

Article



# Luminescence Properties of Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> Modified with Sm(III) and Tb(III) for Potential LED Applications

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**Abstract:** Light-emitting phosphors, doped with lanthanide ions of Tb(III) and Sm(III) of the type  $Gd_{1.97-y}$  Sm<sub>y</sub>Tb<sub>0.03</sub>(MoO<sub>4</sub>)<sub>3</sub> (y = 0.01–0.11, step 0.02) and  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$  (x = 0.01–0.09, step 0.02), were synthesized and characterized by X-ray diffraction, UV-Vis spectroscopy, scanning and transmitting electron microscopy (SEM, TEM) as well as photoluminescence spectroscopy. The effect of the doping content of Tb/Sm was followed. The unit cell parameters for  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  and  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$  changed with the increase in the Tb/Sm content. The microstrain values also increased, proposing an increased concentration of defects. The mean particle size was estimated to be approximately 0.6 µm. Based on a Williamson–Hall plot, the size of the crystallites was determined to be in the range of 42–60 nm for modified and pure  $Gd_2(MoO_4)_3$  samples, respectively. The samples excited at 406 nm exhibited characteristic emission lines of Sm (485, 555, 646 nm). The host material  $Gd_2(MoO_4)_3$  emission in visible light was explained by the crystal structure defects, namely, oxygen vacancies. The CIE x/y color coordinates of the phosphors were determined and the related points were located in the green-yellow/pale yellow region of the visible light. The excited state lifetimes were determined for both groups of the samples, showing values in the millisecond range and indicating the samples as promising phosphors.

Keywords: phosphors; gadolinium molybdate; terbium; samarium; optical properties; luminescence

# 1. Introduction

Phosphors modified with rare earth elements have been of great interest in the last few decades due to their potential applications in various fields such as displays, LEDs, optical fibers, sensors, secret inks and biochemical markers [1]. In addition to their excellent optical properties, the materials based on rare earth elements are also thermally [2] and chemically stable [1]. Their capability has been found to release ozone-depleting substances as well as reducing electricity consumption, which makes them environmentally friendly materials [1]. The most popular method for making white LEDs (wLED) is the combination of a blue LED (InGaN) with yellow phosphor  $Y_3Al_5O_{12}$ : Ce (YAG:Ce), as white light can be obtained by combining blue and yellow emissions. Nevertheless, such wLEDs suffer from insufficient radiation in the red area, which leads to a low color rendering index and a high radiation temperature (7000 K: blue-white light) [3]. This is the reason to look for new materials including new matrices for modification. Among the matrices suitable for the incorporation of lanthanide ions for LEDs, application oxides [4], fluorides and oxofluorides [5], molybdates [6,7], tungstates [8], vanadates and phosphates [9,10] have been studied.

The matrices that attract a particular interest are the molybdates and tungstates, which have an advantage over the other matrices used due to the presence of a wide excitation band in the UV region as well as the presence of a charge transfer in the bonds O-Mo/O-W [1,11,12].



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Among molybdates,  $Gd_2(MoO_4)_3$  is of particular interest due to its low toxicity as well as its high thermal and photochemical stability [13–17]. In addition, Gd(III) can be easily replaced by other lanthanide ions due to their similar ionic radii and preferably the same coordination.  $Gd_2(MoO_4)_3$  modified with  $Eu^{3+}$ ,  $Tb^{3+}$ ,  $Tm^{3+}$  and  $Er^{3+}/Yb^{3+}$  has been studied for solar cell applications as a spectral converter from UV to NIR [12].

A matrix of CaLa<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub> modified with Tb<sup>3+</sup>/Sm<sup>3+</sup> showed a fluorescence that could be turned to white light because of the energy transfer of Tb<sup>3+</sup> to Sm<sup>3+</sup> [18]. The Tb ion was found to be a sensitizing agent, increasing the luminescent efficiency of Sm<sup>3+</sup> in a phosphate-silicate matrix as well [19]. The ion Tb<sup>3+</sup> is known for its fluorescence in the green area based on  ${}^{5}\text{D4} \rightarrow {}^{7}\text{F}_{J}$  (J = 6, 5, 4, 3) whereas Sm<sup>3+</sup> has a fluorescence in orange-red based on  ${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{I}$  (J = 5/2, 7/2, 9/2, 11/2) [20].

