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KEu(MoO₄)₂: Polymorphism, Structures and Luminescent Properties

Vladimir A. Morozov,^{1,2} Alla V. Arakcheeva,^{3,4} Philip Pattison,^{3,5} Katrien W. Meert^{6,7},
Philippe F. Smet^{6,7}, Dirk Poelman^{6,7}, Nicolas Gauquelin,² Johan Verbeeck,²
Artem M. Abakumov,² Joke Hadermann^{*,2}

¹*Chemistry Department, Moscow State University, 119991, Moscow, Russia*

²*EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020, Antwerp, Belgium.*

³*École Polytechnique Fédérale de Lausanne, Laboratoire de cristallographie, 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, Ghent University, Belgium,*

⁷*Center for Nano- and Biophotonics (NB-Photonics), Ghent University, Belgium*

***Corresponding author: Joke Hadermann**

Tel.: +32-32653245

Fax.: +32-32653257

E-mail: joke.hadermann@uantwerpen.be

EMAT laboratory, University of Antwerp,

B-2020, Antwerp, Belgium

ABSTRACT

In this paper, with the example of two different polymorphs of $\text{KEu}(\text{MoO}_4)_2$, the influence of the ordering of the *A*-cations on the luminescent properties in scheelite related compounds $(A',A'')_n[(B',B'')\text{O}_4]_m$ is investigated. The polymorphs were synthesized using a solid state method. The study confirmed the existence of only two polymorphic forms at annealing temperature range 923-1203 K and ambient pressure: a low temperature anorthic 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 - $\text{KEu}(\text{MoO}_4)_2$ has a (3+1)-dimensional incommensurately modulated structure (superspace group $I2/b(\alpha\beta 0)00$, $a = 5.52645(4)\text{\AA}$, $b = 5.28277(4)\text{\AA}$, $c = 11.73797(8)\text{\AA}$, $\gamma = 91.2189(4)^\circ$, $\mathbf{q} = 0.56821(2)\mathbf{a}^* - 0.12388(3)\mathbf{b}^*$), whereas the anorthic α -phase is (3+1)-dimensional commensurately modulated (superspace group $I\bar{1}(\alpha\beta\gamma)0$, $a = 5.58727(22)\text{\AA}$, $b = 5.29188(18)\text{\AA}$, $c = 11.7120(4)\text{\AA}$, $\alpha = 90.485(3)^\circ$, $\beta = 88.074(3)^\circ$, $\gamma = 91.0270(23)^\circ$, $\mathbf{q} = \frac{1}{2}\mathbf{a}^* + \frac{1}{2}\mathbf{c}^*$). 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 $\text{KEu}(\text{MoO}_4)_2$ samples prepared under different annealing conditions were measured, and the relation between their optical properties and their structures are 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 environment 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 doped 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 , $\text{KGd}(\text{WO}_4)_2$, $\text{NaBi}(\text{WO}_4)_2$ and $M\text{WO}_4$ ($M = \text{Pb}, \text{Cd}, \text{Ca}$) are well known and used while other $M\text{Ln}(\text{BO}_4)_2$ ($M = \text{Li}, \text{Na}, \text{K}, \text{Ag}$; $\text{Ln} = \text{lanthanides}, B = \text{W}, \text{Mo}$) materials with Eu^{3+} cations are frequently suggested as red-phosphors for WLEDs. For example, $\text{NaEu}(\text{WO}_4)_2$ and $\text{KGd}_{0.75}\text{Eu}_{0.25}(\text{MoO}_4)_2$ show strong, saturated red emission.⁹⁻¹⁰

The scheelite-type ABO_4 (CaWO_4) structure is built from columns of [...- AO_8 - BO_4 - ...] directed along the c -axis. The AO_8 polyhedra and BO_4 tetrahedra form a 3D framework by sharing common vertices. The A and/or B cations can be partially substituted to form $(A', A'')_n[(B', B'')\text{O}_4]_m$ ($A', A'' = \text{alkali, alkaline-earth or rare-earth elements}; B', B'' = \text{Mo, W}$). 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 $(A' + A''):(B'\text{O}_4 + B''\text{O}_4)$ ratio different from 1:1. The substitution of Ca^{2+} cations in CaBO_4 ($B = \text{W}, \text{Mo}$) by a combination of M^+ ($M = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Ag}^+$) and a trivalent cation leads to the formation of $M\text{R}(\text{BO}_4)_2$ ($R = \text{rare earth elements, Y, Bi}$) compounds. The existence of $M\text{R}(\text{MoO}_4)_2$ ($M = \text{Li}, \text{Na}, \text{Ag}$) molybdenum oxides with a scheelite-type tetragonal structure has been reported for all rare earth elements.¹¹⁻²⁸

$\text{KR}(\text{MoO}_4)_2$ double molybdates have a variety of crystal structures and polymorphs that can be divided in scheelite-type modifications ($R = \text{La-Dy}$) and non-scheelite modifications ($R = \text{Dy-Lu}$) with the $\text{KY}(\text{MoO}_4)_2$ -type structure (space group $Pbcn$ ²⁹). Three groups of scheelite-type modifications can be selected: 1) tetragonal ($R = \text{La} - \text{Sm}$) phases³⁰⁻³¹ or phases with a small monoclinic distortion of the scheelite subcell;³²⁻³³ 2) phases with the incommensurate

modulated structure ($R = \text{Nd},^{34} \text{Sm}^{35}$) (superspace group $I2/b(\alpha\beta 0)00$); 3) anorthic phases with the α - $\text{KEu}(\text{MoO}_4)_2$ structure (space group $P\bar{1}^{36}$).

In contrast to the tetragonal $MR(\text{MoO}_4)_2$ ($M = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Ag}^+$; $R = \text{Ln}, \text{Y}, \text{Bi}$) compounds where M^+ and R^{3+} are statistically distributed over the structure, the K^+ and Eu^{3+} cations in α - $\text{KEu}(\text{MoO}_4)_2$ are ordered. Among the incommensurately modulated structures, the A site cations are completely ordered in $\text{KNd}(\text{MoO}_4)_2^{34}$, while they are only partially ordered in $\text{KSm}(\text{MoO}_4)_2^{35}$. It should be noted that the data about the number of polymorph modifications for $\text{KEu}(\text{MoO}_4)_2$ are contradictory. *Klevtsov et al.*³⁷ selected five modifications of $\text{KEu}(\text{MoO}_4)_2$ (anorthic α -phase \rightarrow monoclinic β -phase with the α - $\text{KSm}(\text{MoO}_4)_2$ -type structure (IM structure³⁷) \times monoclinic β' -phase with α - $\text{KBi}(\text{MoO}_4)_2$ -type structure (unknown structure) \rightarrow orthorhombic γ -phase with the $\text{KY}(\text{MoO}_4)_2$ -type structure \rightarrow δ -phase (unknown structure) with increasing temperature while other authors only discussed anorthic α - and monoclinic β -modifications (β' -phase in accordance with *Klevtsov et al.*³⁷). According to *Klevtsov et al.*³⁷ the pure orthorhombic γ -phase with the $\text{KY}(\text{MoO}_4)_2$ -type structure can be synthesized by annealing at 1123 K followed by quenching to room temperature. β' - $\text{KEu}(\text{MoO}_4)_2$ was grown from the melt and the crystal structure of this phase was described as monoclinic^{36, 38-40} but not specified in detail. It should be noted that different authors have indexed the X-ray powder diffraction (XRPD) patterns with different unit cell parameters.^{36,38-39} Comparison of data from different authors is difficult because XRPD patterns are almost absent in the papers.³⁵ Using the structural data obtained for $\text{KNd}(\text{MoO}_4)_2$, we have shown that all reflections listed in JCPDS PDF2 No. 31-1006 for the monoclinic (β -phase in accordance with *Klevtsov et al.*³⁷) β - $\text{KEu}(\text{MoO}_4)_2$ can be indexed successfully using the unit cell parameters $a = 5.5241(17) \text{ \AA}$, $b = 5.2864(15) \text{ \AA}$, $c = 11.713(3) \text{ \AA}$, $\gamma = 91.247(17)^\circ$ and $\mathbf{q} = 0.5641(2)\mathbf{a}^* - 0.1335(4)\mathbf{b}^*$ in the monoclinic superspace group, $I2/b(\alpha\beta 0)00$.³⁴

