Influence of the Structure on the Properties of Na\textsubscript{x}Eu\textsubscript{y}(MoO\textsubscript{4})\textsubscript{z} Red Phosphors

Vladimir A. Morozov,
Bogdan I. Lazoryak,
Semen Z. Shmurak,
Oleg I. Lebedev,
Nicolas Gauquelin,
Johan Verbeeck,
Joke Hadermann,
and Gustaaf Van Tendeloo

Chemistry Department, Moscow State University, 119991 Moscow, Russia
Institute of Solid State Physics, 142432 Chernogolovka, Russia
Laboratoire CRISMAT, UMR 6508 CNRS ENSICAEN, 6bd Marechal Juin, 14050 Caen, France
EMAT, University of Antwerp, Groenenborlaan 171, B-2020 Antwerp, Belgium

ABSTRACT: Scheelite related compounds ($A$′$A$″)$_x$($B$′$B$″$O_4$)$_y$ with $B$′$B$″ = W and/or Mo are promising new red phosphors for phosphor-converted white-light-emitting-diode and solid-state lasers. Cation substitution in CaMoO\textsubscript{4} of Ca\textsuperscript{2+} by the combination of Na\textsuperscript{+} and Eu\textsuperscript{3+}, with the creation of A cation vacancies, has been investigated as a factor for controlling the scheelite-type structure and the luminescent properties. Na\textsubscript{5}Eu(MoO\textsubscript{4})\textsubscript{4} and Na\textsubscript{5}Eu\textsuperscript{3+}(1−x)/3MoO\textsubscript{4} (0.138 ≤ x ≤ 0.5) phases with a scheelite-type structure were synthesized by the solid state method; their structural characteristics were investigated using transmission electron microscopy. Contrary to powder synchrotron X-ray diffraction before the study by electron diffraction and high resolution transmission electron microscopy in this paper revealed that Na\textsubscript{0.286}Eu\textsubscript{0.571}MoO\textsubscript{4} has a (3 + 2)D incommensurately modulated structure and that (3 + 2)D incommensurately modulated domains are present in Na\textsubscript{0.200}Eu\textsubscript{0.600}MoO\textsubscript{4}. It also confirmed the (3 + 1)D incommensurately modulated character of Na\textsubscript{0.138}Eu\textsubscript{0.613}MoO\textsubscript{4}. The luminescent properties of all phases under near-ultraviolet (n-UV) light have been investigated. The excitation spectra of these phosphors show the strongest absorption at about 395 nm, which matches well with the commercially available n-UV-emitting GaN-based LED chip. The emission spectra indicate an intense red emission due to the $^5D_0 \rightarrow ^7F_2$ transition of Eu\textsuperscript{3+}, with local minima in the intensity at Na\textsubscript{0.326}Eu\textsubscript{0.557}MoO\textsubscript{4} and Na\textsubscript{0.320}Eu\textsubscript{0.569}MoO\textsubscript{4} for ~613 nm and ~616 nm bands. The phosphor Na\textsubscript{5}Eu(MoO\textsubscript{4})\textsubscript{4} shows the brightest red light emission among the phosphors in the Na\textsubscript{2}MoO\textsubscript{4}−Eu\textsubscript{2}MoO\textsubscript{4} system and the maximum luminescence intensity of Na\textsubscript{5}Eu(MoO\textsubscript{4})\textsubscript{4} ($\lambda_{ex}$ = 395 nm) in the $^5D_0 \rightarrow ^7F_2$ transition region is close to that of the commercially used red phosphor YVO\textsubscript{4}:Eu\textsuperscript{3+} ($\lambda_{ex}$ = 326 nm). Electron energy loss spectroscopy measurements revealed the influence of the structure and Na/Eu cation distribution on the number and positions of bands in the UV-optical-infrared regions of the EELS spectrum.

1. INTRODUCTION

White light-emitting diodes (WLEDs) receive a lot of attention as promising solid-state lighting sources, because of their high reliability, long lifetime, low energy consumption, and environmentally friendly characteristics. WLEDs are used as white light sources to replace traditional incandescent and fluorescent lamps, etc. Phosphor-converted WLEDs can be made by using blue/green/red tricolor phosphors excited by a near-ultraviolet (UV) (360–410 nm) InGaN-based LED and are competitive for applications that require a high quality of light (high color-rendering index, high color reproducibility, etc.). Molybdate and tungstate phosphors have broad and intense absorption bands in the near-UV region due to charge transfer from oxygen to the metal (Mo or W). Rare earth doped molybdates and tungstates with a scheelite-type (CaWO\textsubscript{4}) structure, such as MR(BO\textsubscript{4})\textsubscript{2} (M = Li, Na, K, Ag; R = lanthanides (Ln), Y, Bi; B = W, Mo), have shown potential as WLED and laser materials. For example, Na\textsubscript{0.9}Y\textsubscript{0.1}Eu\textsubscript{0.5}(WO\textsubscript{4})\textsubscript{3} and KGd\textsubscript{0.75}Eu\textsubscript{0.25}(MoO\textsubscript{4})\textsubscript{2} show a much higher light output than Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}, often used as red phosphor for WLEDs.

The scheelite-type ABO\textsubscript{4} structure is built up by \([B\textsuperscript{′}B\textsuperscript{″}O_4]^{−}\) layers and \(A\) cation vacancy (cation deficiency) with a deformed scheelite-type structure and the maximum luminescence intensity of Na\textsubscript{5}Eu(MoO\textsubscript{4})\textsubscript{4} ($\lambda_{ex}$ = 395 nm) in the $^5D_0 \rightarrow ^7F_2$ transition region is close to that of the commercially used red phosphor YVO\textsubscript{4}:Eu\textsuperscript{3+} ($\lambda_{ex}$ = 326 nm). Electron energy loss spectroscopy measurements revealed the influence of the structure and Na/Eu cation distribution on the number and positions of bands in the UV-optical-infrared regions of the EELS spectrum.

