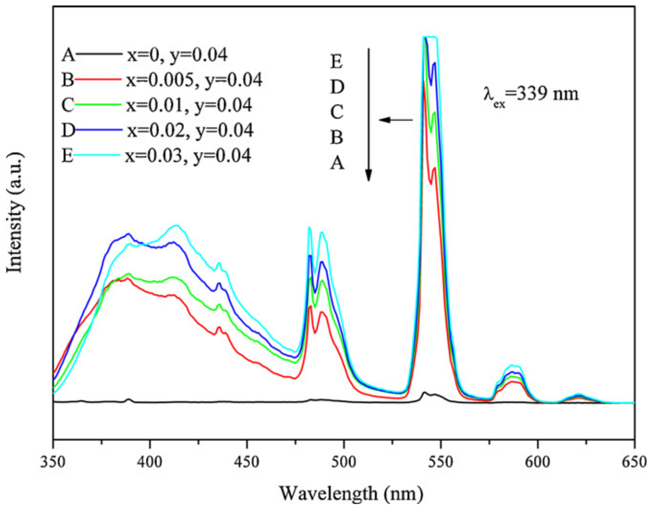

Fig. 5. Emission spectra of $NaLa_{1-x-y}(MoO_4)_2$:xCe^{3+},yTb^{3+} phosphors with increasing Ce^{3+} concentration (x).

decrease in the emission intensity. The phenomenon of decrease in emission intensity after certain concentration is called concentration quenching and is attributed to energy migration among rare earth ions, which brings the excitation energy to killer sites such as surface defects in polycrystalline powder samples [30].

Fig. 5 shows the emission spectra of $NaLa_{0.96-y}(MoO_4)_2$:xCe^{3+},$0.04Tb^{3+}$ ($x = 0$–0.03). Under the excitation of 339 nm, the intense characteristic emission peaks of Ce^{3+} and Tb^{3+} are observed in the emission spectra of all samples. And both emission intensities of Ce^{3+} and Tb^{3+} increase with increasing Ce^{3+} concentrations. Furthermore, the emission intensity of $Ce^{3+}$and Tb^{3+} co-doping $NaLa(MoO_4)_2$ phosphor is higher than that of Tb^{3+} single doped one. The emission spectra of phosphors doped with different Tb^{3+} concentrations at the fixed Ce^{3+} concentrations are shown in Fig. 6. Under the excitation of 339 nm, the emission spectra of $NaLa_{0.98-y}(MoO_4)_2$:$0.02Ce^{3+}$,yTb^{3+} appear not only a band of the Ce^{3+} ions but also a band of the Tb^{3+} ions. With increasing Tb^{3+} concentrations, the Ce^{3+} emissions decrease whereas the Tb^{3+} emissions become stronger and then decreases may due to concentration quenching. Furthermore, the optimum emission intensity of $Ce^{3+}$and Tb^{3+} co-doping $NaLa(MoO_4)_2$ phosphor (Curve D) is about 200 percent higher than that of Tb^{3+} single doped one (Curve G), suggesting that there exists energy transfer from Ce^{3+} to Tb^{3+}. The concentration quenching is due to energy transfer from one activator (donor) to another until an energy sink (acceptor) in the crystal lattice is reached. Hence, the energy transfer will strongly depend on the distance (R) between the Tb^{3+} ions and the Ce^{3+} ions, which can be obtained using the following equation [31]

$$R \approx 2\left[\frac{3V}{4\pi XZ}\right]^{1/3} \tag{1}$$

where V is the volume of the unit cell, X is the number of Ce^{3+} and Tb^{3+} ions, and Z is the number of the host cations in the unit cell. For $NaLa(MoO_4)_2$ host, the optimal concentration of Ce^{3+} and Tb^{3+} is estimated to be about 0.06, $Z = 2$ and $V = 0.335\ nm^3$. The critical distance R is estimated by Eq. (1) to be about 1.75 nm. On the basis of Dexter's energy transfer formula of multipolar interaction and Reisfeld's approximation the following relation can be obtained [31,32]:

$$\frac{I_{S0}}{I_S} \propto C^{n/3} \tag{2}$$

where I_{S0} is the intrinsic luminescence intensity of Ce^{3+}, I_S the luminescence intensity of Ce^{3+} in the presence of the Tb^{3+}, and The factor

