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K₅Eu(MoO₄)₄ red phosphor for solid state lighting applications, prepared by different techniques[†]

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The influence of preparation techniques on the structure and luminescent properties of $K_{z}Eu(MoO_{a})_{a}$ (KEMO) was investigated. KEMO phosphors were synthesized by three different techniques: solid state and sol-gel (sg) methods as well as the Czochralski (CZ) crystal growth technique. Laboratory powder X-ray diffraction (PXRD) studies revealed that all KEMO samples had a structure analogous to that of other high temperature α -K₅R(MoO₄)₄ palmierite-type phases (space group (SG) $R\bar{S}m$). Contrary to laboratory PXRD data, electron diffraction revealed that the KEMO crystal grown by the CZ technique had a (3 + 1)Dincommensurately modulated structure (super space group (SSG) $C2/m(0\beta 0)00$) with the modulation vector $\mathbf{q} = 0.689 \mathbf{b}^*$. A detailed analysis of electron diffraction patterns has shown formation of three twin domains rotated along the c axis of the R-subcell at 60° with respect to each other. Synchrotron XRD patterns showed additional ultra-wide reflexes in addition to reflections of the R-subcell of the palmierite. However, the insufficient number of reflections, their low intensity and large width in the synchrotron X-ray diffraction patterns made it impossible to refine the structure as incommensurately modulated $C2/m(0\beta 0)00$. An average structure was refined in the C2/m space group with random distribution of K1 and Eu1 in [M1A₂O₈]-layers of the palmierite-type structure. The dependence of luminescent properties on utilized synthesis techniques was studied. The emission spectra of all samples exhibit intense red emission originating from the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ Eu³⁺ transition. The integrated intensity of the emission from the Eu^{3+ 5}D₀ term was found to be the highest in the crystal grown by the CZ technique. The quantum vield measured for KEMO crystals demonstrates a very high value of 66.5%. This fact confirms that KEMO crystals are exceptionally attractive for applications as a near-UV converting red phosphor for LEDs.

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heating and cooling cycle (Fig. S2). Fragments of the experimental, calculated and difference synchrotron XPD patterns for K5Eu(MoO4)4 structure in the R3m model (Fig. S3). $[\rho_{dif}: (x; y; z)]$ residual electron density maps for the K₅- $Eu(MoO_4)_4$ structure after the refinement in the $R\bar{3}m$ model in the (001) plane through O1 and M1 (atoms and in the (010) plane (Fig. S4). R3m models tested during the Rietveld refinement of K5Eu(MoO4)4 structure using the SXPD data (annex 1). Crystallographic data for K5Eu(MoO4)4 in different models (Table S3). Fractional atomic coordinates and isotropic atomic displacement parameters (U_{iso}) for K₅Eu(MoO₄)₄ (Table S4). Selected distances and angles for K₅Eu(MoO₄)₄ (Table S5). Photoluminescence emission spectra at temperatures 78, 300 and 500 K of sg893-KEMO, ss-KEMO and crushed crystal measured at E_{ex} = 2.66 eV (a, d and g); 3.14 eV (b, e and h) and 5.63 eV (Fig. S5). M2-layers and K1On polyhedra in the rhombohedral α -K₅Yb(MoO₄)₄ and monoclinic γ -phase (Fig. S6). Photoluminescence emission spectra for the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ and transition of Eu $^{3+}$ in for K5Eu(MoO4)4 prepared by solid state synthesis, sol-gel method followed by annealing at 893 K and the Czochralski techniques (Fig. S7). Positions of the $^5D_0 \rightarrow \ ^7F_0$ transition, integral intensities of the $\ ^5D_0 \rightarrow \ ^7F_1$ and $\ ^5D_0 \rightarrow \ ^7F_2$ transitions, ⁵D₀-⁷F₂/⁵D₀-⁷F₁ ratio, lifetimes and quantum yield for K₅Eu(MoO₄)₄ prepared by different synthesis techniques (Table S6). CCDC 2114453. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/ 10.1039/d2ce01107g

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[†] Electronic supplementary information (ESI) available: EDX analysis results of $K_5Eu(MoO_4)_4$ prepared by different techniques (Table S1). Unit cell parameters and estimated crystallite size for $K_5Eu(MoO_4)_4$ prepared by solid state synthesis, sol-gel method followed by annealing at 893 K and Czochralski techniques (Table S2). Particle size distributions and PXRD patterns of $K_5Eu(MoO_4)_4$ synthesized by various methods (Fig. S1). Fragments of DSC and TG curves for ss-KEMO sample in the temperature ranges of 370–1120 K and 980–1070 K in