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Recently, the combination of transmission electron microscopy (TEM) and X-ray diffraction (XRD) has allowed us to gather new information about the real structure of scheelite-type compounds. A detailed analysis of the satellite reflections located between main reflections on the electron diffraction (ED) patterns has revealed that scheelite-type structures are often incomensurately modulated and require using the superspace (3 + n)-dimensional formalism to index them.

It was shown by TEM that the real Na$_{2/7}$Gd$_{4/7}$MoO$_4$ structure is not the well-known tetragonal structure (space group $I4/1$) with a random distribution of Na$^+$ and Gd$^{3+}$ in the A position as it was thought earlier. Na$_{2/7}$-Gd$_{4/7}$-MoO$_4$ has a (3 + 2)-dimensional (3 + 2D) incomensurately modulated structure with a partially ordered distribution of vacancies, Na and Gd cations. On the other hand, an investigation of the phases in the Na$_2$MoO$_4$ system (3 + 2)D incommensurately modulated phases are present; we also determine the synchrotron PXRD patterns for Na$_{0.286}$Eu$_{0.571}$MoO$_4$ while Na$_{0.286}$Gd$_{0.571}$MoO$_4$ is (3 + 2)D incomensurately modulated phases (0.015 $\leq x \leq 0.5$) have been found on the XRD patterns for Na$_{0.286}$Eu$_{0.571}$MoO$_4$ phases (0.015 $\leq x \leq 0.25$) have a (3 + 1)D structure with different amounts of Eu$^{3+}$ dimers while no satellite reflections have been found on the synchrotron PXRD patterns for x = 0.5 (Na$_{0.286}$Eu$_{0.514}$MoO$_4$) and x = 0.286 (Na$_{0.286}$Eu$_{0.517}$MoO$_4$ or Na$_{0.286}$-Eu$_{0.517}$-MoO$_4$). Therefore, the structure of Na$_{0.286}$Eu$_{0.514}$MoO$_4$ and Na$_{0.286}$Eu$_{0.517}$MoO$_4$ was refined in the conventional 3D space group with a random distribution of Na$^+$ and Eu$^{3+}$ cations. The absence of satellite reflections on the synchrotron PXRD patterns for Na$_{0.286}$Eu$_{0.517}$MoO$_4$ while Na$_{0.286}$Gd$_{0.517}$MoO$_4$ is (3 + 2)D incomensurately modulated demands a detailed TEM investigation of the phases in the Na$_2$MoO$_4$-Eu$_{0.517}$-MoO$_4$ system.

Using a detailed TEM investigation we show that also in the Na$_{0.317}$Eu$_{0.683}$MoO$_4$ system (3 + 2)D incomensurately modulated phases are present; we also determine the luminescent properties of the different phases and prove with electron energy loss spectroscopy (EELS) that the dimensionality influences the luminescent properties.

2. EXPERIMENTAL SECTION

Materials and Sample Preparation. The Na$_2$Eu(MoO$_4$)$_4$ molybdenum oxide was prepared from a stoichiometric mixture of Na$_2$MoO$_4$, Eu$_2$O$_3$ (99.99%), and MoO$_3$ (99.99%) by the solid-state method at 923 K for 48 h. Earlier, Guo C. et al. studied the influence of the annealing temperature on the stability and luminescent properties of Na$_2$La(MoO$_4$)$_4$Eu$^{3+}$. It has been found that an annealing temperature in the range from 873 to 923 K is optimal for the red emission intensity of Eu$^{3+}$ and that increasing the temperature up to 973 K leads to partial decomposition of Na$_2$La(MoO$_4$)$_4$Eu$^{3+}$. Cubic Na$_2$MoO$_4$ was prepared from a stoichiometric mixture of Na$_2$CO$_3$ and MoO$_3$ by the solid-state method at 923 K for 24 h. The monoclinic α-modification of Eu$_{2/3}$MoO$_4$ and Na$_2$Eu$^{3+}$(2−3xo/3)[(1-x/2)-MoO$_4$] (0.138 $\leq x \leq 0.5$) was synthesized by solid-state method at 1023 K for 48 h in air followed by quenching from T = 1023 K to room temperature ($T_R$). A TEM study of Na$_2$Eu$^{3+}(2−3xo/3)[(1-x/2)-MoO$_4$] (0.138 $\leq x \leq 0.5$) was performed on the same samples as the ones that were studied by synchrotron PXRD. The element composition of Na$_2$Eu(MoO$_4$)$_4$ was confirmed by energy dispersive X-ray (EDX) analysis. EDX analysis and electron diffraction (ED) were performed using a Philips CM20 microscope with an Oxford INCA attachment. The EDX analysis results were based on the Eu, and Mo lines in the spectra. EDX analysis is carried out at 4 points for 10 different crystallites, in combination with ED analysis. The cation ratio has been found to be Mo/Eu = 4.04(0.35):1 (80.1 ± 1.5 at% Mo, 19.9 ± 1.5 at% Eu). This is close to the bulk Na$_2$Eu(MoO$_4$)$_4$ composition. The element content of Na$_2$Eu$^{3+}(2−3xo/3)[(1-x/2)-MoO$_4$] (0.138 $\leq x \leq 0.5$) was determined earlier by inductively coupled plasma optical emission spectrometry (ICP-OES), and the Na/Eu ratios for these Na$_2$Eu$^{3+}(2−3xo/3)[(1-x/2)-MoO$_4$] phases are listed in ref 34.

Samples for transmission electron microscopy were prepared by crushing powders in an agate mortar and dispersing them in methanol. A few drops of the suspension were placed on a copper grid with holey carbon film. ED and high-resolution transmission electron microscopy (HRTEM) were carried out with a JEOL 400EX microscope operated at 400 kV and having 0.17 nm point resolution.

Electron energy loss (EELS) spectroscopy measurements were acquired on a Titan$^3$ 80-300 operated at 80 kV equipped with a monochromator giving an energy resolution of 130 meV (full width at half-maximum of the zero-loss peak). A dispersion of 0.01 eV/pixel and an exposure time of 0.2 ms were used. Thin areas of each sample were chosen in order to avoid plural scattering. The tail of the Zero Loss was removed by subtraction of the second order polynomial fit performed in the wavelength regime.