A matrix such as  $Gd_2(MoO4)_3$  modified with  $Tb^{3+}/Sm^{3+}$  can be considered to be a potential candidate for a wLED. In the available literature, the system of  $Gd_2(MoO_4)_3$  as a host with  $Tb^{3+}/Sm^{3+}$  as modifying agents and the fluorescent properties of Tb/Sm-doped  $Gd_2(MoO_4)_3$  have not been studied. In the present work, samples of  $Gd_2(MoO_4)_3$  doped with different  $Sm^{3+}$  and  $Tb^{3+}$  contents were synthesized by a solid state reaction process characterized by different methods to observe their luminescent properties.

### 2. Materials and Method

 $MoO_3$  oxide was produced after  $MoO_2$  calcination in air at 600 °C/5 h and the phase purity was confirmed by an XRD analysis (not included). The lanthanide oxides used in the experiments were  $Sm_2O_3$ ,  $Gd_2O_3$  and  $Tb_4O_7$  as well as  $NH_4F$  as a flux. All reagents of 99.99% purity were purchased from Sigma-Aldrich (Chemie GmbH, Taufkirchen, Germany). Prior to synthesis, the lanthanide oxides were annealed at 900 °C overnight to remove any physisorbed moisture or carbonate species.

A solid state reaction was applied for the synthesis of the samples. The procedure was followed by grinding for homogenization for 30 min in a corundum mortar. Considering the diffusion limitations in the solid state reaction to speed up the reaction, NH<sub>4</sub>F acting as flux was added in the last 5 min of grinding (5 wt% of the total mass of the final product). The final thermal calcination was implemented at 800 °C for 5 h in a corundum crucible with a heating rate of 10 °C/min.

Following the procedure, two groups of samples with the general formula  $Gd_{2-x-y}Sm_y$   $Tb_x(MoO_4)_3$  were synthesized. The first one had a fixed y = 0.05 mol and the content of Tb(III) and  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$  was varied where x = 0.01, 0.03, 0.05, 0.07 and 0.09; the second one had a fixed x = 0.03 and the content of Sm(III) and  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  was varied where y = 0.01, 0.03, 0.05, 0.07, 0.09 and 0.11. In the case of x = 0 and y = 0, pure  $Gd_2(MoO_4)_3$  was obtained. Small quantities of Sm(III) and Tb(III) were used, considering the potential quenching of the luminescence.

XRD measurements were performed on a PANalytical Empyrean diffractometer (Malvern PANalytical Empyrean, Almelo, Netherlands) with a PIXcel 3D detector and a Cu K $\alpha$  tube ( $\lambda$  = 0.1542 nm). The microstructural information was extracted by a full profile Rietveld method using the FullProf Suite software (v01-2021, Grenoble, France) [21].

The fluorescence was measured in the solid state (powder) by a Varian Cary Eclipse spectrometer (Agilent, Santa Clara, California, USA) equipped with a 150 W Xe flash lamp as an excitation source. The measurements were performed at room temperature. Scanning electron microscopy (SEM) was performed using a JEOL 5510 (JEOL, Tokyo, Japan) microscope under different magnifications with an 80 keV accelerating voltage. Transmission electron microscopy (HRTEM) was applied to follow the morphology of the samples using a JEM 2100 (JEOL Tokyo, Japan)) with an accelerator voltage of 200 kV and up to 1,500,000 times magnification. UV-Vis absorption spectroscopy was applied using an Evolution 300 UV-Vis spectrometer (Thermo Scientific, Waltham, Massachusetts, USA) for measuring the absorption in the range of 200 nm.