1. Introduction

Phosphor converted light emission diodes (pc-WLEDs) in lighting technologies represent modern and commonly used light sources. pc-WLEDs are used as back lights for various electronic devices, general lightning, new LED screens, *etc.*^{1,2} The pc-WLEDs are characterized by minimal energy losses and consumption, non-toxicity, multiple easy ways of fabrication and cost efficiency.^{3–9}

Molybdates of alkali-earth and transition metals attract attention due to their applications as phosphors, scintillators, acousto-optical, photocatalytic materials, and so on.¹⁰⁻¹⁴ Doped with rare earth elements (RE) Mo-based compounds are promising materials for pc-WLEDs applications due to the opportunity for luminescence spectra tuning and excellent thermal stability.¹⁵⁻²⁶ Molybdenum oxides $M_5R(MOO_4)_4$ (M = Rb, K, Tl; R = RE) with the palmierite-type $(K_2Pb(SO_4)_2)^{27-28}$ structure can be also under consideration due to their high luminescence intensity.^{15,29,30} Another important advantage of these compounds is the possibility to grow sufficiently large crystals by the Czochralski method at sufficiently low temperatures.^{17-20,22,31-33}

This allows expanding the variety of experimental methods to study the physical properties of the compounds, and to compare luminescent properties of crystals with those of powders or ceramics. Luminescence properties are strongly dependent on various factors such as synthesis techniques, annealing temperature, grain diameter, size of coherent scattering regions (crystal size), and others.^{34,35}

In this work, we prepared $K_5 Eu(MoO_4)_4$ by various methods and tried to reveal the influence of synthesis techniques on material structure and luminescence properties.

2. Experimental section

2.1. Sample preparation

Different synthesis methods were used to prepare KEMO samples: solid state (ss) and sol–gel (sg) synthesis as well as Czochralski (CZ) crystal growth technique. The stoichiometric amounts of such raw materials as MoO₃ (99.99%, Rushim), Eu₂O₃ (99.99%, Rushim), and K₂CO₃ (99.99%, Rushim) were mixed together. Then the mixture was heated in an alumina crucible at the temperature of 893 ± 10 K for 30 h in air conditions (ss-KEMO sample). The cooling procedure was carried out in the furnace starting with the highest 893 K and gradually decreasing to room temperature ($T_{\rm R}$).

sg-KEMO was prepared by a sol-gel method. All chemicals used in the experiments were of analytical grade. Firstly, stoichiometric amounts of K_2CO_3 and Eu_2O_3 according to the chemical formula $K_5Eu(MoO_4)$ were dissolved in diluted HNO₃ to get a nitrate solution. Secondly, an appropriate amount of citric acid was added to the above solution and stirred for 30 min to get a homogeneous solution. Thirdly, a stoichiometric amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was added to the mixed solution and the pH of the solution was then adjusted to 7 with $NH_3\cdot H_2O$. Finally, the solution was



Fig. 1 Images of the $K_5Eu(MoO_4)_4crystal$ grown by a Czochralski technique in daily light (a) and under excitation ~395 nm (b).

evaporated in a water bath at 353 K to get a slightly yellow gel. Then the gel was dried at 403 K in an oven until it became black and dry. The dried gel was sintered at 893 ± 10 K for 8 h (sg893-KEMO) in a muffle furnace and the final product in the form of white powder was obtained.

The process of crystal growth by the CZ technique included the preparation of raw materials by solid state reaction from K_2CO_3 , Eu_2O_3 (spectroscopic pure $\geq 99.995\%$) and MoO_3 in a Pt crucible at 773–823 K for 15 h. The polycrystalline raw materials were placed in a Pt crucible (40 mm diameter) and melted in a 17 KHz frequency induction furnace. As a seed, a small-sized, non-oriented single crystal bar was used. A light-rose crystal (20 mm in diameter and 15 mm in length) was grown at 1073 K in air by the CZ technique (drawing rate 0.5–1.5 mm h⁻¹; rotation speed 50 rpm). The images of the KEMO crystal grown by CZ technique under different external shooting conditions: daily light and ~395 nm excitation are shown in Fig. 1.

2.2. Characterization

The scanning electron microscope (Tescan VEGA3) provided with an Oxford Instruments X-Max 50 silicon drift energydispersive X-ray spectrometry (EDXs) system (AZtec and INCA software) was used for the scanning electron microscopy–energy dispersive X-ray (SEM–EDX) analysis. The content of elements was determined by measuring at 10 points for each sample. The K_K , Eu_L , and Mo_L lines were used to obtain the results of the EDX analysis.

We used a CILAS 1180 laser diffraction particle size analyser for particle sizes determination of ss-KEMO and sg893-KEMO samples. Measurements were taken in isopropyl alcohol/aqueous suspension (20:80) in the range from 0.04 to 2500 μ m for five times for each sample.