Optical spectroscopic studies were carried out on a setup consisting of two monochromators MDR-4 and MDR-6 (wavelength range 200–1000 nm, dispersion 1.3 nm/mm), a photoelectric multiplier FEU-106 (spectral sensitivity in the range 220–800 nm), and a recording system. The MDR-4 monochromator was used to analyze the luminescence excitation spectra of the samples in the wavelength range 275–500 nm (4.51–2.48 eV). The MDR-6 monochromator was used for studying the luminescence spectra of the samples. A DKSSh-150 xenon lamp served as the light source. Photoluminescence spectra of all samples were measured under nearly the same condition to reduce the error. All measurements were performed at $T_R$ and corrected for the sensitivity of the spectrometer.

3. RESULTS AND DISCUSSION

3.1. Electron Diffraction Study. Na$_2$Eu(MoO$_4$)$_4$ Phase (Na/Eu Ratio = 5:1). ED patterns of Na$_2$Eu(MoO$_4$)$_4$ along some of the main zone axes are shown in Figure 2. All strong reflections in the ED patterns can be indexed using the scheelite tetragonal $I4/1/a$ cell with unit cell parameters a = 0.517 nm and c$_s$ = 1.15 nm (s refers to the scheelite-type unit cell) (Figure 2b). The appearance of lower intensity superstructure reflections in the [001] ED pattern necessitates the use of a supercell to be able to index all reflections.

All reflections can be indexed in the tetragonal $I4/1/a$ space group with unit cell parameters a ≈ 1.156 nm, c $\approx$ 1.149 nm (Figure 2a). Thereby, Na$_2$Eu(MoO$_4$)$_4$ exhibits a structure similar to other Na$_2$Ln(MoO$_4$)$_4$ (Na$_2$Ln[Na$_{(2−3xo)}$(MoO$_4$)$_3$]) compounds and is characterized by an ordered replacement of part of the anionic [Mo$O_4$] groups by Na$^+$ cations. However, inspired by the example of Na$_2$Y(MoO$_4$)$_4$ by Arakcheeva and Chapuis, all reflections observed for Na$_2$Eu(MoO$_4$)$_4$ can also...
be indexed as a commensurally modulated scheelite-related structure with four $hkilm$ indexes given by the diffraction vector $H = ha^* + kb^* + lc^* + mc^*$, using the superspace group (SSG) $I2/b(a\overline{3}0)00$ with unit cell parameters $a = 0.52318$ nm, $c = 1.15$ nm, and $\gamma \approx 90^\circ$. The modulation vector $\mathbf{q} = 0.59a^* + 1.21b^*$ is close to the modulation vector $q = 0.59h - 0.79k$ taken from the synchrotron PXRD patterns. A more obvious choice for the domains after rotation by $90^\circ$ is the reduction of the satellite reflections observed in the [001] ED pattern to detect the formation of twins in the crystal. As a consequence of the insignificant difference in the unit cell parameters and the very small deviation of the monoclinic $\gamma$-angle from $90^\circ$ ($a = 0.52318$ nm, $b = 0.52310$ nm, and $\gamma = 90.232^\circ$), the positions of the main reflections are (within the limited resolution on the ED patterns) not different for the domains after rotation by $90^\circ$.

Figure 4 shows a [001] ED pattern of $Na_{0.138}Eu_{0.621}MoO_4$ which is the superposition of two [001] ED patterns of $Na_{0.138}Eu_{0.621}MoO_4$ twinned domains rotated along the $c$ axis over $90^\circ$ with respect to each other. Remark that only the satellite reflections allow to detect the formation of twins in the crystal. As a consequence of the insignificant difference in the unit cell parameters and the very small deviation of the monoclinic $\gamma$-angle from $90^\circ$ ($a = 0.52318$ nm, $b = 0.52310$ nm, and $\gamma = 90.232^\circ$), the positions of the main reflections are (within the limited resolution on the ED patterns) not different for the domains after rotation by $90^\circ$. The white rectangles in Figure 4 based on the first order (0001 and 2201) and second order (2202) satellites for the two domains clearly show the rotation of the domains by $90^\circ$. The deviation of the monoclinic $\gamma$-angle from $90^\circ$ results in the splitting of some low-intensity spots. Furthermore, the intensity of the satellite reflections for the second domain is much less than for the first domain, suggesting different amounts of both domains. The schematic drawing is shown in Figure 4b.

$Na_{x}Eu_{1-x}MoO_4$ Phases ($x = 0.5, 0.286$ ($Na/Eu \sim 1:2$), $0.200$ ($Na/Eu \sim 1:3$)). [001] ED patterns of the $Na_{x}Eu_{1-x}MoO_4$ phases ($x = 0.5, 0.286, 0.200$) are shown in Figure 5.
In the [001] ED pattern of Na$_{0.286}$Eu$_{0.571}$MoO$_4$ (Figure 5a), no weaker reflections are observed, in contrast to other phases in the Na$_2$MoO$_4$–Eu$_2$MoO$_4$ system. All reflections can be indexed in the tetragonal scheelite $I4_1/a$ space group with unit cell parameters $a_0 \approx 0.52$ nm and $c_0 \approx 1.15$ nm assuming a random distribution of Na$^+$ and Eu$^{3+}$ cations in the structure.