*C. Guo et al.*¹³ studied the influence of the calcination temperature from 823 K to 1173 K on the luminescent properties of $\text{KEu}(\text{MoO}_4)_2$ and showed that the anorthic α - $\text{KEu}(\text{MoO}_4)_2$ structure does not change by increasing the calcination temperature from 823 K to 973 K. According to *C. Guo et al.*, XRPD patterns of $\text{KEu}(\text{MoO}_4)_2$ samples prepared at calcination temperatures above 1073 K are in agreement with the JCPDS PDF2 No. 32-0782. It was found that the intensity of the red emission line peaking at 616 nm owing to the electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ for $\text{KEu}(\text{MoO}_4)_2$ increases with increasing sintering temperature and reaches a maximum at 1073 K. Thus, the luminescent intensity of monoclinic $\text{KEu}(\text{MoO}_4)_2$ is stronger than that of the phosphors with an anorthic structure. The intensities of the phosphors

decrease as the processing temperature increases up to 1173 K.¹³ It should be noted that the authors completely ignore the presence of small intensity reflections over the 2θ range 10-20° on the XRPD patterns of the $\text{KEu}(\text{MoO}_4)_2$ samples prepared at calcination temperatures above 1073 K. These small intensity reflections were not listed in JCPDS PDF2 No.32-0782 for $\text{KEu}(\text{MoO}_4)_2$, but they are clearly observed on the XRPD patterns. The high luminescent intensity for the sample prepared at 1073 K can result from a small amount of $\text{KEu}(\text{MoO}_4)_2$ phase with an incommensurately modulated scheelite-type structure.

The aim of the present paper is to reveal the relation between the luminescent properties and structure for different modifications of $\text{KEu}(\text{MoO}_4)_2$.

2. EXPERIMENTAL SECTION

2.1. Materials and Sample Preparation. The low-temperature (LT) α -modification of $\text{KEu}(\text{MoO}_4)_2$ was prepared from a (1:1:4) stoichiometric mixture of K_2CO_3 (99.99 %), Eu_2O_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_R). α - $\text{KEu}(\text{MoO}_4)_2$ was annealed at different temperatures (973 K, 1023 K, 1073 K, 1123 K, 1173 K and 1203 K) for 12 h and cooled under different cooling conditions (slow cooling from the annealing temperature to T_R , 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) β - $\text{KEu}(\text{MoO}_4)_2$ was synthesized from the α -phase by annealing at 1203 ± 10 K for 10 h in air followed by quick quenching from the high temperature to liquid nitrogen temperature.

2.2. Characterization. Powder X-ray diffraction (PXRD) patterns were collected on a Huber G670 Guinier diffractometer ($\text{CuK}_{\alpha 1}$ radiation, $\lambda = 1.5406 \text{ \AA}$, 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 4° – 100° 2θ range with steps of 0.005° . To determine the unit cell parameters, the PXRD data were refined by Le Bail decomposition⁴¹ using the JANA2006 software⁴²⁻⁴³.

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 K_K , Eu_L and Mo_L lines.

High resolution high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a FEI Titan 50-80 transmission electron microscope equipped with a probe aberration corrector, operated at 300 kV.

The synchrotron X-ray powder diffraction (SXP) 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 focussed on a spot size of 0.3mm×0.3mm using a combination of curved mirrors and sagittal bent second crystal. The sample was put into a borosilicate capillary of 0.5mm 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 $1^\circ s^{-1}$. 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 programme 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 80keV to reduce knock-on damage with an energy resolution of 100meV. Data were acquired with a 0.01eV/pixel dispersion and a 0.2ms 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.

3. RESULTS AND DISCUSSION

3.1. Elemental Composition. The composition of both $KEu(MoO_4)_2$ modifications was verified using EDX analysis at 4 points for 10 different crystallites of which also electron

diffraction patterns were taken. The compositions were found to be 24.5(2) at.% K : 25.3(4) at.% Eu : 50.2(4) at.% Mo and 24.7(7) at.% K : 25.1(1) at.% Eu : 50.2(7) at.% Mo for the β - and α -modification, respectively. This is close to the nominal $\text{KEu}(\text{MoO}_4)_2$ composition.

3.2. Preliminary Characterization. PXRD patterns of α - $\text{KEu}(\text{MoO}_4)_2$ and the samples prepared from the α -phase under different annealing and cooling conditions are shown in Figure 1. All reflections of the PXRD pattern of the α -phase correspond to the anorthic structure (space group $P\bar{1}^{36}$) with unit cell parameters refined by Le Bail decomposition: $a = 11.1869(2)$ Å, $b = 5.30038(6)$ Å, $c = 6.93707(8)$ Å, $\alpha = 112.4276(8)$ °, $\beta = 111.5964(9)$ °, $\gamma = 90.9988(9)$ °. PXRD patterns of other samples prepared from the α -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° 2θ range (shown in the green ellipse in Figure 1a). Earlier similar reflections were observed on PXRD patterns of $\text{KR}(\text{MoO}_4)_2$ ($R = \text{Nd}^{34}, \text{Sm}^{35}$) with incommensurately modulated structures and indexed as 0001 and $101\bar{1}$, 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 $\text{KNd}(\text{MoO}_4)_2$ 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 γ - $\text{K}_{0.5}\text{Eu}_{0.5}\text{MoO}_4$ phase with the $\text{KY}(\text{MoO}_4)_2$ -type structure but show the existence of only two modifications for $\text{KEu}(\text{MoO}_4)_2$: an anorthic α -phase and a monoclinic β -modification with incommensurate modulated structure.

3.3. Electron Diffraction Study. *HT β -phase.* $[001]^*_\beta$, $[100]^*_\beta$ and $[1\bar{1}0]^*_\beta$ ED patterns of β - $\text{KEu}(\text{MoO}_4)_2$ (Fig. 2) show a high likeness with those of $\text{KR}(\text{MoO}_4)_2$ ($R = \text{Nd}^{17}, \text{Sm}^{18}$), which have a (3+1)D incommensurately modulated structure. The reflections in the $[1\bar{1}0]^*_\beta$ and $[100]^*_\beta$ ED patterns all correspond to the tetragonal scheelite subcell with parameters $a_s \approx 5.46$ Å, $c_s \approx 11.86$ 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, $[001]^*_\beta$ and $[111]^*_\beta$. These are satellite reflections that need four $hklm$ integers to be indexed, corresponding to $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$, with modulation vector $\mathbf{q} \approx 0.57\mathbf{a}_s^* - 0.122\mathbf{b}_s^*$ and $m \neq 0$. The $m = 0$ reflections are the main reflections. The values of

the \mathbf{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 $hk0m: h, k = 2n$ correspond to the (3+1)D superspace group $I2/b(\alpha\beta0)00$ (unique axis c) (15.1.4.1 in Stokes - Campbell - van Smaalen notations, $B2/b(\alpha\beta0)00$ in a standard setting).⁴⁵

The $[1\bar{1}0]^*$ pattern shows $hk00: h, k = 2n+1$ reflections that are forbidden by the $I2/b$ symmetry. However, on tilting the sample around the $[hk00]$ direction, these reflections become weaker and finally disappear in the $[001]^*$ pattern. Therefore, these reflections are due to double diffraction, not violating the $I2/b$ symmetry.