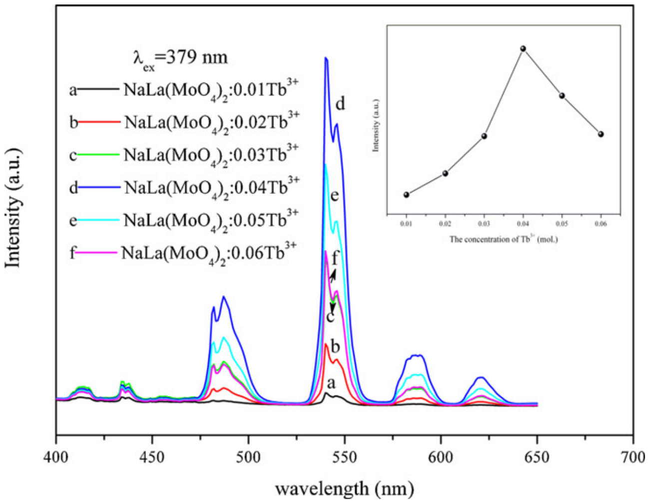

Fig. 4. Emission spectra of $NaLa_{1-x}(MoO_4)_2$:xTb^{3+} phosphors with various Tb concentrations.

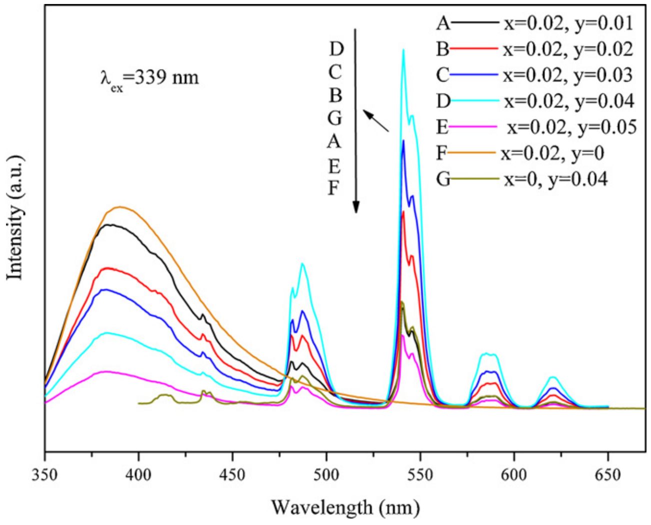

Fig. 6. Emission spectra of $NaLa_{1-x-y}(MoO_4)_2$:xCe^{3+},yTb^{3+} phosphors with increasing Tb^{3+} concentration (y).

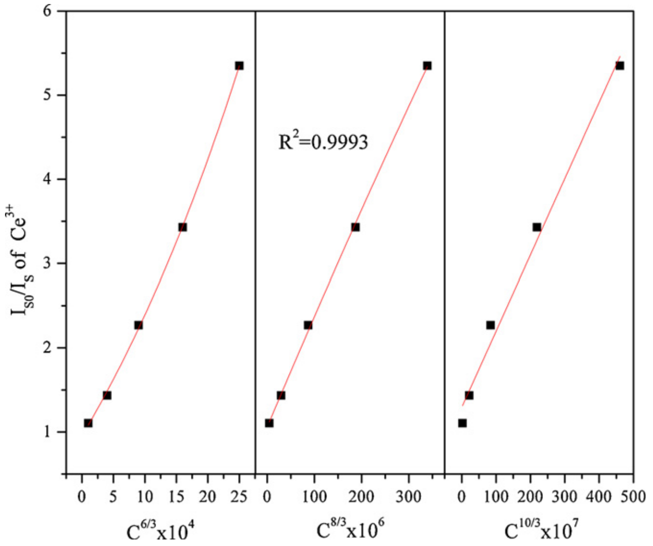

Fig. 7. Dependence of I_{S0}/I_S of $C^{n/3}$ on the exponent (a) $n = 6$, (b) $n = 8$ and (c) $n = 10$.

C is the concentration of Tb^{3+}. The value for exponent n is 6, 8 and 10 for dipole–dipole, dipole–quadrupole, or quadrupole–quadrupole interactions, respectively. Using the emission intensity values of Ce^{3+} at 383 nm under excitation of 339 nm, the I_{S0}/I_S vs $C^{n/3}$ curves corresponding to $n = 6$, 8 and 10 are plotted in Fig. 7. From this approximate relation, the I_{S0}/I_S values follows in the linear growth law for $n = 8$ much better than for $n = 6$ or 10. This clearly indicates that the energy transfer from the Ce^{3+} to the Tb^{3+} ions is the dipole–quadrupole mechanism, which is similar to the results in the literature [33,34].