The [001] ED pattern of Na$_{0.286}$Eu$_{0.571}$MoO$_4$ is very similar to the one reported previously for Na$_{2/7}$Gd$_{4/7}$MoO$_4$ with a $3 + 2$D incommensurately modulated structure$^{32}$ and indicates that Na$_{0.286}$Eu$_{0.571}$MoO$_4$ behaves in a way similar to Na$_{2/7}$Gd$_{4/7}$MoO$_4$. Both have a partially ordered distribution of vacancies, Na$^+$ and Eu$^{3+}$ cations. In contrast to the $[001]$ ED pattern for the $(3 + 1)D$ Na$_2$Eu$_{0.621}$MoO$_4$, the weaker reflections observed in the $[001]$ ED pattern for Na$_{0.286}$Eu$_{0.571}$MoO$_4$ cannot be indexed with four digit indices $hk0mn$, corresponding to the diffraction wave vector $H = ha^* + kb^* + lc^* + mq_1^* + nq_2^*$, with modulation vectors $q_1 \approx 0.57a^*$ + 0.80$b^*$ and $q_2 \approx -0.80a^*$ + 0.57$b^*$. The presence of reflections with $m$ and $n$ both equal to 1 or 0 on the $[001]$ ED pattern proves that Na$_{0.286}$Eu$_{0.571}$MoO$_4$ is tetragonal with two modulation vectors (Figure 5b). The $q_1$ and $q_2$ vectors are symmetrically dependent according to the tetragonal symmetry of the underlying basic scheelite structure for this composition. The $hk0mn$: $h + k + l = 2n$ and $hk0mn$: $h = 2n$ reflection conditions are in agreement with the space group $I4_1/a$ for the basic structure. Thus, the ED patterns of Na$_{0.286}$Eu$_{0.571}$MoO$_4$ can be completely indexed (similar to Na$_{2/7}$Gd$_{4/7}$MoO$_4$) in the tetragonal superspace group with unit cell parameters $a_0 \approx 0.524$ nm, $c_0 \approx 1.150$ nm and two modulation vectors $q_1 \approx 0.57a^* + 0.80$b^* and $q_2 \approx -0.80a^* + 0.57b^*$. These ED results clearly show the presence of satellite reflections, whereas they were absent on the synchrotron PXRD data.$^{34}$ They are much weaker than those previously found for Na$_{2/7}$Gd$_{4/7}$MoO$_4$,$^{32}$ which could explain why for Na$_{0.286}$Eu$_{0.571}$MoO$_4$ they were not detected by synchrotron PXRD.

In contrast to other Na$_x$Eu$_{(2-x)/3}$MoO$_4$ phases, two types of $[001]$ ED patterns are observed for the composition with $x = 0.200$ (Figure 5c and d). The ED pattern in Figure 5c is very similar to the $[001]$ ED pattern of Na$_{0.138}$Eu$_{0.621}$MoO$_4$ (Figure 3) and can be completely indexed using the $I2/b$($a/0$)00 SSG with the unit cell parameters and modulation vector determined earlier from the synchrotron PXRD pattern.$^{34}$ However, other ED patterns, of which an example is shown in Figure 5d are similar to the $[001]$ ED pattern of Na$_{0.286}$Eu$_{0.571}$MoO$_4$ with two modulation vectors $q_1 \approx 0.55a^* + 0.79b^*$ and $q_2 \approx -0.79a^* + 0.55b^*$. The reflections $hk0mn$ with $m$ and $n$ both different from 0 are also present here, although much weaker than in Figure 5b.

3.2. High Resolution Transmission Electron Microscopy. HRTEM observations were performed along the most informative zone axis $[001]$ where the structure of the Na$_{2/7}$Gd$_{4/7}$MoO$_4$ phases can be interpreted in terms of columns of A cations and MoO$_4$ groups. Also, among the main zones, only the $[001]$ ED patterns exhibit superstructure reflections (Figure 3). In order to understand the origin of these superstructure reflections, HRTEM has been performed. $[001]$ HRTEM images of the Na$_{2/7}$Gd$_{4/7}$MoO$_4$ phases ($x = 0.138, 0.200$) together with the corresponding ED patterns are shown in Figures 6–8, respectively. On these images the bright dots represent the projected cationic columns. Along the $[001]$ direction, the A and B cations are projected on top of each other.

Figure 6 shows $[001]$ HRTEM images of Na$_{0.138}$Eu$_{0.621}$MoO$_4$ and the corresponding ED patterns. Two different modulation types can be detected on the $[001]$ HRTEM images. In the first one (Figure 6a), the variation in the brightness of the dots in the image is in agreement with the modulation vector derived from the ED patterns (Figure 3) and corresponds to the $(3 + 1)D$ structure. The difference in brightness between the dots is clearly visible resulting in a wavy contrast due to the compositional modulation.$^{34}$ In other areas though, the modulation waves propagate along two perpendicular directions (marked with arrows) (Figure 6b). The image of the $(3 + 1)D$ structure in Figure 6a consists of chains of four linear

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**Figure 4.** Superposition of $[001]$ ED patterns for two Na$_{0.138}$Eu$_{0.621}$MoO$_4$ domains due to the $90^\circ$ rotating twinning along $c$ axis and schematic representation of the diffraction pattern (1 and 2 refer to the first and second domains). Full circles are main reflections; rings are satellite reflections of the first domain; squares are satellite reflections of the second domain.

**Figure 5.** $[001]$ ED patterns of Na$_x$Eu$_{(2-x)/3}$MoO$_4$ phases ($x = 0.5$ (a), 0.286 (b), 0.200 (c, d)). White rings mark $hk0mn$ reflections with $|n| = |l| = 1$. 

In the $[001]$ ED pattern of Na$_{0.286}$Eu$_{0.571}$MoO$_4$, the origin of these superstructure reflections, whereas they were absent on the synchrotron PXRD data.$^{34}$ However, other ED patterns, of which an example is shown in Figure 5d are similar to the $[001]$ ED pattern of Na$_{0.286}$Eu$_{0.571}$MoO$_4$ with two modulation vectors $q_1 \approx 0.55a^* + 0.79b^*$ and $q_2 \approx -0.79a^* + 0.55b^*$. The reflections $hk0mn$ with $m$ and $n$ both different from 0 are also present here, although much weaker than in Figure 5b.

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bright dots corresponding to [⋯−AO₄−MoO₄−⋯] columns of atoms (marked by white rectangles) along the c-axis, similarly oriented and shifted with respect to each other in accordance to the modulated vector. The image in Figure 6b with modulation waves along two perpendicular directions clearly consists of two families of the same chains as in Figure 6a but rotated with respect to each other over 90° and is therefore a twinned area. This observation confirms the structural model and the interpretation proposed for the ED patterns in Figure 4.