# 3. Results and Discussion

# 3.1. Characterization of Polycrystalline Samples by XRD

The XRD patterns of the samples  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  and  $Gd_{1.95-x}Sm_{0.05}Tb_x$  (MoO<sub>4</sub>)<sub>3</sub> are presented in Figure 1a,b. The Rietveld analysis of the XRD data for one of the samples,  $Gd_{1.92}Sm_{0.05}Tb_{0.03}(MoO_4)_3$ , is presented in Figure 1c. Significant differences could not be observed in the diffraction patterns of the samples containing different amounts of Sm or Tb. This was expected, taking into account the almost identical ionic radii of Sm, Gd and Tb.



**Figure 1.** XRD of the samples: (**a**)  $Gd_{2-x-y}Sm_xTb_y(MoO_4)_3$  and (**b**)  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$ . (**c**) Experimentally observed (dots), Rietveld-calculated (continuous line) and difference (continuous bottom line) profiles, obtained after Rietveld analysis of the  $Gd_{1.92}Sm_{0.05}Tb_{0.03}(MoO_4)_3$  sample. Peak positions are shown on the base line as small markers.

The unit cell parameters of the samples  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  and  $Gd_{1.95-x}Sm_{0.05}$ Tb<sub>x</sub>(MoO<sub>4</sub>)<sub>3</sub> are presented in Table 1. It is known that the molybdates of the middle lanthanides (including Sm, Gd and Tb) crystalize in a monoclinic Eu<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>-type (C2/c) ( $\alpha$ -polymorph) structure [22]. According to [23], in Ln<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> (Ln = lanthanide) with a monoclinic structure of an Eu<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>-type, each W atom has 4 oxygen nearest neighbors and each Ln is surrounded by 8 oxygen atoms. The WO<sub>4</sub> tetrahedra of tungsten share their 4 vertices with  $LnO_8$  trigondodecahedra and several  $LnO_8$  trigondodecahedra share an edge with each other. Following this, the structure of the  $Ln_2(MoO_4)_3$  in question (Ln = Sm, Gd, Tb) could be considered to be a framework formed by  $MoO_4$  tetrahedrons (Mo atom tetrahedral coordinated by oxygen) and  $LnO_8$  polyhedrons linked by corners.

Sample	a, Å	b, Å	c, Å	β, °	Volume, Å <sup>3</sup>
x = 0; y = 0	7.529 (1)	11.429 (1)	11.460 (1)	109.09 (3)	931.01 (1)
Gd <sub>1.97-y</sub> Sm <sub>y</sub> Tb <sub>0.03</sub> (MoO <sub>4</sub> ) <sub>3</sub>					
y = 0.01	7.536 (1)	11.434 (1)	11.463 (2)	109.14 (4)	932.10 (1)
y = 0.03	7.538 (1)	11.428 (2)	11.452 (1)	109.11 (7)	932.58 (1)
y = 0.05	7.538 (2)	11.431 (2)	11.453 (2)	109.08 (2)	932.73 (2)
y = 0.07	7.538 (1)	11.432 (1)	11.454 (1)	109.07 (1)	933.21 (1)
y = 0.09	7.538 (2)	11.433 (1)	11.457 (2)	109.08 (2)	933.59 (2)
y = 0.11	7.540 (3)	11.437 (3)	11.458 (3)	109.07 (1)	933.63 (3)
Gd <sub>1.95-x</sub> Sm <sub>0.05</sub> Tb <sub>x</sub> (MoO <sub>4</sub> ) <sub>3</sub>					
x = 0.01	7.537 (2)	11.428 (3)	11.451 (4)	109.08 (3)	932.12 (2)
x = 0.05	7.540 (2)	11.427 (1)	11.450 (2)	109.06 (3)	932.44 (6)
x = 0.07	7.542 (1)	11.430 (2)	11.448 (3)	109.05 (4)	932.83 (5)
x = 0.09	7.544 (2)	11.433 (3)	11.450 (2)	109.01 (1)	933.71 (10)

**Table 1.** Unit cell parameters of the samples of  $Gd_{2-x-y}Sm_yTb_x(MoO_4)_3$ .

All the unit cell parameters for  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  and  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$  changed with the increase in the Tb/Sm content but there was a difference in the tendency, i.e., excluding the parameter a, the others did not change monotonously in both group samples. The unit cell volume monotonously increased with the Tb/Sm doping content for the samples (Table 1).