LT α -phase. $[010]^*_\alpha$, $[100]^*_\alpha$, $[120]^*_\alpha$ and $[001]^*_\alpha$ ED patterns of α -KEu(MoO₄)₂ are shown in Figure 3. They can be indexed using the space group $P\bar{1}$ with the unit-cell parameters refined from the PXRD pattern. The relation between the unit-cell vectors of the monoclinic (β -phase) and the anorthic unit cell (α -phase) is as follows: $[010]^*_\alpha = [001]^*_\beta$, $[100]^*_\alpha = [100]^*_\beta$ and $[120]^*_\alpha = [1\bar{1}0]^*_\beta$. The difference between the β -phase and the α -phase is clearly observed when comparing the $[010]^*_\alpha$ and $[001]^*_\beta$ ED patterns, whereas the $[100]^*_\alpha$ and $[120]^*_\alpha$ differ only slightly from $[100]^*_\beta$ and $[1\bar{1}0]^*_\beta$, respectively.

3.4. Refinement of the KEu(MoO₄)₂ Crystal Structures. *HT β -phase.* The SXPD data were collected in the 2θ range of 3.002-34.298° with steps of 0.004°. The structure was refined against the SXPD data in the scheelite-type setting with superspace group $I2/b(\alpha\beta0)00$. The cell parameters and \mathbf{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, $\gamma = 91.2189(4)$ °, $\mathbf{q} \approx 0.568a^* - 0.1239b^*$. 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 ($3.002 \leq 2\theta \leq 11.6^\circ$), 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(MoO₄)₂³⁴ 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(MoO₄)₂³⁴ model of the occupation modulation in the A site, two Crenel functions (Figure S2 of Supporting information) were chosen for the K and Eu atomic domains with parameters $x_4^0 = 0$ (K) and x_4^0

= 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 $A = (\text{K}_{0.5}\text{Eu}_{0.5})$ position showed that the assumption of an average half occupation along the internal axis x_4 by both K and Eu was not correct.

The crenel-I model was improved by refining the occupation parameters to $o[\text{K1}] = 0.9851(1)$ and $o[\text{Eu2}] = 0.015(1)$ ($0 < t < 0.5$) and $o[\text{Eu1}] = 0.985(1)$ and $o[\text{K2}] = 0.015(1)$ ($0.5 < t < 1$) (crenel-II model). The coordinates (x, y, z), ADPs and displacive modulations of K1 and K2, and of Eu1 and Eu2 were fixed to be equal, and further restraints $o[\text{K1}] = o[\text{Eu1}] = 1 - o[\text{Eu2}]$, $o[\text{Eu2}] = o[\text{K2}]$ were used. Overall only $o[\text{Eu1}]$ was included as an additional refined parameter compared to the crenel-I model. Two harmonic terms were included in the 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 $R_{\text{all}} = 1.15\%$, $R_p = 2.35\%$ showed that the experimental and calculated profile agree well. Table 1 shows further numerical data on the data collection and refinement. Table S2-S3 of the Supporting information lists the atomic coordinates, crystallographic parameters, modulation parameters and interatomic distances for β -KEu(MoO₄)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.*³⁶ and our PXRD and ED study, the α -KEu(MoO₄)₂ has the anorthic scheelite-type structure (space group $P\bar{1}$), but can also be considered in the scheelite-type settings as a commensurately modulated structure with the anorthic superspace group $I\bar{1}(\alpha\beta\gamma)0$ and the modulation vector $\mathbf{q} = 1/2\mathbf{a}_s^* + 0\mathbf{b}_s^* + 1/2\mathbf{c}_s^*$.^{*} The fractional atomic coordinates of CaWO₄ were used as the initial parameters for the refinement of the average

* The transformation matrix from the commensurately modulated subcell (s) to the anorthic supercell

$$(P\bar{1}) \text{ is } T = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 1/2 & 0 & 1/2 \end{pmatrix} \text{ in the matrix equation } A_{P\bar{1}} = A_s * T$$

structure after their transformation from space group $I4_1/a$ to $I\bar{1}$. According to the analysis of the residual electron density maps, two Crenel functions were applied for the K and Eu atoms with occupation parameter $o = 0.5$ 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 displacive 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 $R_{\text{all}} = 1.53\%$, $R_p = 2.96\%$ indicate that the experimental and calculated profiles agree well. Table 1 lists further data on the refinement. Table S4-S5 lists the atomic coordinates, crystallographic parameters, modulation parameters and interatomic distances of α -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 β -phase has strong satellite reflections on the X-ray diffraction patterns, some 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 β -phases.

The scheelite-type ABO_4 (CaWO₄) structure exists of [...-AO₈ - BO₄- ...] 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 β -phase is demonstrated in Fig. 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 – 1.70Å) or bending of the O-Mo-O bond angles ($\sim 132 - 93^\circ$) are active, similar to the situation observed in other incommensurately modulated cation-ordered scheelite-type structures.⁴⁶

The structure of β -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 $\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^*$. Four $\{\text{KMoO}_4\}$ or $\{\text{EuMoO}_4\}$ columns form 4-membered blocks grouped into "dimers" and "trimers" (respectively indicated in orange and yellow on 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 β -phase.

The ac projections of the crystal structure are shown in Fig. 7 for the two $\text{KEu}(\text{MoO}_4)_2$ 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 α -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 of and alternate along the [100] direction of the scheelite-type unit cell (Fig. 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 Supporting information). Six Eu^{3+} cations form six-membered rings (Fig. 8a), and a Eu^{3+} -layer can be represented as constructed from these rings (Fig. 8b). Thus, the cation ordering in the α -phase leads to the formation of a 2D Eu^{3+} network. In the β -phase, similar six-membered Eu^{3+} -rings can be selected (Fig. 8c) with Eu^{3+} - Eu^{3+} distances between 3.83(7) Å and 4.20(9) Å (Table S4 of Supporting information). However, unlike in the α -phase, these rings form a 3D Eu^{3+} framework (Fig. 8d).

In a previous paper, we summarized the crystal structure data for all $(A',A'')_{1-x}\text{BO}_4$ ($B = \text{Mo}, \text{W}$) 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 .⁴⁶ Like other $\text{NaR}(\text{MoO}_4)_2$ ($R = \text{rare earth elements}$) molybdenum oxides, $\text{NaEu}(\text{MoO}_4)_2$ ⁴⁷⁻⁴⁸ has only the tetragonal scheelite-type structure with a statistical distribution of M^+ and R^{3+} . $\text{KR}(\text{MoO}_4)_2$ ($R = \text{La}^{30-31}$ - Ce^{49}) has similar statistical distribution of K^+ and R^{3+} . Increasing the $r(\text{K})-r(R)$ difference from 0.367 Å (Ce) to 0.401 (Nd) turns the K^+ and R^{3+} distribution into an ordered one, forming the incommensurately modulated structures ($R = \text{Nd-Eu}$). Up to $R = \text{Dy}$, anorthic scheelite-type phases with the α - $\text{KEu}(\text{MoO}_4)_2$ structure are formed⁵⁰. Increasing the $r(\text{K})-r(R)$ difference further, from 0.483 Å (Dy) to 0.491 (Y) results in phases with the non-scheelite $\text{KY}(\text{MoO}_4)_2$ -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 β -K₂Eu(MoO₄)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 brightness of the dots on HAADF-STEM images is related to the average Z of the whole projected atomic column ($Z_{\text{Eu}} = 63$; $Z_{\text{K}} = 19$; $Z_{\text{Mo}} = 42$). 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 β -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 α -phase, the samples annealed at 973 K and 1173 K and the high temperature β -phase. In Fig. 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 Eu³⁺ 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 β -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 $^5\text{D}_0 - ^7\text{F}_2$ forced electric dipole transition at around 615 nm, indicating that the site symmetry of the A position, and thus the position of the Eu³⁺ ion, possesses no inversion center.⁵¹ This confirms the relatively low site symmetry as established by the structural data. Typically, the local environment of the Eu³⁺ 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 $^5\text{D}_0$ level for the studied samples. In all materials, the $^5\text{D}_0 - ^7\text{F}_0$ transition is well separated from the three peaks of the $^5\text{D}_0 - ^7\text{F}_1$ transition between 590 and 600 nm. For the α -phase, the $^5\text{D}_0 - ^7\text{F}_0$ transition is observed at 579.0 nm, but it is shifted to 579 nm for the annealed and the high temperature β -phase samples. Apparently, the $^5\text{D}_0$ - level shifts 2meV to higher energies after annealing the

