KEu(MoO$_4$)$_2$: Polymorphism, Structures, and Luminescent Properties

Vladimir A. Morozov,$^{1,‡}$ Alla V. Arakcheeva,$^{8,‖}$ Philip Pattison,$^{8,†}$ Katrien W. Meert,$^{‡}$ Philippe F. Smet,$^{9,†}$ Dirk Poelman,$^{9,‡}$ Nicolas Gauquelin,$^{‡}$ Johan Verbeeck,$^{‡}$ Artem M. Abakumov,$^{‡}$ and Joke Hadermann$^{8,‡}$

$^1$Chemistry Department, Moscow State University, 119991 Moscow, Russia
$^2$EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
$^3$Laboratoire de Crystallographie, École Polytechnique Fédérale de Lausanne, BSP, CH-1015 Lausanne, Switzerland
$^4$Phase Solutions Ltd., CH-1012 Lausanne, Switzerland
$^5$Swiss-Norwegian Beamline, ESRF, BP-220, F-38043 Grenoble CEDEX, France
$^6$Lumilab, Department of Solid State Sciences and $^3$Center for Nano- and Biophotonics (NB-Photonics), Ghent University, 9000 Gent, Belgium

ABSTRACT: In this paper, with the example of two different polymorphs of KEu(MoO$_4$)$_2$, the influence of the ordering of the A-cations on the luminescent properties in scheelite related compounds (A’,A$^+$)$_n$(B’,B$^+$)O$_{4m}$ is investigated. The polymorphs were synthesized using a solid state method. The study confirmed the existence of only two polymorphic forms at annealing temperature 923–1203 K and ambient pressure: a low temperature anorhthic α-phase and a monoclinic high temperature β-phase with an incommensurately modulated structure. The structures of both polymorphs were solved using transmission electron microscopy and refined from synchrotron powder X-ray diffraction data. The monoclinic β-KEu(MoO$_4$)$_2$ has a (3+1)-dimensional incommensurately modulated structure (superspace group $I2/b$(αβ0)00, $a = 5.52645(4)\ \AA$, $b = 5.28277(4)\ \AA$, $c = 11.73797(8)\ \AA$, $\alpha = 91.2189(4)^\circ$, $q = 0.56821(2)a^*−0.12388(3)b^*$), whereas the anorhthic α-phase is (3+1)-dimensional commensurately modulated (superspace group $I\bar{1}(αβγ0)$0, $a = 5.58727(22)\ \AA$, $b = 5.29188(18)\ \AA$, $c = 11.7120(4)\ \AA$, $\alpha = 90.485(3)^\circ$, $\beta = 88.074(3)^\circ$, $\gamma = 91.0270(23)^\circ$, $q = 1/2a^*+1/2c^*$). In both cases the modulation arises due to Eu/K cation ordering at the A site: the formation of a 2-dimensional Eu$^{3+}$ network is characteristic for the α-phase, while a 3-dimensional Eu$^{3+}$-framework is observed for the β-phase structure. The luminescent properties of KEu(MoO$_4$)$_2$ samples prepared under different annealing conditions were measured, and the relation between their optical properties and their structures is discussed.

1. INTRODUCTION

White light-emitting diodes (WLEDs) are promising for replacing conventional fluorescent and incandescent lamps. They are highly reliable, have a long lifetime with low energy consumption, and are environmentally friendly.$^1$ Their availability can result in exciting new applications as medical and architecture lighting, portable electronics backlights, etc.$^2$

Rare earth doped solid-state molybdates and tungstates exhibit outstanding chemical stability and long wavelength emission. Among these, rare earth scheelite-type (CaWO$_4$) molybdates and tungstates have a large potential for use in WLEDs.$^{3−7}$ Recently a new application field has emerged for these materials as thermographic phosphors, due to their capacity to accurately visualize temperature gradients with high spatial resolution.$^8$ Due to charge transfer from oxygen to metal, tungstate and molybdate phosphors have intense, broad absorption bands in the near-UV region. Some scheelite-type compounds, such as PbMoO$_4$, K$_2$MoO$_4$, NaBi(WO$_4$)$_2$, and MWO$_4$ (M = Pb, Cd, Ca) are well-known and used, while other MLn(BO$_4$)$_2$ (M = Li, Na, K, Ag; Ln = lanthanides, B = W, Mo) materials with Eu$^{3+}$ cations are frequently suggested as red phosphors for WLEDs. For example, NaEu(WO$_4$)$_2$ and K$_2$Eu$_{0.75}$Eu$_{0.25}$(MoO$_4$)$_2$ show strong, saturated red emission.$^{9,10}$

The scheelite-type ABO$_4$ (CaWO$_4$) structure is built from columns of [...] AO$_4$ - BO$_4$ - ...] directed along the c-axis. The A and/or B cations can be partially substituted to form (A’,A$^+$)$_n$(B’,B$^+$)O$_{4m}$ (A’, A$^+$ = alkali, alkaline-earth, or rare-earth elements; B’, B$^+$ = Mo, W). Such compounds are relatively simple to prepare and often have good stability and good optical properties. A large amount of vacancies can be present at the A cation site, resulting in a (A$'^+$+A$^+$/2):(B$'^+$+B$^+$) ratio different from 1:1. The substitution of Ca$^{2+}$ cations in Ca$_2$MoO$_4$ (B = Mo), by a combination of $M^+$ (M = Li, Na, K, Ag$^+$) and a trivalent cation leads to the