As seen in Table 1, the Tb content increased for  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$ , which led to significant changes in the lattice parameters and distortion of the unit cell. This could be attributed to the fact that the pure  $Tb_2(MoO_4)_3$  crystallizes mainly in the orthorhombic (space group Pba2)  $\beta$ -phase under these conditions [24] or as a mixture of orthorhombic and monoclinic phases [25] where Tb was 7-coordinated in contrast to 8-coordinated in the Tb-doped  $\alpha$ -Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>.

A Williamson–Hall (W–H) analysis [26] was used to estimate the effect of Tb(III) and Sm(III) on the XRD peak broadening of the samples (Figure S1). The W–H analysis was governed by the following equation:

$$\beta = K\lambda/L\cos(\theta) + \varepsilon \tan(\theta)$$

where  $\beta$  is the observed peak broadening, K is the shape factor (0.94),  $\lambda$  is the wavelength of the Cu K $\alpha$  (0.15406 nm),  $\theta$  is the angle,  $\varepsilon$  are the microstrains and L is the crystallite size. The crystallite size (intercept =  $K\lambda/L$ ) and the microstrains (slope) were calculated by a linear fit of the plot between  $\beta$  cos( $\theta$ ) versus 4 sin( $\theta$ ) (W–H plot).

The slope of the W–H plot of all samples had a positive sign, indicating the presence of tensile strains in the samples. The microstrain level increased with the content of Tb and Sm for both series, indicating an increased concentration of defects in the crystal structure, most likely  $V_o$  (Table S1). The presence of defects also played a role in the grain boundaries inhibiting the crystal growth of the samples, leading to smaller crystallites with the increase in the content of Tb/Sm.

## 3.2. Electron Microscopy (SEM and TEM)

Crystallite size and morphology can influence the luminescent properties of phosphor materials. The SEM and TEM images of  $Gd_{1.92}Sm_{0.05}Tb_{0.03}(MoO_4)_3$  (Figure 2a–d) showed the formation of rhombohedron-shaped microcrystals with well-formed edges (Figure 2d) and a few of them were glued together (Figure 2a–c). The observation of well-faceted

microcrystals was an indication of their high crystallinity and it was in good relation to the sharp diffraction peaks observed in Figure 1. This relation has also been detected for other compounds [27].



**Figure 2.** SEM images (**a**–**c**) and TEM image (**d**) of the sample  $Gd_{1.92}Sm_{0.05}Tb_{0.03}(MoO_4)_3$ . (**e**) Particle size distribution as obtained from the SEM images.

The particle size distribution (taken as a particle area) was obtained from the SEM images by using ImageJ software [28] and is presented in Figure 2e. The mean particle size was estimated to be 0.598  $\mu$ m.

# 3.3. Optical Properties

# 3.3.1. UV-Vis Absorption

There were two major absorption regions appearing in the absorption spectra of the samples. The absorbance in the UV-Vis range (200–350 nm) showed a clear maximum at approximately 300 nm. A very weak band at approximately 406 nm was also observed (Figure 3a).



**Figure 3.** (a) UV-Vis spectra of  $Gd_{1.97-x}Sm_xTb_{0.03}(MoO_4)_3$  and (b) band gap energy calculated for the samples.