[001] HRTEM images of Na₀.₂₀₀Eu₀.₆₀₀MoO₄ are shown in Figures 7 and 8. The Fourier transforms obtained from the HRTEM image; and (c) lower magnification low pass filtered “image of a larger area around part a”, using a Bragg-mask filter, basic reflections marked as the black square in part b were used to improve the signal-to-noise ratio. A thick region is shown because the modulation quickly disappears under the electron beam, thin regions first.

Figure 6. [001] HRTEM images of Na₀.₁₃₈Eu₀.₆₂₁MoO₄.

Figure 7. (a) [001] HRTEM image of Na₀.₂₀₀Eu₀.₆₀₀MoO₄; (b) Fourier transform obtained from the HRTEM image; and (c) lower magnification low pass filtered “image of a larger area around part a”, using a Bragg-mask filter, basic reflections marked as the black square in part b were used to improve the signal-to-noise ratio. A thick region is shown because the modulation quickly disappears under the electron beam, thin regions first.

to enhance the signal-to-noise ratio in the HRTEM image and clarify the nature of the satellite reflections on the ED patterns, Fourier filtering was applied using a Bragg mask. The mask size was chosen in such way that no structural information was lost and no artifacts were introduced, as proven by the persisting similarity between the filtered images (Figures 7c and 8c) and the experimental images (Figure 7a and 8a). Figures 7c and 8c show filtered HRTEM images of the Na₀.₂₀₀Eu₀.₆₀₀MoO₄ phase using the basic reflections marked with black squares in the Fourier transforms (Figures 7b and 8b).

The [001] HRTEM image of Na₀.₂₀₀Eu₀.₆₀₀MoO₄ shown in Figure 7 consists of square blocks of brighter dots (marked by a white square) containing inside four dots with lower intensity. Previously such type of blocks were observed on the [001] HRTEM image of Na₀.₇₅Gd₀.₆₇MoO₄. The shift of the blocks of brighter dots relative to each other along two perpendicular directions corresponds to the satellite reflections on the ED pattern (Figure 5d). Thus, the HRTEM image confirms that the fragment of the Na₀.₂₀₀Eu₀.₆₀₀MoO₄ structure shown in Figure 7 is (3 + 2)-dimensionally modulated, and not simply twinned, since the modulation waves propagate along two perpendicular directions in all observed areas and both modulation vectors q₁ and q₂ are clearly present on the Fourier transform (Figure 7b). The [001] HRTEM image of a second fragment of the Na₀.₂₀₀Eu₀.₆₀₀MoO₄ structure shown in Figure 7 is (3 + 2)-dimensionally modulated, and not simply twinned, since the modulation waves propagate along two perpendicular directions in all observed areas and both modulation vectors q₁ and q₂ are clearly present on the Fourier transform (Figure 7b). The [001] HRTEM image of a second fragment of the Na₀.₂₀₀Eu₀.₆₀₀MoO₄ structure shown in Figure 8c is similar to the [001] HRTEM image of the (3 + 1)D Na₀.₁₃₈Eu₀.₆₂₁MoO₄ (Figure 6a). It also consists of chains of four linear bright dots, similarly oriented and shifted with respect to each other in accordance with the modulation vector. In conclusion, two types of modulated structures have been found for Na₀.₂₀₀Eu₀.₆₀₀MoO₄: a (3 + 1)D incommensurately modulated structure and a (3 + 2)D incommensurately modulated one. The change from (3 + 1)D to (3 + 2)D here involves the occurrence of a second modulation vector perpendicular to the one in the (3 + 1)D structure, with the same length.

3.3. Luminescent Properties. The photoluminescent excitation (PLE) and the photoluminescent emission (PL) spectra of the Na₅Eu(MoO₄)₄ and Na₀.₅Eu₀.₅MoO₄ phosphors are shown in Figures 9 and 10. The PLE spectrum of Na₀.₅Eu₀.₅MoO₄ shown in Figure 9b, is representative for all Na₀.ₓEu₀.₅₋ₓMoO₄ (0.138 ≤ x ≤ 0.5) phases. The PL spectra of all phases are shown in Figure 11. Positions and intensities of two maximum bands on the PL and PLE spectra...
of phases in the Na$_2$MoO$_4$–Eu$_{2/3}$MoO$_4$ system are given in Table 1. As shown in Figure 9, the PLE spectra were measured in the spectral range from 275 to 500 nm by monitoring the emission at 617.4 nm and 615.6 nm, which is attributed to the 5D$_0$ → 7F$_2$ transition of Eu$^{3+}$ ions. Both PLE excitation spectra show a broad excitation band in the range 275–300 nm and 275–350 nm as well as a group of sharp lines in the range 300–500 nm and 350–500 nm for Na$_5$Eu(MoO$_4$)$_4$ and Na$_{0.5}$Eu$_{0.5}$MoO$_4$, respectively. The broad excitation bands centered at ∼290 nm for Na$_5$Eu(MoO$_4$)$_4$ (Figure 9a) and at ∼315 nm for Na$_{0.5}$Eu$_{0.5}$MoO$_4$ (Figure 9b) are attributed to a charge transfer (CT) from oxygen to molybdenum inside the MoO$_4^{2−}$ groups. In the spectral region from 350 to 500 nm all phases in the Na$_2$MoO$_4$–Eu$_{2/3}$MoO$_4$ system show characteristic intracon­figurational 4f−4f emissive transitions of Eu$^{3+}$: a sharp 7F$_0$ → 5L$_6$ transition for 394.5–395 nm, a 7F$_0$ → 5D$_2$ transition for 465.5–466 nm (Table 1). In accordance with Table 1 and Figure 9, the change of the crystal structure from Na$_5$Eu(MoO$_4$)$_4$ to Na$_{0.5}$Eu$_{0.5}$MoO$_4$ practically does not change positions of the bands of 7F$_0$ → 5L$_6$/7F$_0$ → 5D$_2$ ratio and a shift of the center of the broad excitation band toward longer wavelengths.