samples. The annealing induces also changes in the 7F_2 multiplet splitting, as reflected in the ${}^5D_0 - {}^7F_2$ transition (Figure 11(bottom)). However, calculating the barycenter energy 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 5D_2 – and 5D_1 – level is relatively much more prominent for the high temperature β -phase as compared to the other modifications. In general, the non-radiative depopulation of the higher lying 5D_J levels to the 5D_0 level can occur by two mechanisms, cross-relaxation and multiphonon relaxation. Cross-relaxation between two neighboring ions involves an energy transfer of the ${}^5D_1 - {}^5D_0$ energy difference from one ion to the other. A relatively small distance between the luminescent ions is necessary for this transfer process to occur and thus a (locally) high Eu^{3+} 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 ($\lambda_{\text{exc}} = 337 \text{ nm}$) of the 5D_0 – emission of all the samples both at 10 K and at T_R are shown to be very different. The modulated monoclinic sample annealed at 973 K shows a monoexponential decay and fitting the expression $I(t) = I_0 \cdot \exp(-t/\tau)$ to the experimental data yields a single decay constant of $\tau = 540 \mu\text{s}$ 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 $\tau = 280 \mu\text{s}$ for the α -phase and the sample annealed at 1173K and $\tau = 160 \mu\text{s}$ for the β -modification. In both cases, the fraction of fast decay ($f_2 = \frac{I_2\tau_2}{I_1\tau_1 + I_2\tau_2}$) is circa 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 non-radiative decay paths, each with their own rate constant, the non-radiative decay starts to dominate if its rate constant becomes of the same order of magnitude as the intrinsic radiative decay rate. The greyish 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 5D_1 -level is of the order of a microsecond for all four samples (Fig.S4).

At room temperature (T_R), the decay of the 5D_0 emission all samples is much faster as compared to the situation at 10 K. Apparently, at T_R the emission is already partially quenched. The decay constant of the 5D_1 emission is similar for all four samples ($\tau = 200$ ns), whereas the decay profile of the 5D_0 emission differs largely. The invariance of the 5D_1 decay reflects an equally efficient relaxation process from the 5D_1 to the 5D_0 level for the investigated samples. Therefore, the increased $^5D_{1,2} - ^7F_J$ emission relative to the 5D_0 emission of the β -phase in the steady state spectra should be linked with the fast decay of the 5D_0 emission. This fast decay originates from an increased probability for non-radiative decay, which is reflected in a decrease of the internal quantum efficiency of the emission from the 5D_0 level. Due to the 3D framework of Eu^{3+} atoms in the β -phase, the Eu ions are highly connected to each other, making energy transfer from one Eu^{3+} 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 non-radiative decay paths. Given that the decay from the 5D_0 level is several orders of magnitude slower than from the 5D_1 level, the influence of the non-radiative decay rate is much larger for the 5D_0 level. This results in a relatively stronger reduction for the emission intensity for the transitions starting from the 5D_0 level, compared to those from the 5D_1 level.

However, it should be noted that for stoichiometric phosphors much lower quantum efficiencies are usually observed. For high Eu^{3+} concentrations, distances between Eu^{3+} atoms become so small that cross-relaxation and other energy transfer process 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 Eu^{3+} concentration. In this way, the relatively low absorption strength of the 4f-4f transitions in Eu^{3+} 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 $Na_xEu_y(MoO_4)_z$

and $R_2(\text{MoO}_4)_3$ ($R = \text{Eu, Gd}$)^{48,52}, 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 8eV) (Figure 13), covering three different regions of the electromagnetic spectrum: Ultraviolet (UV) below 380nm (region I), Visible (Vis) from 380 to 740nm (region II) and Infrared (IR) above 780nm (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 $\text{Na}_x\text{Eu}_y(\text{MoO}_4)_z$ ²⁸ and $R_2(\text{MoO}_4)_3$ ($R = \text{Gd, Eu}$).⁵²

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 non-dipole and transitions involving momentum transfer. As these non-optical transitions probe a wider range of the band structure of the material, the EELS spectra contains less sharp features, but nevertheless clear differences between the different materials are apparent.

Changing the $\text{KEu}(\text{MoO}_4)_2$ structure from the anorthic α -phase to the modulated monoclinic phase during the annealing at 973 K (Table S1 of Supporting information) leads to a shift of the maximum from ~215 nm to ~180 nm (Fig. 13). Further increase of the annealing temperature from 973 K to 1173 K returns to an initial maximum value ~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 Fig. 13, the EELS spectrum of K_2MoO_4 is characterized by the presence of a second absorption band at ~500 nm while the EELS spectra of $\text{KEu}(\text{MoO}_4)_2$ prepared at 973K, 1173 K (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 α - $\text{K}_{0.5}\text{Eu}_{0.5}\text{MoO}_4$. The EELS spectrum of α - $\text{KEu}(\text{MoO}_4)_2$ in the region from 380 to 1200 nm shows the presence of one absorption band at ~680 nm in the visible range. The position of this band is close to the positions of the same bands on the EELS spectra of earlier studied $\text{Na}_{0.286}\text{Eu}_{0.571}\text{MoO}_4$ (~735 nm)⁴⁸ and β' - $R_2(\text{MoO}_4)_3$ ($R = \text{Gd, Eu}$; 680-700 nm)⁵² providing hints that it is related to the Eu^{3+} excitation. Thermal annealing of α - $\text{KEu}(\text{MoO}_4)_2$ and the transformation from the anorthic structure to the modulated monoclinic structure leads to a

vanishing of the band at ~ 680 nm and the appearance of a new broad absorption band at ~ 875 nm which remains for both types of cooling of the β - $\text{K}_{0.5}\text{Eu}_{0.5}\text{MoO}_4$. In contrast with $\text{Na}_5\text{Eu}(\text{MoO}_4)_4$ ⁴⁸ and both modifications of $\text{Eu}_2(\text{MoO}_4)_3$ ⁵², EELS spectra of all $\text{KEu}(\text{MoO}_4)_2$ 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 (1-3eV) 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’’⁵³ $|\Delta L| \leq 2$, $|\Delta J| \leq 2$, $\Delta S = 0$) are usually observed in optical excitation and emission spectra⁵⁴⁻⁵⁶ 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 ago⁵⁷⁻⁵⁸ 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 ${}^7\text{F}_0$, ${}^7\text{F}_1 \rightarrow {}^5\text{D}_j$ 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 α - $\text{KEu}(\text{MoO}_4)_2$ and the modulated monoclinic β -phase and an influence of the preparing conditions on the band positions.

4. Conclusion

The α - and β -polymorphs of $\text{KEu}(\text{MoO}_4)_2$ 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 α -phase and a monoclinic high temperature β -phase with an incommensurately modulated structure. The structures of both $\text{KEu}(\text{MoO}_4)_2$ 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 Eu^{3+} -framework is observed for the β -phase. The most intense luminescence provided by Eu^{3+} is observed in the case of the minimum size of the Eu^{3+} clusters (isolated from other Eu^{3+} ions).⁵⁹ The higher the concentration of the smallest clusters, the better luminescence properties can be

observed.⁴⁷ The present report shows that a layered network of Eu³⁺ ions 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.