Band gap energy calculations were accomplished based on the UV-Vis data (Figure 3b). The UV-Vis data were analyzed for the relation between the optical band gap, absorption coefficient and energy (hv) of the incident photon for the near edge optical absorption. The calculations were performed from the measured curves by fits according to Tauc's equation [29],  $\alpha hv = A(hv - Eg)^n$ , where A is a constant independent of hv, Eg is the band gap and n depends on the type of transition. In addition, the well-known approach for Eg determination from the intersection of the linear fits of  $(\alpha hv)1/n$  versus hv on the *x*-axis was used with n being 1/2 and 2 for the direct and indirect band gaps, respectively. A direct band gap of ~3.65 eV was obtained for the pure Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, which was in the range of the Eg values earlier reported for several other molybdates (i.e., 3.74 eV (Eu<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>), 3.2 eV (PbMoO<sub>4</sub>), 3.98 eV (SrMoO<sub>4</sub>) and 4.3 eV (ZnMoO<sub>4</sub>)) [30].

The direct band gaps of the  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  samples are presented in Table 2. The band gap values decreased compared with those of the pure  $Gd_2(MoO_4)_3$  sample. The changes were not monotonous with the Sm content increase.

Sample	Band Gap, eV
$Gd_2(MoO_4)_3$	3.65
Gd <sub>1.96</sub> Sm <sub>0.01</sub> Tb <sub>0.03</sub> (MoO <sub>4</sub> ) <sub>3</sub>	3.60
Gd <sub>1.94</sub> Sm <sub>0.03</sub> Tb <sub>0.03</sub> (MoO <sub>4</sub> ) <sub>3</sub>	3.57
Gd <sub>1.92</sub> Sm <sub>0.05</sub> Tb <sub>0.03</sub> (MoO <sub>4</sub> ) <sub>3</sub>	3.57
Gd <sub>1.90</sub> Sm <sub>0.07</sub> Tb <sub>0.03</sub> (MoO <sub>4</sub> ) <sub>3</sub>	3.62
Gd <sub>1.88</sub> Sm <sub>0.09</sub> Tb <sub>0.03</sub> (MoO <sub>4</sub> ) <sub>3</sub>	3.61
$Gd_{1.86}Sm_{0.11}Tb_{0.03}(MoO_4)_3$	3.59

Table 2. Band gap values of the  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  samples.

## 3.3.2. Excitation Spectra

In Figure 4a, the excitation spectra are shown for the samples of Gd<sub>1.97-y</sub>Sm<sub>y</sub>Tb<sub>0.03</sub>(MoO<sub>4</sub>)<sub>3</sub> monitored by the 645 nm fluorescence emission (electric dipole transition  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ ), which is one of the characteristic bands of an Sm<sup>3+</sup> ion. Very weak broad bands between 225 and 300 nm were considered because bands appeared by the charge transfer due to the O<sup>2-</sup>-Sm<sup>3+</sup> interactions [31,32]. A series of excitation bands presented between 225 and 450 nm corresponded with the typical f–f transition of Sm<sup>3+</sup> ions centered at 332, 345, 361, 376, 391, 406, 418 and 440 nm. The strongest intensity band was the one at 406 nm, transition  ${}^{4}H_{5/2} \rightarrow {}^{4}K_{11/2}$  [33]. This band intensity increased when the Sm content increased up to x = 0.05 and then it decreased with the further increase in Sm content (x = 0.07, 0.09)

and 0.11). It is known that a host matrix containing a transition metal (such as  $VO_4^{3-}$ ,  $NbO_4^{3-}$ ,  $WO_4^{2-}$  or  $MoO_4^{2-}$ ) has an advantage over the host matrices absorbing in the UV region due to the charge transfer between the transition metal ion (electron deficient) and the oxygen ion (electron rich). Thus, the energy transfer between the transition metal atom and oxygen is considered to be an important factor to increase the luminescent properties of inorganic phosphors [12].



**Figure 4.** (a) Excitation spectra of the  $Gd_{1.97-x}Sm_xTb_{0.03}(MoO_4)_3$  sample monitored at 645 nm and emission spectra of the samples (b)  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$  and (c)  $Gd_{2-x-y}Sm_xTb_y(MoO_4)_3$  upon excitation with a 406 nm light.