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PL spectra of Na$_5$Eu(MoO$_4$)$_4$ and Na$_x$Eu$_{(2−x)/3}$□$_{(1−2x)/3}$MoO$_4$ (0.138 ≤ x ≤ 0.5) phases are shown in Figures 10 and 11. PL spectra in the spectral range from 570 to 650 nm show the typical red emitting features of
Eu$^{3+}$, including $^5\Delta_0 \rightarrow ^7F_j$ ($j = 0, 1, 2$) emissions. The most intense peak in the region from 600 to 620 nm is due to the electric dipole transition $^5\Delta_0 \rightarrow ^7F_2$, $^5\Delta_0 \rightarrow ^7F_3$ transition bands at $\sim 613$ nm and at $\sim 616$ nm on the PL spectrum of Na$_2$Eu(MoO$_4$)$_x$ have more intensity than those of all Na$_5$Eu$_x$MoO$_4$ (0.0138 $\leq x \leq 0.5$) phases (Figure 10, Table 1). The transition at 590 nm is the $^3\Delta_0 \rightarrow ^1F_5$ magnetic dipole transition. Emission wavelengths of these $4f$--$4f$ transitions are only moderately influenced by the environment of the lanthanide ions since the partially filled 4f shell is well shielded by the environment of the Al$^{3+}$ polyhedron. Nevertheless, it is possible to correlate the spectrum with the symmetry of the site.

CaWO$_4$ with the tetragonal symmetry (space group $I4_1/a$) has $C_{4h}$ as 3D point group. The Ca$^2+$O distances in the CaO$_4$ polyhedron vary from 0.2450 to 0.2486 nm (difference between the distances of 1.5%) and from 0.2559 to 0.2568 nm (difference of 2.2%) respectively. The substitution of Ca$^{2+}$ in CaMoO$_4$ by Na$^+$ and R$^{3+}$ (R = Ln, Y, Bi) leads to the formation of double molybdates Na$_2$Eu$_x$R$_2$MoO$_{14}$ and Na$_3$Eu$_x$R$_3$MoO$_{15}$ with ordering or random distribution of Na$^+$ and R$^{3+}$ cations, respectively. Both types of compounds also have the tetragonal symmetry (space group $I4_1/a$) and $C_{4h}$ as 3D point group. However, the distortion of the RO$_8$ polyhedron is different for both compounds and much larger for Na$_2$Eu$_x$R$_3$MoO$_{15}$. For example, the La$^3+$--O distances in the LaO$_8$ polyhedron in Na$_5$La(MoO$_4$)$_4$ and NaLa(MoO$_4$)$_2$ vary from 0.2495 to 0.2498 nm (difference between the distances of 0.1%) and from 0.2559 to 0.2616 nm (a difference of 2.2%), respectively.

Due to the distortion of the RO$_8$ polyhedron for Na$_2$Eu$_x$MoO$_4$ (0.138 $\leq x \leq 0.5$) structures, the Na$^+$ and R$^{3+}$ cations occupy a site with maximal $C_2$ site symmetry. The lack of inversion symmetry induces a high intensity of the hypersensitive $^5\Delta_0 \rightarrow ^7F_2$ transition. Another intensity is the appearance of a band of the $^5\Delta_0 \rightarrow ^7F_0$ transition at 580 nm on the PL spectra of the Na$_2$Eu$_x$MoO$_4$ (0.138 $\leq x \leq 0.5$) phases (Figure 10 and 11). Since the $^5\Delta_0 \rightarrow ^7F_0$ transition is forbidden both for electric and magnetic dipole interactions, the intensity can be very low or even nonobservable. Yet, for $C_2$ symmetry the transition is induced, so a peak can be expected at that position. As splitting of the initial and final level, both characterized by $j = 0$, is not possible, observing more than one transition would be an indication of the presence of more than one nonequivalent site for the luminescent Eu$^{3+}$ ions. Since we observe only one peak for all Na$_5$Eu$_x$MoO$_4$ (0.138 $\leq x \leq 0.5$) phases, the local environment of the Eu$^{3+}$ ions probably remains the same over the whole crystal.\(^{37}\)

Figure 11 shows PL spectra ($\lambda_{\text{ex}} = 395$ nm) of Na$_2$Eu$_x$MoO$_4$ (0 $\leq x \leq 0.5$) phases with the ordered distribution of vacancies, Na and Eu cations, a correlation has been proposed between the relative amount of Eu$^{3+}$ dimers and the characteristic parameters ($Q_{\text{Eu}}(\lambda_{\text{ex}})$), intrinsic quantum yields ($\eta_{\text{in}}(\lambda_{\text{ex}})$) of the Eu$^{3+}$-centered luminescence.\(^{38}\) At the same time, it was believed that Na$_5$Eu$_x$MoO$_4$ phases with $x = 0.286$ and $x = 0.5$ have 3D nonmodulated structures with one crystallographic cation position statistically occupied by Eu$^{3+}$ and Na$^+$. However, our detailed TEM study has revealed that Na$_2$Eu$_x$MoO$_4$ has a (3 + 2)D incommensurately modulated structure, such as the Na$_3$Gd$_2$MoO$_6$ structure,\(^{32}\) in which there is a full ordering of vacancies and a partially ordered distribution of Eu$^{3+}$ and Na$^+$ cations. In addition, similar domains with the (3 + 2)D structure have been found next to (3 + 1)D domains in Na$_{0.200}$Eu$^{3+}_{0.600}$MoO$_4$. Thus, the occurrence of the (3 + 2)D modulation coincides with the local minima in the luminescence properties.

There are two possible reasons for the decreasing $^5\Delta_0 \rightarrow ^7F_2$ emission intensity of Na$_2$Eu$_x$(MoO$_4$)$_x$ red phosphors (Figures 10 and 11) as the Na$_2$/Eu$_2$ ratio varies from 5:1 to 1:2. 1) A quenching effect because usually the luminescent intensity decreases with increasing concentration of the luminescent centers; 2) changing the structure from 3D with an ordered distribution of Eu$^{3+}$ and Na$^+$ cations (Na$_2$/Eu$_2$ = 5:1) to a (3 + 2)D incommensurately modulated structure with a partially ordered distribution (Na$_2$/Eu$_2$ = 1:2) via a 3D structure for Na/ Eu = 1:1 with a random distribution of Eu$^{3+}$ and Na$^+$ cations.