The Commission Internationale de L'Eclairage (CIE) chromaticity coordinates for $NaLa_{1-m-n}MoO_4$:mCe^{3+},nTb^{3+} are represented in Fig. 8. From Fig. 8, it can be seen that the as-obtained purely Ce^{3+}-doped $NaLa(MoO_4)_2$ sample shows indigo emission under excitation with UV light. By co-doping the $NaLa(MoO_4)_2$ host lattice with Tb^{3+} ions, the characteristic emission of the Tb^{3+} ions could be observed besides the Ce^{3+} emission. By changing the concentration of the Ce and Tb, the tunable emission properties of the $NaLa(MoO_4)_2$ samples can be obtained. With increasing Tb^{3+} content, the chromaticity coordinates (x, y) vary systematically from (0.163, 0.075) to (0.269, 0.450), corresponding color tone of the samples changes gradually from indigo to green by simply adjusting the relative doping concentrations of the Ce^{3+} and Tb^{3+} ions.

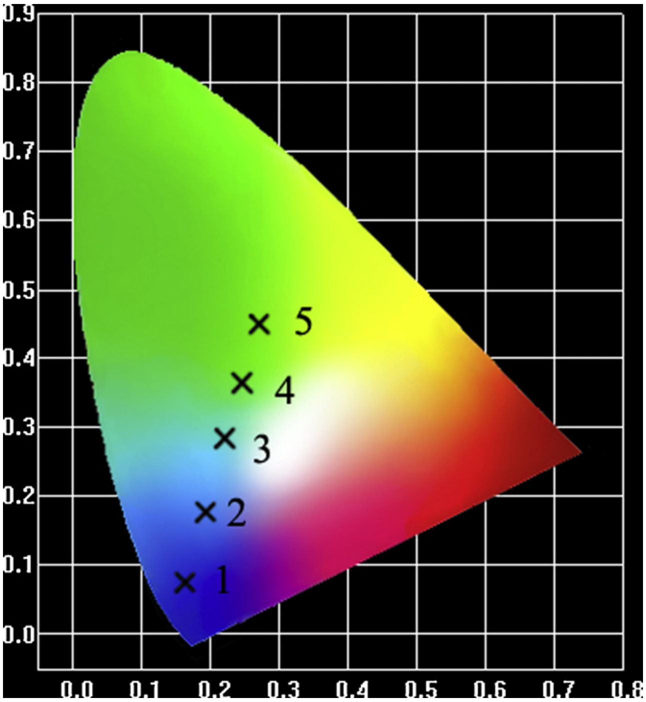

Fig. 8. CIE chromaticity diagram for $NaLa_{1-m-n}MoO_4$:mCe^{3+},nTb^{3+} phosphors excited at 339 nm. (1) $m = 0.02$, $n = 0$; (2) $m = 0.02$, $n = 0.01$; (3) $m = 0.02$, $n = 0.02$; (4) $m = 0.02$, $n = 0.03$; (5) $m = 0.02$, $n = 0.04$.

4. Conclusions

We have synthesized $NaLa(MoO_4)_2$:Ce^{3+},Tb^{3+} phosphors and investigated their luminescence. The spectroscopic data indicate that the energy transfer from the Ce^{3+} to the Tb^{3+} ions takes place in the host matrix of $NaLa(MoO_4)_2$. The mechanism of the energy transfer is a resonant type that takes place through a dipole–quadrupole reaction. The green emission of the Tb^{3+} ions is observed in $NaLa(MoO_4)_2$:Ce^{3+},Tb^{3+} under UV excitation due to the energy transfer from the Ce^{3+} to the Tb^{3+} ions. The efficiencies from the Ce^{3+} to Tb^{3+} ions were calculated by the changes of their relative emission intensity. The distance between the Tb^{3+} ions and the Ce^{3+} ions of the energy transfer is about 1.75 nm. Furthermore, we have demonstrated that the $NaLa(MoO_4)_2$:Ce^{3+},Tb^{3+} phosphors can be tuned to generate from indigo to green light under UV radiation. Preliminary studies have shown that the $NaLa(MoO_4)_2$:Ce^{3+},Tb^{3+} phosphor may serve as a potential UV-convertible phosphor under UV excitation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2011.10.008.

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