3.3.3. Emission of  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$  and  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  in the Visible Light Region

All samples were activated by irradiation with light at 406 nm. The emission spectra of the samples are presented in Figure 4b,c. The samples possessed three emission bands at 600 ( ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ ), 645 ( ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ ) and 705 nm, which were not observed in the pure Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (without Sm and Tb, x = 0.00, y = 0.00). The sequence of the bands in the region of 450–575 nm, observed in all the samples both with and without Tb/Sm, could be due to photoluminescence of the Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> matrix. It was not expected to yield an emission of visible light from the Gd(III) because the lowest excited state of the ion has

a very high energy (32,000 cm<sup>-1</sup>) and Gd(III) complexes usually show a ligand-centered emission. The microstrains and defects in the structure, quite likely oxygen vacancies, could be considered to be a reason for the luminescence of Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> in the visible region. As discussed in Section 3.1, the microstrains and, consequently, the number of defects increased with an increase in the Tb/Sm ion content.

The Sm(III) ion had an emission in the visible area due to its  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{J}$  (J = 5/2, 7/2, 9/2, 11/2) transitions where  ${}^{4}G_{5/2}$  (17,800 cm<sup>-1</sup>) was the main resonance level for Sm(III). The sharp band at 560 nm and the weak shoulder at 570 nm as well as the band at 598 nm corresponded with the Sm(III) intra-4f transition from the excited level to the lower levels  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$  and  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$  [34,35].

The  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$  emission is a magnetic dipole-allowed transition and so its intensity hardly changes with the local structure symmetry of the Sm<sup>3+</sup> ions [35]. In our samples, this band was fragmented into two bands of a lower intensity. The higher intensity for the  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$  transition could be related to the symmetry of the ion coordination in the lattice [35]. For Gd<sub>1.95-x</sub>Sm<sub>0.05</sub>Tb<sub>x</sub>(MoO<sub>4</sub>)<sub>3</sub>, the strongest intensity of the band at 645 nm was provided by the sample with the Tb content of 0.03 mol and, accordingly, the most intensive photoluminescence was obtained in Gd<sub>1.92</sub>Sm<sub>0.05</sub>Tb<sub>0.03</sub>(MoO<sub>4</sub>)<sub>3</sub>.

The emission spectra analysis of the samples showed that Tb(III) played the role of a sensitizing agent and the energy transfer was in the direction of the Sm<sup>3+</sup> emitting levels.

The variation in the luminescence intensity of the emission bands at 600 and 646 nm with the doping concentration of  $\text{Sm}^{3+}$  and  $\text{Tb}^{3+}$  is presented in Figure S2a,b. The  $\text{Gd}_{2-x-y}$   $\text{Sm}_{y}\text{Tb}_{x}(\text{MoO}_{4})_{3}$  samples with a higher Sm(III) content (Figure S2a) showed a decrease in the emission intensity at 600 and 646 nm with the highest intensity of the bands for the composition  $\text{Gd}_{1.92}\text{Sm}_{0.05}\text{Tb}_{0.03}(\text{MoO}_{4})_{3}$  (Figure S2a). For the samples with Sm contents of 0.07, 0.09 and 0.11 mol, the intensity of the bands was lower. This was a result from the concentration quenching that took place when the Sm(III) ions became closer in the structure, as also observed for other matrices [35]. For  $\text{Gd}_{1.95-x}\text{Sm}_{0.05}\text{Tb}_{x}(\text{MoO}_{4})_{3}$ , a decrease in the intensity of the bands in question was observed for the Tb contents 0.05, 0.07 and 0.09 mol (Figure S2b). This was a result from the concentration quenching of the Tb ions, which became close to each other and, thus, the sensitizing of the Sm(III) was low.