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Supporting Information Available:

Unit cell parameters of KEu(MoO₄)₂ samples prepared under different annealing conditions (Table S1). Final coordinates, isotropic atomic displacement parameters and Fourier amplitudes of the displacive modulation function for β-KEu(MoO₄)₂ (Table S2). Anisotropic atomic displacement parameters in β-KEu(MoO₄)₂ (Table S3). Selected interatomic distances and bond angles in β-KEu(MoO₄)₂ (Table S4). Final coordinates, isotropic atomic displacement parameters and Fourier amplitudes of the displacive modulation function for α-KEu(MoO₄)₂ (Table S5). Selected interatomic distances and bond angles in α-KEu(MoO₄)₂ (Table S6). K and Eu distribution versus *t* for β-KEu(MoO₄)₂ structure (Figure S1). Difference Fourier map of the Eu/K site in β-KEu(MoO₄)₂, *x*₁–*x*₄ section (Figure S2). *t*-dependences of the Eu – O, K – O and Mo – O distances in β-KEu(MoO₄)₂ (Figure S3). Decay profiles of the ⁵D₁ – emission (λ_{exc} = 337nm) at 10 K (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1. Crystal data, data collection and refinement of KEu(MoO₄)₂ polymorphs.

Formula	β -KEu(MoO ₄) ₂	α -KEu(MoO ₄) ₂
Formula weight (g)		510.93
Temperature (K)		293(2)
Cell setting	Monoclinic	Anorthic
Super Space group	<i>I</i> 2/ <i>b</i> ($\alpha\beta$ 0)00	$I\bar{1}$ ($\alpha\beta\gamma$)0
Lattice parameters:		
<i>a</i> (Å)	5.52645(4)	5.58727(22)
<i>b</i> (Å)	5.28277(4)	5.29188(18)
<i>c</i> (Å)	11.73797(8)	11.7120(4)
α (°)		90.485(3)
β (°)		88.074(3)
γ (°)	91.2189(4)	91.0270(23)
<i>V</i> (Å ³)	342.612(5)	346.03(3)
q vector	0.56821(2) a * - 0.12388(3) b *	$\frac{1}{2}$ a * + $\frac{1}{2}$ c *
Formula units, Z	2	2
Calculated density, D _x (g×cm ⁻³)	4.951(8)	4.9038(4)
Color	Light-brown	White
Data collection		
Diffractometer		MAR345
Radiation/ Wavelength (λ , Å)		Synchrotron / 0.6692
Radiation monochromator		Si(111) double crystal
Absorption coefficient, μ (mm ⁻¹)	12.832	12.553
F(000)	460	460
2 θ range (°)	3.002-34.298	2.000-34.708
Step scan (2 θ)	0.004	0.004
<i>I</i> _{max}	20846	20127
Number of points	7825	9346
Refinement		
Refinement		Rietveld

Background function	Legendre polynomials, 16 terms	
The number of reflections		
(All / Observed)	864 / 861	447 / 445
Among them:		
Main	124 / 124	220 / 218
The 1 st order satellites	245 / 245	227 / 227
The 2 nd order satellites	246 / 244	
The 3 rd order satellites	249 / 248	
No. of refined parameters/ refined atomic parameters	97/69	54 / 30
R and R _w (%) for Bragg reflections		
(R _{all} /R _{obs})	1.15/1.12 and 1.43/1.40	1.50/1.49 and 2.05/2.05
Among them:		
Main	0.74/0.74 and 1.09/1.09	1.25/1.24 and 1.90/1.89
The 1 st order satellites	1.26 / 1.26 and 1.40 / 1.40	1.85/1.85 and 2.22/2.22
The 2 nd order satellites	1.90 / 1.72 and 1.66 / 1.55	
The 3 rd order satellites	1.57 / 1.52 and 1.41 / 1.40	
R _p and R _{wp} ; R _{exp}	2.35 and 3.30; 3.32	2.96 and 4.16; 3.04
Goodness of fit (ChiQ)	0.99	1.37
Max./min. residual density (e×Å ⁻³)	0.13/-0.12	0.30/-0.26

Figure captions

- Fig. 1. (*Color online*). Part of the PXRD patterns of the $\text{KEu}(\text{MoO}_4)_2$ samples prepared from $\alpha\text{-KEu}(\text{MoO}_4)_2$ (1) by annealing at 973 K (2), 1023 K (3), 1073 K (4), 1123 K (5), 1173 K (6) and at 1203 ± 10 K followed by fast quenching from the high temperature to liquid nitrogen ($\beta\text{-KEu}(\text{MoO}_4)_2$ (7)) in 2θ ranges of $5\text{-}51^\circ$ (a) and $27\text{-}28.75^\circ$ (b)
- Fig. 2. ED patterns along the main zone axes for the monoclinic $\beta\text{-KEu}(\text{MoO}_4)_2$.
- Fig. 3. ED patterns along the main zone axes for the anorthic $\alpha\text{-KEu}(\text{MoO}_4)_2$.
- Fig. 4. (*Color online*). Experimental, calculated and difference SXP patterns for $\beta\text{-KEu}(\text{MoO}_4)_2$. Tick marks denote the peak positions of possible Bragg reflections for (a) the main reflections and (b) satellites. The inset shows a part of the profile with the indexation of some reflections. The pair of strong low-angle satellites is a characteristic feature of the scheelite-like incommensurate structures.
- Fig. 5. (*Color online*). Experimental, calculated and difference SXP patterns for $\alpha\text{-KEu}(\text{MoO}_4)_2$. Tick marks denote the peak positions of possible Bragg reflections for (a) the main reflections and (b) satellites.
- Fig. 6. (*Color online*). A portion of the $\beta\text{-KEu}(\text{MoO}_4)_2$ aperiodic structure in the ab projection. The red balls and blue rings indicate Eu and K positions, respectively. The $[\text{MoO}_4]$ tetrahedra are represented by their edges. The grey-and-white wave indicates the continuously changing chemical composition from mainly $\{\text{Eu}[\text{MoO}_4]\}$ (center of the grey part) to mainly $\{\text{K}[\text{MoO}_4]\}$ (center of the white part). The direction and length of this wave (arrow) is parallel to the q vector with length $1/|q|$. The dimers (marked in orange) and trimers (marked in yellow) of the $\{\text{EuMoO}_4\}$ columns are marked.
- Fig. 7. (*Color online*). The ac projection of the crystal structure for the two $\text{KEu}(\text{MoO}_4)_2$ modifications (only K, Eu and Mo cations are shown for simplicity): β - (a) and α - (b).
- Fig. 8. (*Color online*). Eu-layers in α - (a,b) and $\beta\text{-KEu}(\text{MoO}_4)_2$ (c,d) structures.
- Fig. 9. (*Color online*). $[001]$ HAADF-STEM image of $\beta\text{-K}_{0.5}\text{Eu}_{0.5}\text{MoO}_4$ and the structural model (only K and Eu cations are shown for simplicity) overlay on the experimental HAADF-STEM image (bottom). Red balls are Eu positions, blue rings are K positions.
- Fig. 10. (*Color online*). Excitation (a) ($\lambda_{\text{em}} = 615$ nm) and emission (b) ($\lambda_{\text{ex}} = 395$ nm) spectra of four $\text{KEu}(\text{MoO}_4)_2$ samples at room temperature. The inset shows the emission of the $^5\text{D}_1$ and $^5\text{D}_2$ level normalized to the peak of the emission of the $^5\text{D}_0$ level for all samples at room temperature.

Fig 11. (*Color online*). Emission ($\lambda_{\text{ex}} = 395 \text{ nm}$) of the $^5\text{D}_0$ – level at 10 K: $^5\text{D}_0 - ^7\text{F}_0$ (up) and $^5\text{D}_0 - ^7\text{F}_2$ (down) transitions.