Received: May 1, 2015
Revised: July 29, 2015
Published: July 29, 2015

DOI: 10.1021/acs.chemmater.5b01622
Chem. Mater. 2015, 27, 5519−5530
formation of MR(BO₃)₃ (R = rare earth elements, Y, Bi) compounds. The existence of MR(MoO₄)₂ (M = Li, Na, Ag) molybdenum oxides with a scheelite-type tetragonal structure has been reported for all rare earth elements.⁴⁰⁻⁴⁸

KR(MoO₄)₂ double molybdates have a variety of crystal structures that can be divided in scheelite-type modifications (R = La–Dy) and non-scheelite modifications (R = Dy–Lu) with the KY(MoO₄)₂-type structure (space group Pbma). Three groups of scheelite-type modifications can be selected: 1) tetragonal (R = La–Sm) phases⁴⁹⁻⁵¹ or phases with a small monoclinic distortion of the scheelite subcell; ²) phases with the incommensurate modulated structure (R = Nd,⁵² Sm) (superspace group I2/b(a/2)00); and ³) anorthic phases with the α-KEu(MoO₄)₂ structure (space group PT).⁵²

In contrast to the tetragonal MR(MoO₄)₂ (M = Li⁺, Na⁺, K⁺, Ag⁺; R = Ln, Y, Bi) compounds where M⁺ and R³⁺ are statistically distributed over the structure, the K⁺ and Eu³⁺ cations in α-KEu(MoO₄)₂ are ordered. Among the incommensurately modulated structures, the A site cations are completely ordered in KNd(MoO₄)₂ while they are only partially ordered in KSm(MoO₄)₂.⁵² It should be noted that the data about the number of polymorph modifications for KEu(MoO₄)₂ are contradictory. Klevtsov et al. selected five modifications of KEu(MoO₄)₂ (anorthic α-phase → monoclinic β-phase with the α-KSm(MoO₄)₂-type structure (IM structure) × monoclinic β'-phase with α-KBi(MoO₄)₂-type structure (unknown structure) → orthorhombic γ-phase with the KY(MoO₄)₂-type structure → δ-phase (unknown struct-

| Table 1. Crystal Data, Data Collection, and Refinement of KEu(MoO₄)₂ Polymorphs |
|---------------------------------|-------------------------------|
| formula weight (g)             | formula | β-KEu(MoO₄)₂ | α-KEu(MoO₄)₂ |
| temperature (K)                |        |             |             |
| cell setting                   |         |             |             |
| super space group              |         |             |             |
| lattice parameters:            |         |             |             |
| a (Å)                          |         |             |             |
| b (Å)                          |         |             |             |
| c (Å)                          |         |             |             |
| α (deg)                        |         |             |             |
| β (deg)                        |         |             |             |
| γ (deg)                        |         |             |             |
| V (Å³)                         |         |             |             |
| q vector                       |         |             |             |
| formula units, Z               |         |             |             |
| calcld density, Dₘ (g × cm⁻³)  |         |             |             |
| color                          |         |             |             |
| Data collection                |         |             |             |
| d:riectrod                   | MAR345  |             |             |
| radiation/wavelength (λ, Å)    | synchrotron/0.6692 |         |             |
| radiation monochromator        | Si(111) |             |             |
| absorption coefficient, μ (mm⁻¹) |         |             |             |
| F(000)                         |         |             |             |
| 2θ range (deg)                 |         |             |             |
| step scan (2θ)                 |         |             |             |
| no. of reflections (all/observed) |         |             |             |
| among them:                    |         |             |             |
| main                           |         |             |             |
| the first-order satellites     |         |             |             |
| the second-order satellites    |         |             |             |
| the third-order satellites     |         |             |             |
| no. of refined parameters      |         |             |             |
| R and Rₑ (%) for Bragg reflections (Rₑ/Rₑ) |         |             |             |
| among them:                    |         |             |             |
| main                           |         |             |             |
| the first-order satellites     |         |             |             |
| the second-order satellites    |         |             |             |
| the third-order satellites     |         |             |             |
| Refinement                     |         |             |             |
| refinement                     | Rietveld|             |             |
| background function            | Legandre polynomials, 16 terms |         |             |
| the number of reflections      |         |             |             |
| among them:                    |         |             |             |
| no. of refined parameters      |         |             |             |
| R and Rₑ (%) for Bragg reflections (Rₑ/Rₑ) |         |             |             |
| among them:                    |         |             |             |
| Rₑ and Rₑ<sup>II</sup> Rₑ<sup>III</sup> |         |             |             |
| goodness of fit (Chi²Q)        |         |             |             |
| max./min. residual density      |         |             |             |
2.2. Characterization. Powder X-ray diffraction (PXRD) patterns were collected on a Huber G670 Guinier diffractometer (CuKα\(_1\) radiation, \(\lambda = 1.5406 \, \text{Å}\), curved Ge(111) monochromator, transmission geometry, image plate detector) for the determination of the unit cell parameters. PXRD data were collected at room temperature over the 2\(\Theta\)−100° range with steps of 0.005°. To determine the unit cell parameters, the PXRD data were refined by Le Bail decomposition\(^{43}\) using the JANA2006 software.\(^{12,49}\)

For the transmission electron microscopy study, the samples were made by crushing the powder in an agate mortar and dispersing the crushed powder in methanol. Several drops of this solution were deposited on a copper grid covered with a holey carbon film. Selected area electron diffraction (SAED) patterns were obtained using a Philips CM20 transmission electron microscope operated at 200 kV, equipped with a CCD camera. The elemental composition of the samples was confirmed by energy dispersive X-ray (EDX) analysis performed with a Philips CM20 microscope with an Oxford INCA attachment. For the EDX analysis, the results were based on the KEu, Eu\(_2\), and Mo\(_2\) lines.

High resolution angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a FEI Titan 60-300 transmission electron microscope equipped with a probe aberration corrector, operated at 300 kV.