A NETZSCH STA Jupiter 449 simultaneous thermal analyzer was used to carry out differential scanning calorimetry (DSC) and thermogravimetry (TG) studies for ss-KEMO. Samples weighing \sim 30 mg were placed into platinum crucibles with lids. The study was conducted in air conditions in the temperature range of 300–1097 K (heating/cooling rate was 3 K min⁻¹).

A test for the center of symmetry in ss-KEMO sample and CZ-KEMO crystal was performed with the second-harmonic generation (SHG) powder technique similar to the one first described by Kurtz and Perry.³⁶ The CZ-KEMO crystal was previously crushed into 3–5 µm powder for the sake of comparability with all other samples. The SHG at the wavelength $\lambda_{\omega} = 0.532$ µm was excited with a Minilite-I YAG:Nd-laser operating in a Q-switched mode at $\lambda_{\omega} = 1.064$ µm and registered in reflection geometry as described previously.³⁷ Polycrystal-line α -SiO₂ with 3–5 µm size particles was used as a standard in order to calibrate intensity of the SHG response $I_{2\omega}$ according to $q = I_{2\omega}/I_{2\omega}(SiO_2)$ relation.

We used a Thermo ARL X'TRA powder diffractometer (CuK α radiation, $\lambda = 1.5418$ Å, Bragg–Brentano geometry, scintillation detector) for powder X-ray diffraction (PXRD) data. PXRD patterns were collected at $T_{\rm R}$ in the range 2θ equal to 5–65° with a step of 0.02°. Checking of the presence of any initial or intermediate phase reflections was done using the JCPDS PDF-2 Database. The lattice parameters were determined by Le Bail decomposition³⁸ applying the JANA2006 software.³⁹ The Debye–Scherrer's (D–S) equation⁴⁰ was implemented to count coherent scattering regions (crystallite sizes). LaB₆ (SRM 660c) as a line shape standard was applied to determine instrumental broadening.

Synchrotron XRD (SXRD) patterns for the crushed KEMO crystal were measured at the BL15XU beamline of SPring-8 using $\lambda = 0.65297$ Å.^{41,42} The sample was inside rotated Lindemann glass capillaries with the inner diameter of 0.1 mm). Data were collected between 2 and 61° with a step of 0.003° in 2θ . Absorption coefficients were also measured, and the Rietveld analysis was performed using JANA2006.³⁹ Illustrations were produced with this package in combination with the DIAMOND⁴³ program.

A Philips CM20 transmission electron microscope operating at 200 kV with a CCD camera was used to record selected area electron diffraction (SAED) patterns. KEMO crystal was crushed in an agate mortar and dispersed in methanol for SAED observations. After the treatment in an ultrasonic bath, a few drops of the solution were put on a copper grid with a holey carbon film to disperse the crystallites.

Photoluminescence emission (PL) spectra were recorded on a Lot-Oriel MS-257 spectrograph fitted with a Marconi CCD detector and 150 W Xe arc as an excitation source over the wavelength range of 570–720 nm with 0.3 nm spectral resolution. Approximately the same conditions were created during the photoluminescence spectra measurements of all samples which allowed to obtain information on their relative luminescence intensity. The measurements were carried out under $T_{\rm R}$ conditions, the spectral values were given taking into account adjustments for the sensitivity of the spectrometer.

PLE spectra were measured over the 130–550 nm wavelength range at $T_{\rm R}$ using a specialized laboratory set-up for VUV luminescent spectroscopy with 5 nm spectral resolution. As an excitation source a Hamamatsu L11798 deuterium lamp was used. A McPherson 234/302 vacuum primary monoView Article Online

chromator was used to monochromatize the lamp radiation. Samples were settled down into a vacuum closed-cycle ARS cryostat. The luminescence registration was provided using a Shamrock 303i (Andor Technology) monochromator supplied with a Hamamatsu H8259-02 photon counting head. Emission decay curves were measured at $T_{\rm R}$ using 1 µs pulsed xenon Perkin-Elmer FX-1152 Flashtube as an excitation source and an Ortec MCS-PCI Card with 100 ns resolution for signal processing.

Internal quantum efficiency usually evaluated using the relation of the amount of emitted photons to the amount of absorbed photons, was estimated at $T_{\rm R}$ on Edinburgh FS5 Instruments using a 450 W xenon light source. Quantum yield (QY) was determined under excitation of the Eu (⁵D₂) level at λ = 395 nm using an absolute method based on an integration sphere module. A fluoroplastic cuvette served as a reference for the reflection. Measurements of each sample were carried out several times in slightly different external conditions.