Concentration quenching is caused by the energy transfer between luminescent centers, and these energy-transfer chains trigger the energy migration to the energy sink such as crystalline defects or trace ions. As the concentration of Eu$^{3+}$ ions increases, the distance between the Eu$^{3+}$ ions decreases.
due to difference between the size of the EuIII and Na+ cations ($r_{\text{VIII}(Na^+) = 1.18 \text{ Å}}$ and $r_{\text{VIII}(Eu^{3+}) = 1.066 \text{ Å}}$), favoring a nonradiative energy transfer among EuIII ions. For example, the $R - R$ distances in Na$_5$R(MoO$_4$)$_4$ (R = La, Y) and Na$_{0.5}$R$_{0.5}$MoO$_4$ (R = La, Y) vary from 0.6475 to 0.3969 nm (La–La) and from 0.6366 to 0.3844 nm (Y–Y), respectively. On one hand, the $^5D_0 \rightarrow ^7F_2$ emission intensity of Na$_{5+x}$La$_{1-x}$Eu$_x$(MoO$_4$)$_4$ and Na$_{0.5(Gd_{1-x}Eu_x)}_{0.5}$MoO$_4$ solid solutions is reported to increase with an increasing concentration of EuIII ions and to reach a maximum at $x = 1$. On the other hand, Zhao et al. found that the $^5D_0 \rightarrow ^7F_2$ emission increases with an increase of the EuIII content up to $x = 0.7$ in Na$_{2/7}$Gd$_{0.3}$Eu$_{0.7}$MoO$_4$ solid solutions, followed by a decrease due to a concentration quenching effect. The $^5D_0 \rightarrow ^7F_2$ emission intensity of Na$_{2/7}$Gd$_{0.3}$Eu$_{0.7}$MoO$_4$ is about five times higher than that of Y$_2$O$_3$:EuIII phosphor under blue excitations $\lambda_{\text{ex}} = 466$ nm and changing excitations from $\lambda_{\text{ex}} = 466$ nm to $\lambda_{\text{ex}} = 396$ nm does not lead to a noticeable change of the emission intensity of Na$_{2/7}$Gd$_{0.3}$Eu$_{0.7}$MoO$_4$. The $^5D_0 \rightarrow ^7F_2$ emission intensity of pure Na$_{2/7}$Eu$_{5/7}$MoO$_4$ is approximately 75% of the intensity for Na$_{2/7}$Gd$_{0.3}$Eu$_{0.7}$MoO$_4$ under both excitations. Such high quenching concentrations are caused by the scheelite-related structure and are observed for other EuIII-doped molybdates. Thus, the relation between the decrease in the $^5D_0 \rightarrow ^7F_2$ emission and the increase of the EuIII concentration in our view could be more complex than only a concentration quenching effect, since the increase of the EuIII concentration also leads to changes in the structure and in the EuIII distribution. To determine this complex relation between structure and properties, a material is required for which the reflections corresponding to the (3 + 2)D structure are observable with bulk diffraction or single crystal techniques to enable a refinement of the structures. For the current material, these reflections were only observed by electron microscopy.

The second local minimum of the EuIII emission observed on the PL spectra of Na$_{5+x}$Eu(MoO$_4$)$_4$ (0 $\leq x \leq 0.5$) for $x = 0.2$ has been associated with the number ordering of the EuIII dimers. The successful solution of the Na$_{2/7}$Eu$_{5/7}$MoO$_4$ structure as (3 + 1)D incommensurately modulated indicates that this is the main phase. It cannot be excluded that the change in dimensionality anyway has an effect on the luminescence, while it can go undetected by bulk diffraction techniques, therefore these phases will be investigated using the local technique of electron energy loss spectroscopy (EELS) in the next section.

As shown in Figure 10 and 11, among the phases in the system Na$_2$MoO$_4$–Eu$_{2/3}$MoO$_4$, the maximum intensity of luminescence in the region from 600 to 620 nm ($^5D_0 \rightarrow ^7F_2$ transition) is observed for Na$_5$Eu(MoO$_4$)$_4$. Concerning applications, the color chromaticity of phosphors is considered to be a critical parameter for evaluating the performance of LED phosphors. In literature, the luminescent properties of Na$_5$Eu(MoO$_4$)$_4$ are compared against those of the commodity Y$_2$O$_2$:EuIII and La$_2$O$_2$:EuIII. Here, we compare the luminescent properties of Na$_5$Eu(MoO$_4$)$_4$ red-emitting phosphor and compared against those of the commodity Y$_2$O$_2$:EuIII and La$_2$O$_2$:EuIII. It was found that the CIE color coordinates ($x, y$) and relative luminance ($r_l$) of Na$_5$Eu(MoO$_4$)$_4$ ($x = 0.66, y = 0.33$, $r_l = 1.3$) are similar to those of Y$_2$O$_2$:EuIII. Figure 12 shows the comparison of PLE and PE spectra of Na$_5$Eu(MoO$_4$)$_4$ and YVO$_4$:EuIII. As shown in Figure 12d, the maximum
The luminescence intensity of Na$_{5}$Eu(MoO$_4$)$_4$ ($\lambda_{\text{ex}} = 395$ nm) in the $^3D_0 \rightarrow ^5F_2$ transition region is close to the luminescence intensity of YVO$_4$:Eu$^{3+}$ ($\lambda_{\text{ex}} = 326$ nm). This confirms that Na$_{5}$Eu(MoO$_4$)$_4$ is exceptionally attractive as a near-UV convertible phosphor applied as a red-emitting phosphor for LEDs as suggested in ref 16a.