The synchrotron X-ray powder diffraction (SXPD) data were collected at the BM01A beamline (Swiss-Norwegian Beamline) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). A wavelength of 0.6692 Å was selected using a Si(111) double crystal monochromator, and the synchrotron beam was focused on a spot size of 0.3 mm \(\times\) 0.3 mm using a combination of curved mirrors and sagittal bent second crystal. The sample was put into a borosilicate capillary of 0.5 mm diameter, and the data were collected at room temperature. A Mar345 image plate detector was used to register the powder patterns. The sample-to-detector distance of 250 mm was calibrated using a LaB\(_6\) reference powder. Exposure times per sample were typically 30 s per image, and the samples were rotated during data collection at a speed of 1° s\(^{-1}\). Exposure times were chosen to avoid any pixel saturation. Details of experiments and characteristics of the final structure refinements are listed in Table 1. Rietveld analysis of the incommensurately modulated structure was performed using the JANA2006 program package.\(^{42,43}\) Illustrations were produced with this package in combination with the program DIAMOND.\(^{44}\)

Electron Energy Loss Spectroscopy (EELS) was performed on a monochromated Titan 80-300 microscope operated at 80 keV to reduce knock-on damage with an energy resolution of 100 meV. Data were acquired with a 0.01 eV/pixel dispersion and a 0.2 ms exposure time in thin areas of the sample to avoid multiple scattering to alter the results. The tail of the Zero-Loss was removed by subtraction of a second-order polynomial background fit.

Luminescent emission and excitation spectra were recorded on an Edinburgh Instruments FS920 fluorescence spectrometer with a monochromated 450W Xe arc as the excitation source. Decay profiles were collected using an Andor intensified CCD (Andor DH720) connected to a 500 mm spectrograph, combined with a dye laser as excitation source. Temperature dependent measurements were performed using an Oxford Optistat CF cryostat.

2. EXPERIMENTAL SECTION

2.1. Materials and Sample Preparation. The low-temperature (LT) \(\alpha\)-modification of KEu(MoO\(_4\))\(_2\) was prepared from a 1:1 stoichiometric mixture of K\(_2\)CO\(_3\) (99.99%), Eu\(_2\)O\(_3\) (99.99%), and MoO\(_3\) (99.99%) by a routine ceramic technique in a Pt crucible at 923 ± 10 K for 30 h in air followed by slow cooling in the furnace from 923 K to room temperature (\(T_{\text{RT}}\)). \(\alpha\)-KEu(MoO\(_4\))\(_2\) was annealed at different temperatures (973, 1023, 1073, 1123, 1173, and 1203 K) for 12 h and cooled under different cooling conditions (slow cooling from the annealing temperature to \(T_W\) quenching from the annealing temperature to liquid nitrogen (N\(_2\)) to solve the unclear problem with the number of polymorph modifications (Table S1). The high-temperature (HT) \(\beta\)-KEu(MoO\(_4\))\(_2\) was synthesized from the \(\alpha\)-phase by annealing at 1203 ± 10 K for 10 h in air followed by quick quenching from the high temperature to liquid nitrogen temperature.

2.3. Preliminary Characterization. PXRD patterns of \(\alpha\)-KEu(MoO\(_4\))\(_2\) and the samples prepared from the \(\alpha\)-phase under different annealing and cooling conditions are shown in
All reflections of the PXRD pattern of the \( \alpha \)-phase correspond to the anorthic structure (space group \( P\overline{1}36 \)) with unit cell parameters refined by Le Bail decomposition: \( a = 11.1869(2) \, \text{Å}, b = 5.30038(6) \, \text{Å}, c = 6.93707(8) \, \text{Å}, \alpha = 112.4276(8)^\circ, \beta = 111.5964(9)^\circ, \gamma = 90.9988(9)^\circ \). PXRD patterns of other samples prepared from the \( \alpha \)-phase differ insignificantly (Figure 1). The main feature of all PXRD patterns of these samples is the presence of two fairly intense reflections in the 8°–11° 2\( \theta \) range (shown in the green ellipse in Figure 1a). Earlier similar reflections were observed on PXRD patterns of \( \text{Kr(MoO}_4)_2 \) \( (R = \text{Nd}, \text{Sm}) \) with incommensurately modulated structures and indexed as 0001 and 1011, respectively. The positions of these satellite reflections on PXRD patterns are almost independent of the heating and cooling conditions, while the positions of the basic reflections change significantly (Figure 1b). The unit cell parameters were refined by Le Bail decomposition using the data of the incommensurately modulated \( \text{Kn(MoO}_4)_2 \) crystal structure as initial parameters. The unit cell parameters determined by Le Bail decomposition from the PXRD patterns are given in Table S1. According to Table S1 and Figure 1 the \( \alpha \rightarrow \beta \) phase transition is not reversible. Thus, PXRD studies do not show any orthorhombic \( \gamma \)-\( \text{Keu(MoO}_4)_2 \) phase with the \( \text{Ki(MoO}_4)_2 \)-type structure but show the existence of only two modifications for \( \text{Keu(MoO}_4)_2 \): an anorthic \( \alpha \)-phase and a monoclinic \( \beta \)-modification with incommensurate modulated structure.