Fig 12. (*Color online*). Decay profiles of the $^5\text{D}_0$ – emission ($\lambda_{\text{exc}} = 337\text{nm}$) at 10 K (up) and at room temperature (down). The dashed lines are exponential fits.

Fig. 13. (*Color online*). a) EELS spectra of K_2MoO_4 (1), $\alpha\text{-KEu}(\text{MoO}_4)_2$ (2), $\text{KEu}(\text{MoO}_4)_2$ annealed at 973 K (3) and 1173 K (4) followed by slow cooling to room temperature and $\beta\text{-KEu}(\text{MoO}_4)_2$ (5) prepared at $1203 \pm 10 \text{ K}$ followed by fast quenching to liquid nitrogen plotted as a function of energy loss. b) Same spectra plotted in wavelength scale. (I - ultraviolet region, II - visible light and III - infrared region). Spectra are normalized in the displayed region and shifted vertically for clarity of display. Scales were matched for easy comparison with PLE and PL spectra.

Figures

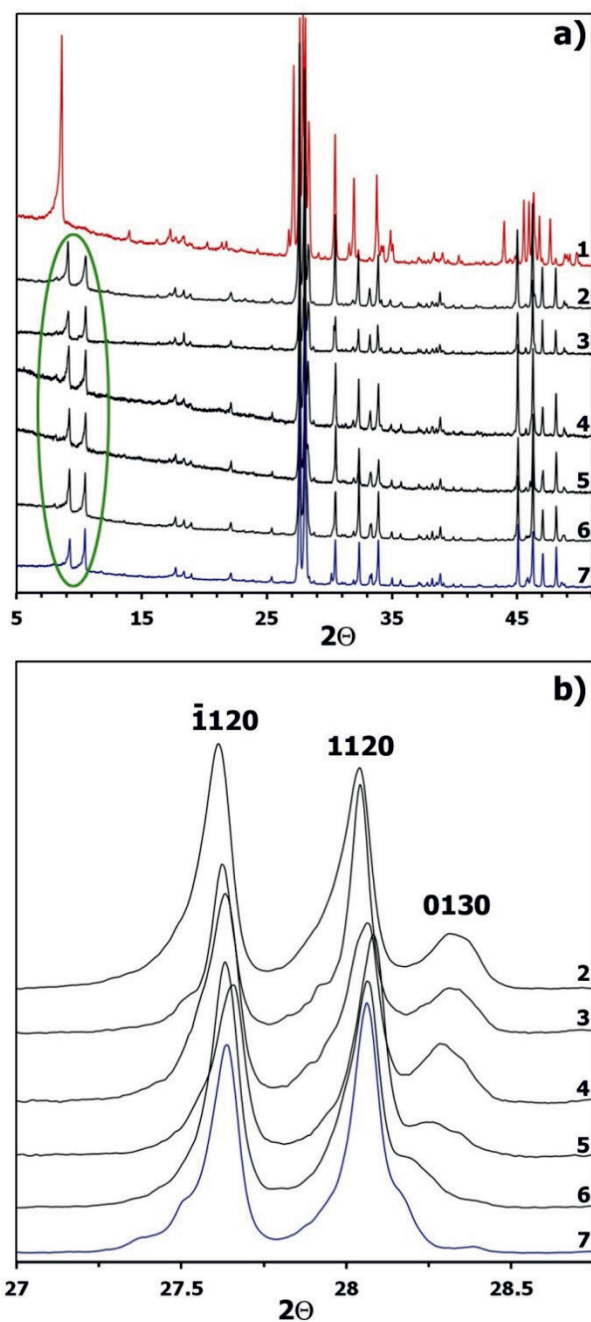


Fig. 1. (Color online). Part of the PXR D patterns of the $\text{KEu}(\text{MoO}_4)_2$ samples prepared from $\alpha\text{-KEu}(\text{MoO}_4)_2$ (1) by annealing at 973 K (2), 1023 K (3), 1073 K (4), 1123 K (5), 1173 K (6) and at 1203 ± 10 K followed by fast quenching from the high temperature to liquid nitrogen ($\beta\text{-KEu}(\text{MoO}_4)_2$ (7)) in 2θ ranges of $5\text{-}51^\circ$ (a) and $27\text{-}28.75^\circ$ (b).

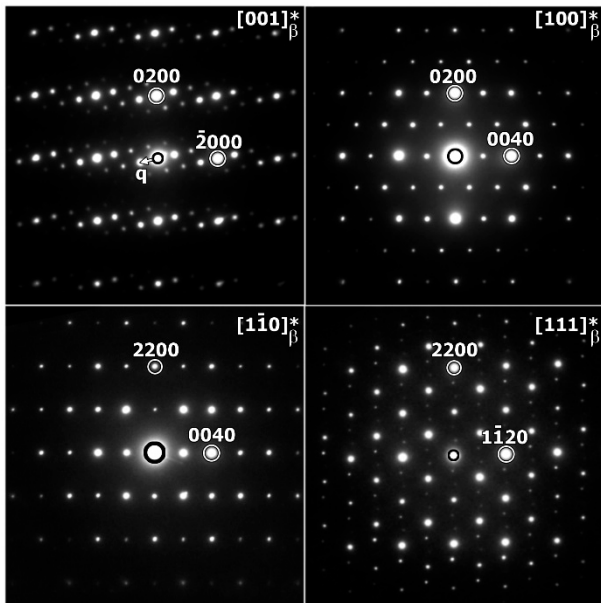


Fig. 2. ED patterns along the main zone axes for the monoclinic β -KEu(MoO₄)₂.

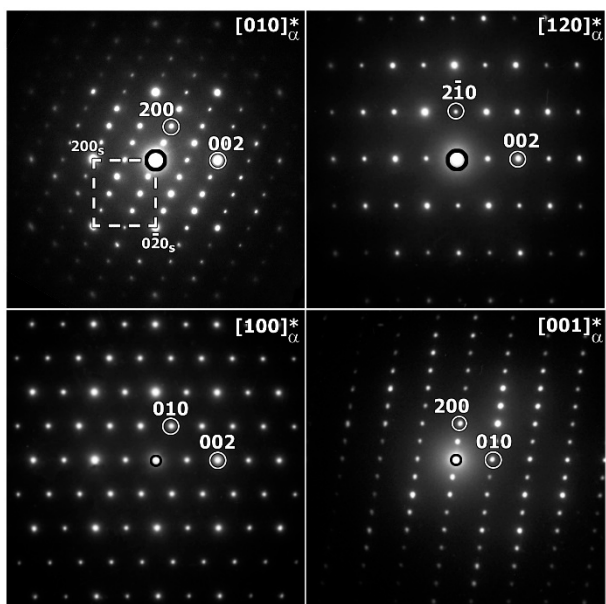


Fig. 3. ED patterns along the main zone axes for the anorthic α - $\text{KEu}(\text{MoO}_4)_2$ (s refers to the scheelite-type unit cell).

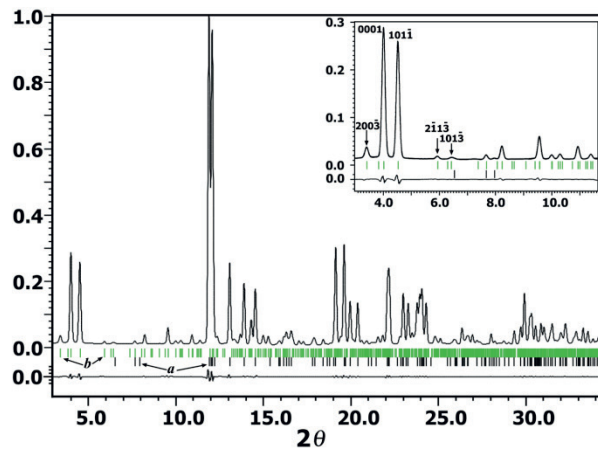


Fig. 4. (*Color online*). Experimental, calculated and difference XPD patterns for β -KEu(MoO₄)₂. Tick marks denote the peak positions of possible Bragg reflections for (*a*) the main reflections and (*b*) satellites. The inset shows a part of the profile with the indexation of some reflections. The pair of strong low-angle satellites is a characteristic feature of the scheelite-like incommensurate structures.