## 3.3.4. Lifetime ( $\tau$ ), Decay Half-Life ( $\tau_{1/2}$ ) and Decay Rate (k)

The lifetime ( $\tau$ ) was calculated by using the one-component exponential decay function  $I(t) = I_0 \exp(-t/\tau)$ ; the decay rate (k) was calculated by  $k = 1/\tau$  and the decay half-life by  $\tau_{1/2} = \tau \ln 2$ . In Figure 5, the decay curves are presented for the  ${}^6G_{5/2} \rightarrow {}^6H_{9/2}$  transition of the Sm<sup>3+</sup> ion in the Gd<sub>1.97-y</sub>Sm<sub>y</sub>Tb<sub>0.03</sub>(MoO<sub>4</sub>)<sub>3</sub> and Gd<sub>1.95-x</sub>Sm<sub>0.05</sub>Tb<sub>x</sub>(MoO<sub>4</sub>)<sub>3</sub> samples where the excitation and the emission wavelengths were fixed at 406 and 645 nm, respectively.

The lifetime and decay half-life decreased with an increase in the Sm<sup>3+</sup> concentration for Gd<sub>1.97-y</sub>Sm<sub>y</sub>Tb<sub>0.03</sub>(MoO<sub>4</sub>)<sub>3</sub> (Table 3). A similar tendency was also observed for other phosphors [35]. For Gd<sub>1.97-y</sub>Sm<sub>y</sub>Tb<sub>0.03</sub>(MoO<sub>4</sub>)<sub>3</sub>, the lifetime decreased monotonously from 0.515 ms to 0.308 ms as the Sm<sup>3+</sup> content increased from 0.01 to 0.11 mol. In the same mode, the decay half-life decreased and the decay rate increased from 1.944  $\pm$  0.023 to 3.247  $\pm$  0.068 ms<sup>-1</sup> with an increase in the Sm<sup>3+</sup> content. For Gd<sub>1.95-x</sub>Sm<sub>0.05</sub>Tb<sub>x</sub>(MoO<sub>4</sub>)<sub>3</sub>, a non-monotonous change with an increase in the Tb content as well as very close values for all the parameters were observed. The differences were within the possible error ranges so it could be concluded that Tb influenced the emission intensity of Sm but hardly influenced the lifetime of the excited state.



Figure 5. Decay curves recorded for (a)  $Gd_{1.97-x}Sm_xTb_{0.03}(MoO_4)_3$  and (b)  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$ .

Gd <sub>1.97-y</sub> Sm <sub>y</sub> Tb <sub>0.03</sub> (MoO <sub>4</sub> ) <sub>3</sub>				
Sample	t, ms	t <sub>1/2</sub> , ms	k, ms $^{-1}$	
y = 0.01	$0.515\pm0.005$	$0.357\pm0.004$	$1.944\pm0.023$	
y = 0.03	$0.443 \pm 0.006$	$0.307\pm0.004$	$2.257\pm0.031$	
y = 0.05	$0.380\pm0.003$	$0.263 \pm 0.004$	$2.641\pm0.025$	
y = 0.07	$0.371\pm0.006$	$0.257\pm0.004$	$2.684\pm0.046$	
y = 0.09	$0.359\pm0.007$	$0.250\pm0.005$	$2.778\pm0.051$	
y = 0.11	$0.308\pm0.006$	$0.214 \pm 0.004$	$3.247\pm0.068$	
Gd <sub>1.95-x</sub> Sm <sub>0.05</sub> Tb <sub>x</sub> (MoO <sub>4</sub> ) <sub>3</sub>				
Sample	t, ms	t <sub>1/2</sub> , ms	k, ms $^{-1}$	
x = 0.01	$0.379\pm0.004$	$0.262\pm0.003$	$2.642\pm0.028$	
x = 0.03	$0.380\pm0.003$	$0.263\pm0.004$	$2.641\pm0.025$	
x = 0.05	$0.385\pm0.004$	$0.268 \pm 0.002$	$2.640\pm0.023$	
x = 0.07	$0.378\pm0.004$	$0.261 \pm 0.003$	$2.644\pm0.029$	
x = 0.09	$0.384 \pm 0.005$	$0.267\pm0.003$	$2.648\pm0.027$	

Table 3. Lifetime (	(τ), decar	y half-life (	$(\tau_{1/2})$	and decar	y rate (	$(\mathbf{k})$	)
,		/			/		

3.3.5. Chromaticity Diagrams and Coordinates

In Figure 6, the CIE 1931 (x, y) chromaticity diagrams for the emission at a 406 nm excitation are presented.