3.3. Electron Diffraction Study. \( HT \beta \)-Phase. [001]*, [100]* and [11\( \overline{1} \)]* \( \beta \) ED patterns of \( \beta \)-\( \text{Keu(MoO}_4)_2 \) (Figure 2) show a high likeness with those of \( \text{Kr(MoO}_4)_2 \) \( \beta \) ED patterns along the main zone axes for the monoclinic \( \beta \)-\( \text{Keu(MoO}_4)_2 \).
which have a (3+1)D incommensurately modulated structure. The reflections in the [1\bar{1}0]*_β and [100]*_β ED patterns all correspond to the tetragonal scheelite subcell with parameters a_1 \approx 5.46 Å, c_1 \approx 11.86 Å (s refers to the scheelite-type unit cell) and thus are considered main reflections. However, next to main reflections, low intensity reflections are observed in the other ED patterns, [001]*_β and [111]*_β. These are satellite reflections that need four hklm integers to be indexed, corresponding to H = ha* + kb* + lc* + mα, with modulation vector q \approx 0.57α* - 0.122β*, and m ≠ 0. The m = 0 reflections are the main reflections. The values of the q vector components cannot be expressed as rational values and therefore designate the structure as incommensurately modulated. The reflection conditions hklm: h + k + l = 2n and hklm: h, k, l = 2n correspond to the (3+1)D superspace group \Gamma_2/b(a\bar{q}b)00 (unique axis c) (15.1.4.1 in Stokes-Campbell-van Smaalen notations, B2/b(a\bar{q}b)00 in a standard setting). The [1\bar{1}0]*_β pattern shows h00: h, k = 2n+1 reflections that are forbidden by the \Gamma_2/b symmetry. However, on tilting the sample around the [hk00] direction, these reflections become weaker and finally disappear in the [001]*_β pattern. Therefore, these reflections are due to double diffraction, not violating the \Gamma_2/b symmetry.

**LT α-Phase.** [010]*_α, [100]*_α, [120]*_α, and [001]*_α ED patterns of α-KEu(MoO_4)_2 are shown in Figure 3. They can be indexed using the space group P6 with the unit-cell parameters refined from the PXRD pattern. The relation between the unit-cell vectors of the monoclinic (β-phase) and the anorhctic unit cell (α-phase) is as follows: [010]*_α = [001]*_β, [100]*_α = [100]*_β, and [120]*_α = [110]*_β. The difference between the β- and the α-phase is clearly observed when comparing the [010]*_α and [001]*_β ED patterns, whereas the [100]*_α and [120]*_α differ only slightly from [100]*_β and [110]*_β, respectively.

**3.4. Refinement of the KEu(MoO_4)_2 Crystal Structures.**

**HT β-Phase.** The SXPD data were collected in the 2θ range of 3.002–34.708° with steps of 0.004°. The structure was refined against the SXPD data in the scheelite-type setting with superspace group \Gamma_2/b(a\bar{q}b)00. The cell parameters and q vector from electron microscopy were used as input and refined as a = 5.52645(4) Å, b = 5.28277(4) Å, c = 11.73797(8) Å, β = 91.2189(4)°, q ≈ 0.568α* - 0.1239β*. Refining the unit cell and profile parameters together allowed to index 864 of the main reflections and up to third-order satellite reflections (Table 1 and Figure 4). In the lower-angle range (3° ≤ 2θ ≤ 11.6°), the first-order satellites are the strongest reflections and also the third-order satellites are clearly present, whereas of the main reflections only three weak ones are present (Figure 4).

For the initial parameters of the refinement, the Mo and O atomic parameters of KNd(MoO_4)_2 were used, including the displacive modulation function’s first-order Fourier amplitudes, completed by K and Eu occupying the A position statistically (x_1 = 0.5, x_2 = 0.25, x_3 = 0.88). The displacive modulation functions, atomic coordinates, and isotropic atomic displacement parameters were subsequently refined. According to the KNd(MoO_4)_2 model of the occupation modulation in the A site, two Crenel functions (Figure S2 of the Supporting Information) were chosen for the K and Eu atomic domains with parameters x_0^A = 0 (K) and x_0^E = 0.5 (Eu) and an occupation parameter o = 0.5 for both A atoms (crenel-I model). The occupation parameters were fixed to satisfy the EDX results. Acceptable values of R were obtained for the main reflections and higher R values for satellite reflections. The calculated electron and residual electron density near the A = (K0,0,Eu0,s) position showed that the assumption of an average half occupation along the internal axis x_1 by both K and Eu was not correct.

The crenel-I model was improved by refining the occupation parameters to o[K1] = 0.9851(1) and o[Eu2] = 0.015(1) (0 < t < 0.5) and o[Eu1] = 0.985(1) and o[K2] = 0.015(1) (0.5 < t < 1) (crenel-II model). The coordinates (x, y, z), ADPs, and displacive modulations for the Eu/K cations, three for the Mo and O atoms.

The crenel-II model was successfully refined using isotropic atomic displacement parameters (ADP). The sufficiently large ratio between observed reflections and atomic refined parameters (864/69 > 8.9) allowed the refinement of the anisotropic ADP for K, Eu, and Mo cations. The reliability factors R_all = 1.15%, R_w = 2.35% showed that the experimental and calculated profile agree well. Table 1 shows further numerical data on the data collection and refinement. Tables S2 and S3 of the Supporting Information list the atomic coordinates, crystallographic parameters, modulation parameters, and interatomic distances for β-KEu(MoO_4)_2. Figure 4 shows the experimental, calculated, and difference XRD patterns.