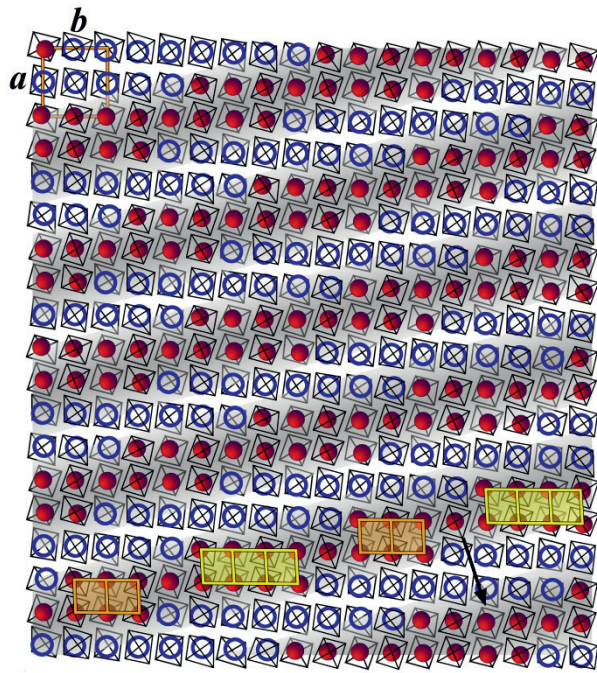


Fig. 5. (*Color online*). A portion of the β -KEu(MoO₄)₂ aperiodic structure in the ab projection. The red balls and blue rings indicate Eu (0.981Eu1+0.019K2) and K (0.981K1+0.019Eu2) positions, respectively. The [MoO₄] tetrahedra are represented by their edges. The grey-and-white wave indicates the continuously changing chemical composition from mainly {EuMoO₄} (center of the grey part) to mainly {KMoO₄} (center of the white part). The direction of this wave (arrow) is parallel to the q vector with length $1/|q|$. The dimers (marked in orange) and trimers (marked in yellow) of the {EuMoO₄} columns are marked.

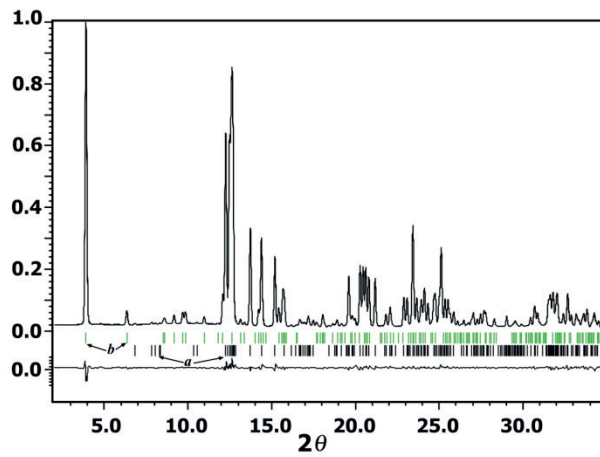


Fig. 6. (*Color online*). Experimental, calculated and difference XPD patterns for α -KEu(MoO₄)₂. Tick marks denote the peak positions of possible Bragg reflections for (a) the main reflections and (b) satellites.

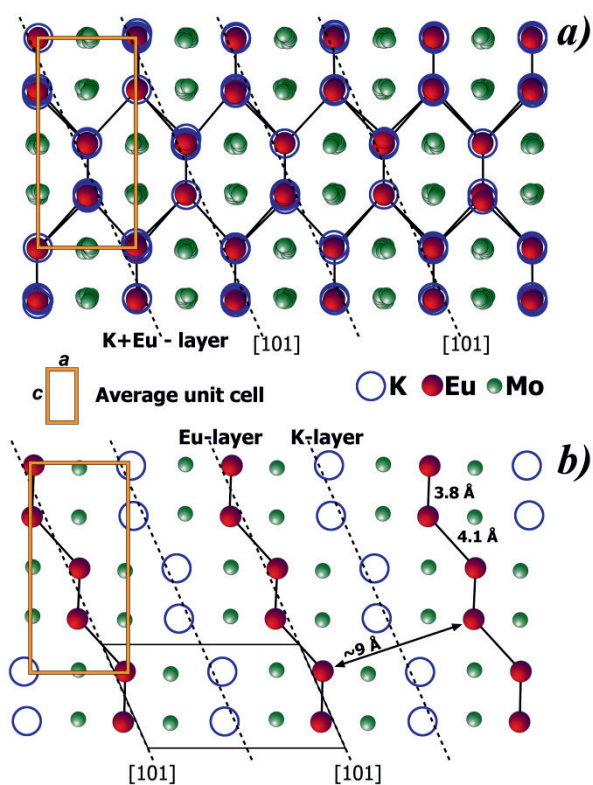


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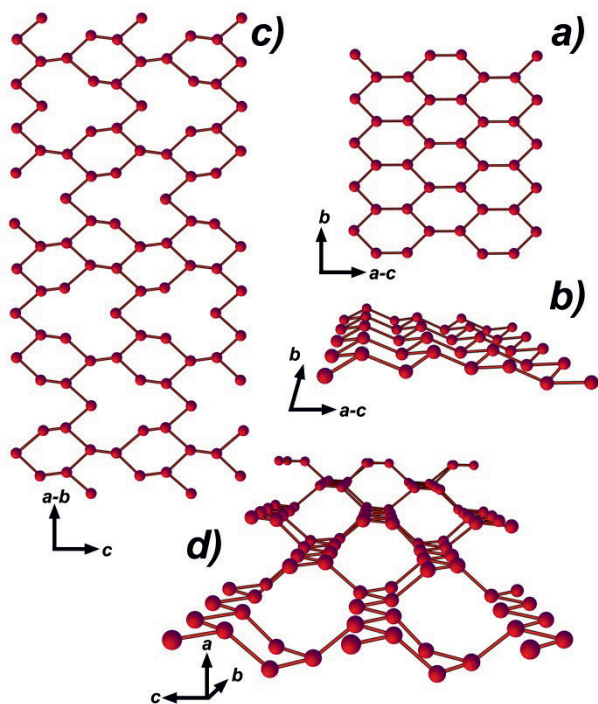


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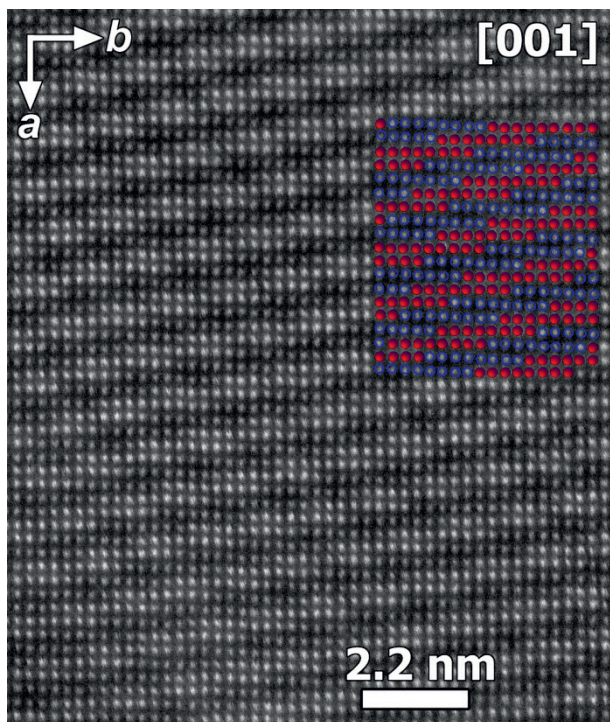