3.4. Electron Energy Loss Spectroscopy. To determine whether the change in dimensionality has an effect on the luminescent properties, a local technique such as EELS needs to be applied, which allows to correlate spectra with specific crystallites or even domains. Figure 13 shows the comparison of EELS spectra of Na$_2$MoO$_4$, Na$_{5}$Eu(MoO$_4$)$_4$, Na$_{0.138}$Eu$_{0.621}$MoO$_4$ (5) and Na$_{5}$Eu(MoO$_4$)$_4$ (2), Na$_{0.5}$Eu$_{0.5}$MoO$_4$ (3), Na$_{0.286}$Eu$_{0.571}$MoO$_4$ (4), Na$_{x}$Eu$_{2/3}$MoO$_4$ (6) plotted as a function of $\lambda_{\text{ex}} = 395$ nm in the ultraviolet region (I, ultraviolet region; II, vision light (a, region of PLE spectra; b, region of PL spectra); and III, infrared region). Scales were matched for easy comparison with PLE and PL spectra.

Figure 13. (a) Background subtracted EELS spectra of Na$_2$MoO$_4$ (1), Na$_{5}$Eu(MoO$_4$)$_4$ (2), Na$_{0.5}$Eu$_{0.5}$MoO$_4$ (3), Na$_{0.286}$Eu$_{0.571}$MoO$_4$ (4), Na$_{0.138}$Eu$_{0.621}$MoO$_4$ (5) and $\alpha$-Eu$_{2/3}$MoO$_4$ (6) plotted as a function of energy loss. (b) Same spectra plotted in wavelength scale. (I, ultraviolet region; II, vision light (a, region of PLE spectra; b, region of PL spectra); and III, infrared region). Scales were matched for easy comparison with PLE and PL spectra.

All EELS spectra are similar in the range from 150 to 380 nm (ultraviolet region) and show only one broad absorption band. Broad absorption band positions ($\sim 215$ to $240$ nm) are close to the positions of the CT bands observed on the PLE spectra (Figure 9). These broad absorption bands can be therefore assigned to the charge transfer (CT) from oxygen to molybdenum inside the MoO$_4^{2-}$ groups. Increasing the Eu$^{3+}$ concentration from Na$_5$Eu(MoO$_4$)$_4$ to Na$_{0.5}$Eu$_{0.5}$MoO$_4$ leads to a clear broadening of the CT bands and a shift of the maximum from $\sim 215$ nm (A in Figure 13) to $\sim 240$ nm (B in Figure 13).

A similar modification of the center of the CT bands with increasing Eu$^{3+}$ concentration from Na$_5$Eu(MoO$_4$)$_4$ to Na$_{0.5}$Eu$_{0.5}$MoO$_4$ is observed onPLE spectra.

Peculiarities of EELS spectra of studied compounds are clearly observed in the regions of the visible light and infrared regime (Figure 13). As shown in Figure 13, the EELS spectrum of Na$_2$MoO$_4$ contains no other peaks except a broad absorption band while the EELS spectrum of $\alpha$-Eu$_{2/3}$MoO$_4$ besides shifting the maximum of this peak from $\sim 215$ nm to $\sim 240$ nm is characterized by the presence of a second broad absorption band in the region from 350 to 1000 nm. The maximum of the second broad absorption band is about $\sim 610$ nm which is in agreement with the $^3D_0 \rightarrow ^5F_2$ transition bands at $\sim 613$ nm and at $\sim 616$ nm on the PL spectrum (Table 1, Figure 11). The EELS spectrum of Na$_5$Eu(MoO$_4$)$_4$ in the region from 350 to 1300 nm shows the presence of three absorption bands: a first broad absorption band in the visible range and two bands at $\sim 940$ nm and at $\sim 1180$ nm in the infrared region. Changing of the Na and Eu cation distribution from ordered in Na$_5$Eu$_{2/3}$MoO$_4$ to random in the Na$_{0.5}$Eu$_{0.5}$MoO$_4$ structure leads to a vanishing of the band at $\sim 1180$ nm, a significant increasing intensity of the band at $\sim 940$ nm and the appearance of a new band at $\sim 476$ nm. Further increase of Eu$^{3+}$ concentration and modification of the cation distribution due to formation of incommensurately modulated structures leads to a change in the number of bands in the spectra, broadening of the most intense band and a change in its center from $\sim 940$ nm to $\sim 990$ nm but does not lead to its disappearance. Absorption bands at $\sim 940$ nm and $\sim 1180$ nm in the infrared regime may be associated with the Eu–Eu or Eu–Na interactions, respectively.

On one hand, Na$_5$Eu(MoO$_4$)$_4$ shows the maximum intensity of luminescence in the region from 600 to 620 nm ($^3D_0 \rightarrow ^5F_2$ transition) among the Na$_5$Eu$_{2/3}$MoO$_4$ red phosphors and the band at $\sim 1180$ nm in the infrared region is observed only on EELS spectrum of Na$_5$Eu(MoO$_4$)$_4$. On the other hand, the Na$_5$Eu(MoO$_4$)$_4$ structure has the longest Eu–Eu bond length among the Na$_5$Eu$_{2/3}$MoO$_4$ series, and thus the weakest Eu–Eu interactions.

Although the PLE spectra of the bulk samples were the same and the PL spectra differ only in the intensities of the peaks, the local low loss EELS measurements show a clear difference between the samples with different dimensionalities. This could also be related with the differences in underlying symmetry for the $(3 + 1)D$ (monoclinic) and $(3 + 2)D$ (tetragonal) incommensurately modulated structures.
4. CONCLUSION

The detailed study of phases in the Na$_2$MoO$_4$–Eu$_2/3$MoO$_4$ system by TEM has allowed us to differentiate between structures with different modulations that were undetected before by bulk diffraction techniques. Moreover, TEM has also shown clear differences in their low loss EELS spectra. Whereas no satellite reflections were detected on the synchrotron PXRD patterns for Na$_3$Eu$_{1+x}$MoO$_{4+2x}$ (x = 0.286, a (3 + 2) D incommensurately modulated structure was clearly revealed by TEM. Moreover, TEM showed that for x = 0.200, next to the (3 + 1) D incommensurately modulated structure, domains with a (3 + 2) D incommensurately modulated structure are present.

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