**LT α-Phase.** The SXPD data were collected in the 2θ range of 2.000–34.708° with steps of 0.004°. In accordance with Klevtsova et al. and our PXRD and ED study, the α-KEu(MoO_4)_2 has the anorhctic scheelite-type structure (space group \Gamma_1) but can also be considered in the scheelite-type settings as a commensurately modulated structure with the anorhctic superspace group \Gamma_1(a\bar{q}y)0 and the modulation vector q = 1/2a* + 0b* + 1/2c*. The transformation matrix from the commensurately modulated subcell (s) to the anorhctic supercell
The fractional atomic coordinates of CaWO₄ were used as the initial parameters for the refinement of the average structure after their transformation from space group $I4_1/a$ to $I\bar{4}$. According to the analysis of the residual electron density maps, two Crenel functions were applied for the K and Eu atoms with occupation parameter $\sigma = 0.5$ for both A atoms, Eu $x_4^0 = 0$ and K $x_4^0 = 0.5$. The occupation parameters were fixed in agreement with the EDX results. The displaceable modulations were approximated with one harmonic term for the Eu, K, Mo, and O atoms. The structure has been refined as commensurately modulated with $t_0 = 1/4$.

The reliability factors $R_{fi} = 1.53\%$, $R_\varepsilon = 2.96\%$ indicate that the experimental and calculated profiles agree well. Table 1 lists further data on the refinement. Tables S4–S5 lists the atomic coordinates, crystallographic parameters, modulation parameters, and interatomic distances of $\alpha$-KEu(MoO₄)₂. Figure 6 shows the experimental, calculated, and difference SXRD patterns.

### 3.5. Specific Features of the KEu(MoO₄)₂ Crystal Structures

The incommensurately modulated scheelite-type $\beta$-phase has strong satellite reflections on the X-ray diffraction patterns, some even stronger than many main reflections (Figure 4), with also strong reflections at low angles (inset Figure 4). These features are characteristic for the incommensurately modulated scheelite-type $\beta$-phases.

The scheelite-type ABO₄ (CaWO₄) structure exists of $[\cdots$-BO₄$^-$ - BO₄$^-$ - $\cdots$] columns oriented along the c-axis. For the A positions, many different distributions of cations have been reported, ordered, and disordered and with positions fully or partially occupied, whereas the B positions were always fully occupied and topologically identical. The K and Eu cation ordering in the $\beta$-phase is demonstrated in Figure 5, showing the $9a \times 8.5b \times 1c$ representative portion of the structure. The distribution of K and Eu in the A position is aperiodic in the $ab$ plane and periodic along the c-axis (Figure 5). The ionic charge and radius of K and Eu cations, as well as their electronic structure and covalent bonding preferences are different, and therefore a different first coordination sphere environment is required. The A-O distances are more spread along the internal coordinate $t$ for the K–O values than for the Eu–O values (Figure S3). The data in Table S4 of the Supporting Information reflect that two distortion modes with either stretching of the Mo-O bonds (1.92–1.70 Å) or bending of the O–Mo–O bond angles (132–93$^\circ$) are active, similar to the situation observed in other incommensurately modulated cation-ordered scheelite-type structures.

The structure of $\beta$-KEu(MoO₄)₂ can, like other scheelite-type compounds, be described as columns along the c-axis consisting of A cations and MoO₄ (Figure 5). Each column consists of either $\{KMoO₄\}$ or $\{EuMoO₄\}$ units. As a result, it can be clearly seen in the $ab$ projection that the K and Eu distribution over the structure follows an incommensurate compositional modulation wave propagating in the direction of vector $q = a\alpha^* + b\beta^*$. Four $\{KMoO₄\}$ or $\{EuMoO₄\}$ columns form 4-membered blocks grouped into “dimers” and “trimers” (respectively indicated in orange and yellow in Figure 5) along the [010] direction of the scheelite subcell. Aperiodic alternation of the “dimers” and “trimers” can be considered as the origin of the incommensurability in the $\beta$-phase.

The $ac$ projections of the crystal structure are shown in Figure 7 for the two KEu(MoO₄)₂ modifications. The difference between them lies in the ordering of the cations in the $A$-sublattice of the scheelite-type structure, clearly observed in these projections. The difference and similarity between the structures can be better understood if we consider the mutual arrangement of Eu$^{3+}$ and the geometry of their surroundings by neighboring Eu$^{3+}$ cations.
In the $\alpha$-phase, the ordering of the Eu$^{3+}$ and K$^+$ cations leads to the formation of similar zigzag Eu$^{3+}$- and K$^+$-layers, which are confined to the (101) plane and alternate along the [100] direction of the scheelite-type unit cell (Figure 7b). Two neighboring Eu$^{3+}$-layers are separated by a similar zigzag K$^+$-layer. The shortest distance between two nearest Eu$^{3+}$ cations is equal to 9 Å between layers, and it varies from 3.889(7) Å to 3.981(7) Å within the layer (Table S6 of the Supporting Information). Six Eu$^{3+}$ cations form six-membered rings (Figure 8a), and a Eu$^{3+}$-layer can be represented as constructed from these rings (Figure 8b). Thus, the cation ordering in the $\alpha$-phase leads to the formation of a 2D Eu$^{3+}$ network. In the $\beta$-phase, similar six-membered Eu$^{3+}$-rings can be selected (Figure 8c) with Eu$^{3+}$−Eu$^{3+}$ distances between 3.83(7) Å and 4.20(9) Å (Table S4 of the Supporting Information). However, unlike in the $\alpha$-phase, these rings form a 3D Eu$^{3+}$ framework (Figure 8d).