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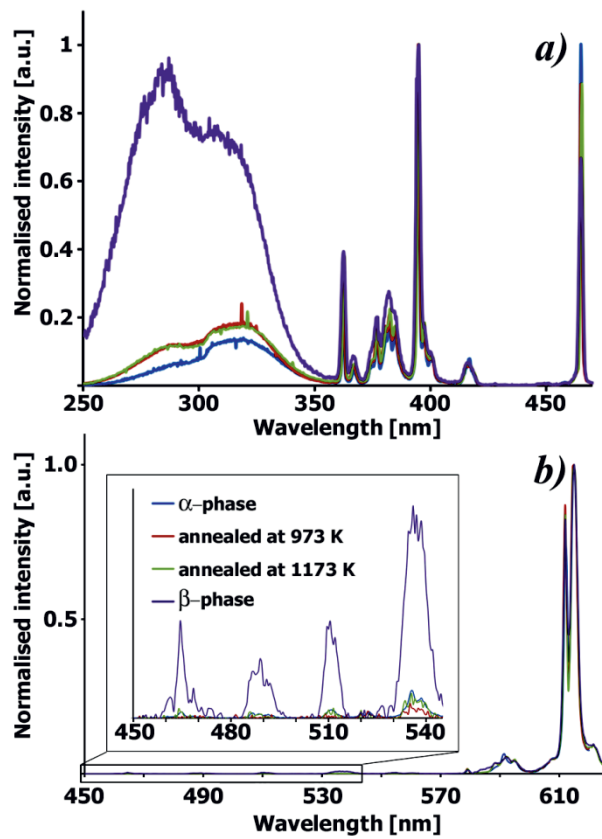


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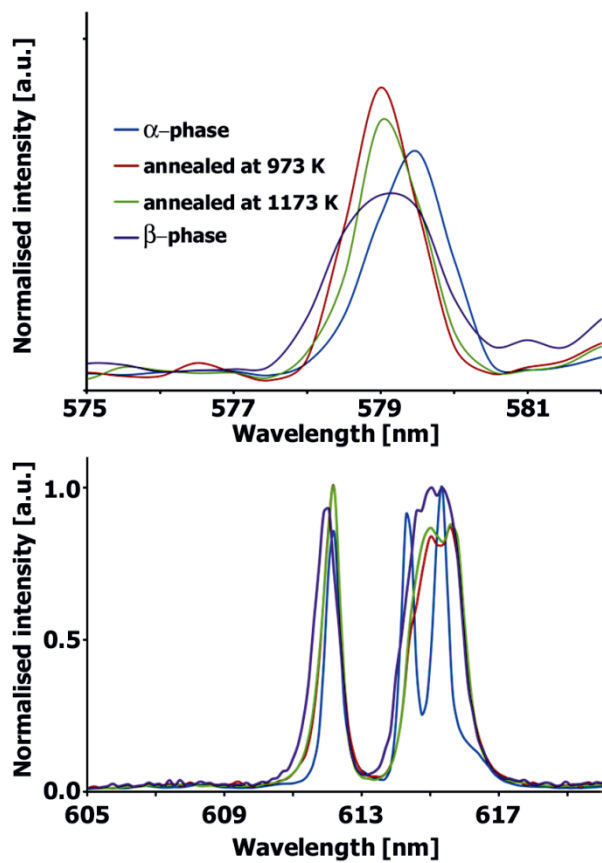


Fig 11. (Color online). Emission ($\lambda_{\text{ex}} = 395 \text{ nm}$) from the ${}^5\text{D}_0$ – level at 10 K: (top) ${}^5\text{D}_0 - {}^7\text{F}_0$ and (bottom) ${}^5\text{D}_0 - {}^7\text{F}_2$ transitions.

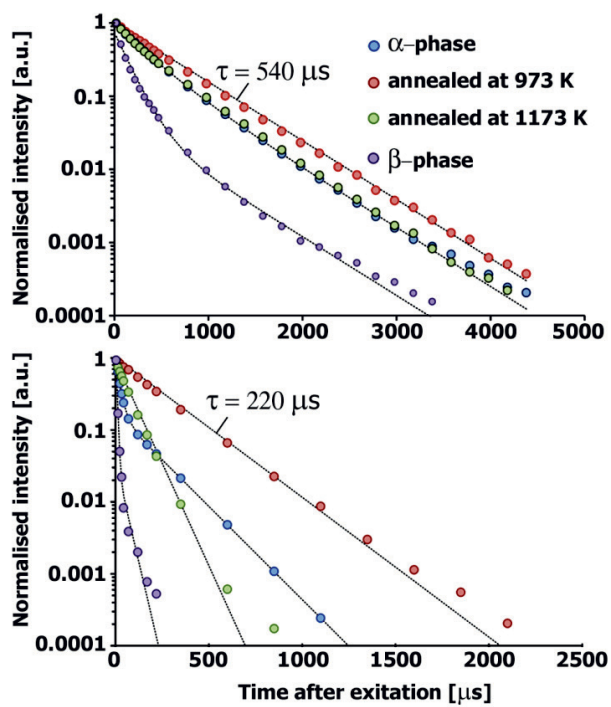


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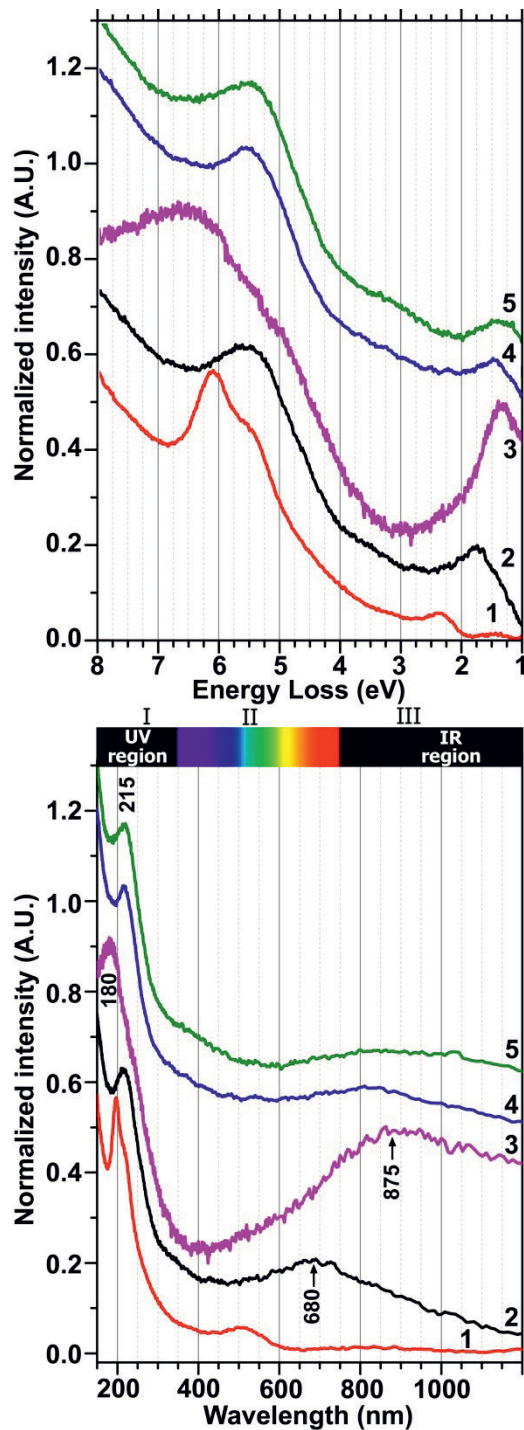


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TOC figure.