All the obtained data fitted in a small area, ranging from 0.3223 to 0.3008 in the x chromaticity coordinate and from 0.3687 to 0.3732 in the y chromaticity coordinate for  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$ ; for  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$ , this was from 0.3223 to 0.3288 in the x chromaticity coordinate and from 0.3598 to 0.3712 in the y chromaticity coordinate, respectively (Table 4). A non-monotonous color point variation with the Tb content variation was observed for  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$ . The color points moved within the yellow-green region and among all samples, the  $Gd_{1.95-x}Sm_{0.05}Tb_{0.05}(MoO_4)_3$  color point was the closest to the green light region (Figure 6a). The variations of the x/y coordinates for  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  were insignificant, resulting in the point overlapping so a single point on the diagram was obtained (Figure 6b). The related emission color was pale yellow.



**Figure 6.** The CIE chromaticity diagrams for the emission under an excitation of 406 nm for (a)  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$  (the content of Tb(III) is shown by x in the Figure field) and (b)  $Gd_{1.97-x}Sm_xTb_{0.03}(MoO_4)_3$  (the x/y coordinates for the samples overlap).

**Table 4.** Chromaticity coordinates (x, y) based on the emission spectra of  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$  and  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$ .

$Gd_{1.95-x}Sm_{0.05}Tb_{x}(MoO_{4})_{3}$				
Sample	x-Coordinate	y-Coordinate		
x = 0.01	0.3014	0.3687		
x = 0.03	0.3223	0.3712		
x = 0.05	0.3140	0.3732		
x = 0.07	0.3029	0.3694		
x = 0.09	0.3008	0.3688		
Gd <sub>1.97-y</sub> Sm <sub>y</sub> Tb <sub>0.03</sub> (MoO <sub>4</sub> ) <sub>3</sub>				
Sample	x-Coordinate	y-Coordinate		
y = 0.01	0.3291	0.3608		
y = 0.03	0.3288	0.3608		
y = 0.05	0.3223	0.3712		
y = 0.07	0.3234	0.3598		
y = 0.09	0.3246	0.3634		
y = 0.11	0.3288	0.3608		

The points of all samples were close to the white light point (x = 0.333, y = 0.333). All the above results revealed that the phosphors have the potential for wLED applications.

# 4. Conclusions

 $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_4)_3$  and  $Gd_{1.97-y}Sm_yTb_{0.03}(MoO_4)_3$  solid solutions were successfully prepared by using the conventional solid state reaction route. All the samples proved to be in the single phase state without crystalline impurities. The UV-Vis and luminescence excitation spectra measurements indicated that the 406 nm excitation wavelength was the appropriate one. The luminescence emission spectra showed an emission close to the white light point. The lifetime of the samples lowered with an increase in the Tb/Sm content. It can be concluded that the samples have the potential for applications in solid state lighting.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/cryst12010120/s1, Table S1: Crystallite size and microstrain of the samples based on Williamson–Hall plot; Figure S1: Williamson–Hall (W–H) plot for a few of the samples of  $Gd_{2}(MoO_{4})_{3}$  and  $Gd_{1.92}Sm_{0.05}Tb_{0.03}(MoO_{4})_{3}$ . These are available for all the samples but not included; Figure S2: Emission band intensity variation for Sm(III) with the doping content of (a)  $Sm^{3+}$  ion and (b)  $Tb^{3+}$  ion where (a)  $Gd_{1.97-v}Sm_vTb_{0.03}(MoO_{4})_{3}$  and (b)  $Gd_{1.95-x}Sm_{0.05}Tb_x(MoO_{4})_{3}$ .

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