In a previous paper, we summarized the crystal structure data for all ($A'$,$A''$)$_{1-x}$BO$_4$ ($B$ = Mo, W) scheelites, showing that the ordering of the $A$-site cations depends on the difference in their ionic radii $r(A')$−$r(A'')$ and on the amount of cation vacancies $x$. Like other NaR(MoO$_4$)$_2$ ($R$ = rare earth elements), NaEu(MoO$_4$)$_2$ has only the tetragonal scheelite-type structure with a statistical distribution of $M'$ and $R^{3+}$. KR(MoO$_4$)$_2$ ($R$ = La$_3$, Ce$_3$) has similar statistical distribution of K$^+$ and $R^{3+}$. Increasing the $r$(K)$-r$(R) difference from 0.367 Å (Ce) to 0.401 Å (Nd) turns the K$^+$ and $R^{3+}$ distribution into an ordered one, forming the incommensurately modulated structures ($R$ = Nd−Eu). Up to $R$ = Dy, anorthic scheelite-type phases with the $\alpha$-KEu(MoO$_4$)$_2$ structure are formed. Increasing the $r$(K)$-r$(R) difference further, from 0.483 Å (Dy) to 0.491 Å (Y) results in phases with the nonscheelite KY(MoO$_4$)$_2$-type structure. Thus, the scheelite-type structure is apparently restricted to $r$(A')−$r$(A'') values below 0.49 Å.

3.6. HAADF-STEM Observations. The HAADF-STEM image of $\beta$-KEu(MoO$_4$)$_2$ along the most informative zone axis [001] is presented in Figure 9, the bright dots corresponding to the projected cationic columns. The $A$ (K or Eu) and $B$ (Mo) cations project onto each other along this direction. The structure overlay on the experimental HAADF-STEM image (bottom). Red balls are Eu positions, blue rings are K positions.
brightness of the dots on HAADF-STEM images is related to the average $Z$ of the whole projected atomic column ($Z_{\text{Eu}} = 63$; $Z_{K} = 19$; $Z_{\text{Mo}} = 42$). The average $Z$ of oxygen columns is low relative to that of cation columns, which makes the oxygen columns invisible on the image. The brighter bands correspond to the Eu/Mo layers. The HAADF-STEM image shows that the $\beta$-phase is (3+1)-dimensionally modulated. The brightness of the dots on the image varies due to the compositional modulation, showing a wavy contrast; the periodicity and orientation of the variation agree with the modulation vector seen on the ED patterns.

3.7. Luminescent Properties. The luminescent properties were measured for four different samples: the low temperature $\alpha$-phase, the samples annealed at 973 and 1173 K, and the high temperature $\beta$-phase. In Figure 10, the excitation ($\lambda_{\text{em}} = 615$ nm) and emission ($\lambda_{\text{ex}} = 395$ nm) spectra are shown, and the characteristic 4f-4f transitions of Eu$^{3+}$ dominate in both spectra. In the excitation spectrum an additional dual broad band can be observed in the short wavelength region. These broad features are in general linked to host related mechanisms like charge transfer states and point to an energy transfer between the host and the luminescent ion. Apparently, the annealing temperature has an influence on the efficiency of this energy transfer. The excitation spectrum of the $\beta$-phase exhibits the highest contribution of the charge transfer band and thus the most efficient energy transfer mechanism between the host and the luminescent ion as compared to direct excitation. For all samples, the majority of the emission can be ascribed to the $^5D_0 \rightarrow ^7F_2$ forced electric dipole transition at around 615 nm, indicating that the site symmetry of the A position, and thus the position of the Eu$^{3+}$ ion, possesses no inversion center. This confirms the relatively low site symmetry as established by the structural data. Typically, the local environment of the Eu$^{3+}$ ions has only a minor influence on the spectra and differences are limited to small shifts in energy levels and thus in the positions of the transitions in the spectra; therefore, measurements at low temperature are needed to avoid thermally induced peak broadening. Figure 11, measured at a temperature of 10 K, reveals small differences in the emission from the $^5D_0$ level for the studied samples. In all materials, the $^5D_0 \rightarrow ^7F_0$ transition is well separated from the three peaks of the $^5D_0 \rightarrow ^7F_2$ transition between 590 and 600 nm. For the $\alpha$-phase, the $^5D_0 \rightarrow ^7F_0$ transition is observed at 579.5 nm, but it is shifted to 579 nm for the annealed and the high temperature $\beta$-phase samples. Apparently, the $^5D_0$ level shifts 2 meV to higher energies after annealing the samples. The annealing induces also changes in the $^7F_2$ multiplet splitting, as reflected in the $^5D_0 \rightarrow ^7F_2$ transition (Figure 11(bottom)). However, calculating the barcenergy for the $^7F_2$ level (i.e., in the absence of crystal field splitting) is not possible with sufficient precision due to the involvement of multiple overlapping energy levels.

The inset of Figure 10 shows that, in addition to the above differences between the samples, the fraction of emission coming from the higher lying $^3D_2$ and $^3D_1$ levels is relatively much more prominent for the high temperature $\beta$-phase as compared to the other modifications. In general, the non-radiative depopulation of the higher lying $^3D_1$ levels to the $^3D_0$ level can occur by two mechanisms, cross-relaxation and multiphonon relaxation. Cross-relaxation between two neigh-

---

**Figure 10.** Excitation (a) ($\lambda_{\text{em}} = 615$ nm) and emission (b) ($\lambda_{\text{ex}} = 395$ nm) spectra of four KEu(MoO$_4$)$_2$ samples at room temperature. The inset shows the emission of the $^5D_1$ and $^5D_2$ level normalized to the peak of the emission of the $^3D_0$ level for all samples at room temperature.

**Figure 11.** Emission ($\lambda_{\text{ex}} = 395$ nm) of the $^5D_0$ level at 10 K: $^5D_0 \rightarrow ^7F_0$ (up) and $^5D_0 \rightarrow ^7F_1$ (down) transitions.
deviation from this single exponential decay is observed, and an exponential contrast, higher annealing temperatures tend to have a negative effect. At 973 K reduces the quenching centers in the material. By this second component in the decay proves that the annealing process to occur, and thus a (locally) high Eu³⁺ concentration is needed. A second way of depopulating higher lying energy levels in ions is by multiphonon relaxation. In this case the energy of the phonons should be resonant with the energy difference between the higher and the lower lying level.

In order to gain more insight in the involved mechanisms, time-resolved measurements were performed. In Figure 12 the decay profiles (λₑₓₑ = 337 nm) of the ⁵D₀ − emission of all the samples both at 10 K and at T₉₀ are shown to be very different. The modulated monoclinic sample annealed at 973 K shows a monoexponential decay and fitting the expression I(t) = I₀ exp(−t/τ) to the experimental data yields a single decay constant of τ = 540 μs at 10K. For the other modifications a deviation from this single exponential decay is observed, and an extra short component appears in the decay, being τ = 280 μs for the α-phase and the sample annealed at 1173 K and τ = 160 μs for the β-modification. In both cases, the fraction of fast decay (f₂ = (I₁/τ₂)/(I₁/τ₁ + I₁/τ₂)) is ca. 0.75. The suppression of this second component in the decay proves that the annealing at 973 K reduces the quenching centers in the material. By contrast, higher annealing temperatures tend to have a negative effect on the internal quantum efficiency of the material. As the internal quantum efficiency of a specific transition is governed by the competition between the radiative and nonradiative decay paths, each with their own rate constant, the nonradiative decay starts to dominate if its rate constant becomes of the same order of magnitude as the intrinsic radiative decay rate. The grayish body color of the β-phase sample reveals indeed an increased absorption by defects as compared to the other samples which have a brighter body color, leading to a lower emission efficiency. The decay constant of the emission from the ³D₁ level is of the order of a microsecond for all four samples (Figure S4).

At room temperature (T₉₀), the decay of the ⁵D₀ emission of all samples is much faster as compared to the situation at 10 K. Apparently, at T₉₀ the emission is already partially quenched. The decay constant of the ³D₁ emission is similar for all four samples (τ = 200 ns), whereas the decay profile of the ⁵D₀ emission differs largely. The invariance of the ³D₁ decay reflects an equally efficient relaxation process from the ³D₁ to the ⁵D₀ level for the investigated samples. Therefore, the increased ³D₁, ⁵D₂ − ²F₁ emission relative to the ⁵D₀ emission of the β-phase in the steady state spectra should be linked with the fast decay of the ⁵D₀ emission. This fast decay originates from an increased probability for nonradiative decay, which is reflected in a decrease of the internal quantum efficiency of the emission from the ⁵D₀ level. Due to the 3D framework of Eu³⁺ atoms in the β-phase, the Eu ions are highly connected to each other, making energy transfer from one Eu³⁺ ion to another and subsequently to defect centers more probable. In addition, additional impurities or defects are created by elevated temperatures in the preparation phase. The combination of this more efficient transfer process and the increased number of defects results in an increase of the rate constant for the nonradiative decay paths. Given that the decay from the ⁵D₀ level is several orders of magnitude slower than from the ³D₁ level, the influence of the nonradiative decay rate is much larger for the ⁵D₀ level. This results in a relatively stronger reduction for the emission intensity for the transitions starting from the ⁵D₀ level, compared to those from the ³D₁ level.

However, it should be noted that for stoichiometric phosphors much lower quantum efficiencies are usually observed. For high Eu³⁺ concentrations, distances between Eu³⁺ atoms become so small that cross-relaxation and other energy transfer processes gain importance, resulting in strong concentration quenching and thus a reduced emission intensity. For these scheelites, however, relatively high emission intensity is found despite the high Eu³⁺ concentration. In this way, the relatively low absorption strength of the 4f-4f transitions in Eu³⁺ can be compensated to yield a reasonable absorption upon direct excitation.

3.8. Electron Energy Loss Spectroscopy. In order to pinpoint the effect of structural changes and of differences in thermal treatments on the luminescent properties, low-loss EELS spectroscopy can be applied since it is a local technique and therefore facilitates correlating spectra with certain individual crystallites or even domains. In our earlier EELS measurements performed on Na₄Eu₄(MoO₄)₁₂ and R₂(MoO₄)₃ (R = Eu, Gd), we determined the relation between the structure/cation distribution and the number and position of bands in the UV−vis-IR regions of the EELS energy spectrum. EELS spectra are shown in the 150 to 1200 nm range (equivalent to 1 to 8 eV) (Figure 13), covering three different regions of the electromagnetic spectrum: ultraviolet (UV) below 380 nm (region I), visible (Vis) from 380 to 740 nm (region II), and infrared (IR) above 780 nm (Region III). All EELS spectra show a broad absorption band in region I. The positions of these broad absorption bands (~180–215 nm) are similar to the positions of the same bands (~215–240 nm) on the EELS spectra of earlier studied Na₄Eu₄(MoO₄)₁₂ and R₂(MoO₄)₃ (R = Gd, Eu).

In comparing the EELS spectra with the optical emission and excitation spectra, one has to keep in mind that EELS probes all interband transitions, also the optically forbidden transitions involving nondipole and transitions involving momentum transfer. As these nonoptical transitions probe a wider range
of the band structure of the material, the EELS spectra contain less sharp features, but nevertheless clear differences between the different materials are apparent.

Changing the $\text{KEu(MoO}_4)_2$ structure from the anorthic $\alpha$-phase to the modulated monoclinic phase during the annealing at 973 K (Table S1 of the Supporting Information) leads to a shift of the maximum from $\sim 215$ nm to $\sim 180$ nm (Figure 13). Further increase of the annealing temperature from 973 to 1173 K returns to an initial maximum value $\sim 215$ nm. Moreover the change of cooling conditions from slow cooling to liquid nitrogen quenching barely changes the EELS spectrum over the entire range of wavelengths.

Some peculiarities are observed in regions II and III of the investigated compound. As shown in Figure 13, the EELS spectrum of $\text{K}_2\text{MoO}_4$ is characterized by the presence of a second absorption band at $\sim 500$ nm, while the EELS spectra of $\text{KEu(MoO}_4)_2$ prepared at 973, 1173 (slow cooling), and 1203 K (quenching) do not contain clearly observed peaks in the visible and infrared regions but broad absorption bands appear around 875 nm and a shoulder in the violet-blue part of the visible range which can further be seen in the spectrum of $\alpha$-$\text{KEu(MoO}_4)_2$. The EELS spectrum of $\alpha$-$\text{KEu(MoO}_4)_2$ in the region from 380 to 1200 nm shows the presence of one absorption band at $\sim 680$ nm in the visible range. The position of this band is close to the positions of the same bands on the emission spectra of earlier studied $\text{Na}_2\text{Eu}_{52}^3\text{MoO}_{27}$ (near 735 nm) and $\beta_2^2\text{MoO}_4$ (860–700 nm) providing hints that it is related to the Eu$^{3+}$ excitation. Thermal annealing of $\alpha$-$\text{KEu(MoO}_4)_2$ and the transformation from the anorthic structure to the modulated monoclinic structure leads to a vanishing of the band at $\sim 680$ nm and the appearance of a new broad absorption band at $\sim 875$ nm which remains for both types of cooling of the $\beta$-$\text{KEu(MoO}_4)_2$. In contrast with $\text{Na}_2\text{Eu(MoO}_4)_2$ and both modifications of $\text{Eu}_2\text{MoO}_4$ EELS spectra of all $\text{KEu(MoO}_4)_2$ samples contain no peaks associated with Eu–Eu interactions in the structure in the infrared region $>1000$ nm.

The band observed in the EELS spectra in the range 400–1000 nm (1–3 eV) is related to 4f–4f transitions of the Eu$^{3+}$ ions. The 4f–4f transitions are forbidden by the Laporte selection rule but forced electric dipole and magnetic dipole transitions (called “hypersensitive transitions” $^{25}$ $|\Delta J| \leq 2$, $|\Delta L| \leq 2$, $\Delta S = 0$) are usually observed in optical excitation and emission spectra $^{24–26}$ and are at the origin of the interest of phosphors as laser or light emitters and usually seen as sharp lines. Some further excitations are optically forbidden (the ones where a small momentum transfer or spin flip is involved) but can be observed in EELS as was demonstrated in reflection EELS mode many years ago $^{27,28}$ by variation of the momentum or the collected spin, where it was demonstrated that 4f–4f transitions give rise to a large band in EELS. As we use large collection angles and much higher electron velocities as compared to reflection EELS in the experiment reported here, dipole-forbidden 4f–4f transitions are accessible. Therefore, the $^{7}\text{F}_0 \rightarrow ^{2}\text{D}_0$ transitions are visible in EELS as well, resulting in the observed broad band.

Thus, the local low loss EELS measurements show a clear difference between the anorthic $\alpha$-$\text{KEu(MoO}_4)_2$ and the modulated monoclinic $\beta$-phase and an influence of the synthesis conditions on the band positions.

4. CONCLUSION

The $\alpha$- and $\beta$-polymorphs of $\text{KEu(MoO}_4)_2$ were synthesized by a solid state method. PXRD study confirmed the existence of only two polymorphic forms at annealing temperature range 923–1203 K and ambient pressure: a low temperature anorthic $\alpha$-phase and a monoclinic high temperature $\beta$-phase with an incommensurately modulated structure. The structures of both $\text{KEu(MoO}_4)_2$ polymorphs were studied using different transmission electron microscopy techniques and refined from synchrotron powder X-ray diffraction data using a (3+1)D formalism. In both cases the modulation arises due to Eu/K cation ordering at the A site: the formation of a 2D Eu$^{3+}$...
network is characteristic for the α-phase, while a 3D Eu³⁺ framework is observed for the β-phase. The most intense luminescence provided by Eu³⁺ is observed in the case of the minimum size of the Eu³⁺ clusters (isolated from other Eu³⁺ ions). The higher the concentration of the smallest clusters, the better luminescence properties can be observed. The present report shows that a layered network of Eu³⁺ results in better luminescence properties in comparison to a 3D framework of Eu³⁺ ions. Hence, the Eu³⁺-framework and the size of the Eu³⁺ clusters affect the luminescence properties of the Eu³⁺ containing compounds.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.0b01622.

Tables S1–S6 and Figures S1–S4 (PDF)

AUTHOR INFORMATION

Corresponding Author

*Phone: 32-32653245. Fax: 32-32653257. E-mail: joker.hadermann@uantwerpen.be.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This research was supported by FWO (project G039211N), Flanders Research Foundation. V.A.M. acknowledges financial support from the European Research Council under an ERC support from the European Research Council under an ERC.

REFERENCES
(21) Wu, J.; Yan, B. Room-temperature solid-state reaction behavior, hydrothermal crystallization and physical characterization of NaRE(MoO₄)₂ and NaLu(MoO₄)₂ compounds. J. Am. Ceram. Soc. 2010, 93, 2188–2194.


(44) Brandenburg, K. DIAMOND, Version 2.1c; Crystal Impact GbR; Bonn, Germany, 1999.


(50) Basovich, O. M.; Khakina, E. G.; Solodovnikov, S. F.; Tsyrenova, G. D. Phase formation in the systems Li2MoO4−K2MoO4−Ln2(MoO4)3 (Ln = La, Nd, Dy, Er) and properties of triple molybdates Li2KLn2(MoO4)3. J. Solid State Chem. 2005, 178, 1580−1588.