A LED device was fabricated by combining a 405 nm SMD UV chip with prepared $K_5Eu(MoO_4)_4$. A polished $K_5Eu(MoO_4)_4$ crystal plate was placed on the surface of this chip and fixed with epoxy resin. Resulting electroluminescence (EL) spectra and optical properties (CIE color coordinates and correlated color temperature (CCT)) were measured using a UPRtek MK350D spectrometer (CMOS Linear Image Sensor, 400 points) over the wavelength range from 380 to 780 nm with steps of 1 nm. Working voltage and driving current of the fabricated LED device were 600 mA and 3 W, respectively.

3. Results

3.1. Element composition and grain size distributions

Table S1 of the ESI† summarizes the results of the EDX analysis. The compositions were found to be in the range of 47.79–50.23 at%, 39.34–42.54 at% and 9.67–10.43 at% for K, Eu and Mo, respectively. The element content is close to $K_5Eu(MoO_4)_4$ composition.

Particle size distributions of sg893-KEMO and ss-KEMO are shown in Fig. S1a of the ESI.† A size distribution can be described using two modes for ss-KEMO particles ($19 \pm 2 \mu m$ (major peak) and $1.4 \pm 0.4 \mu m$; $D_{10}:D_{50}:D_{90} = <2 \mu m$: <14 μm <36 μm), while sg893-KEMO was characterized by a practically unimodal one (36 $\pm 4 \mu m$; $D_{10}:D_{50}:D_{90} = <4 \mu m$: <25 $\mu m < 50 \mu m$). Thus, the sol-gel technique leads to large size particles in the main fraction in comparison with the solid state sample.

3.2. SHG and DSC measurements

SHG study has shown an insignificant value of SHG responses (q < 0.1) for ss-KEMO and crushed KEMO crystal. The comparison of this result with other known complex molybdenum oxides drastically contrasts with noncentrosymmetric powder substances, all of them demonstrating SHG activity at least q > 10. This two-order difference in SHG intensities definitely excludes macroscopic noncentrosymmetry in the KEMO crystal structure and points at bulk centrosymmetry. Nevertheless, it is known that so weak SHG as q = 0.01-0.1 may also correspond to some order–disorder defects in the nano-scale.⁴⁴

DSC and TG curves for ss-KEMO obtained in a heatingcooling cycle at a 3 K min⁻¹ rate are shown in Fig. S2 of the ESI.† An endothermic peak at ~1054 K (heating) and an exothermic peak at ~1031 K (cooling) correspond to melting and crystallization of KEMO, respectively. A slight weight loss (0.2%) is observed on a TG heating curve in the temperature range of 300–973 K. Further heating up to 1097 K as well as subsequent cooling from 1097 K to room temperature does not lead to a change in weight. PXRD study of the sample after the heating-cooling cycle showed the presence of only the KEMO phase. Thus, the phase melts congruently, and the weight loss is associated with removal of adsorbed water.

3.3. Preliminary PXRD characterization and refinement model validation

Parts of PXRD patterns of KEMO synthesized by different methods are shown in Fig. S1b of the ESI,[†] The positions and number of peaks of KEMO synthesized by three different methods are the same as for KEMO (JCPDS, PDF-2, No. 45-0340). KEMO unit cell parameters were determined from PXRD patterns using Le Bail decomposition. All reflections can be indexed in the SG $R\bar{3}m$ (Z = 1.5) (Table S2 of the ESI[†]) that is standard for high temperature α -K₅R(MoO₄)₄ phases with the palmierite-type structure.^{45,46} However, PXRD patterns of sg893-KEMO sample already contained an additional reflection of K₂Mo₂O₇ phase (PDF#2 Card no. 36-0347, Fig. S1b of the ESI[†]) as an impurity.

The D–S equation (neglecting microstrain in the crystal)⁴⁰ from line broadening observed on PXRD patterns were used to estimate crystallite sizes of sg893-KEMO and ss-KEMO. The D–S equation is $D_{hkl} = K\lambda/(B_{hkl}\cos\theta)$, where crystallite size is denoted as D_{hkl} , hkl means Miller indices, crystallite-shape factor – K, which is generally peer to 0.9, the wavelength is indicated as λ , B_{hkl} is a full-width at half-maximum (FWHM) of an X-ray diffraction peak and a Bragg angle defined as θ . D–S crystallite size calculations with correction for instrumental broadening were performed using reflections in the 2θ range of 24–41° on PXRD patterns. Table S2 of the ESI† summarizes crystallite sizes estimated from the D–S equation. According to this data, both samples have similar crystallite size values.

The palmierite-type structure of crushed KEMO crystal was refined from synchrotron XRD data. Several extra broad reflections with low intensities were found in the synchrotron XRD pattern, and they could not be assigned to any previously known phase (Fig. S3 of the ESI†). Two models were tested during preliminary Rietveld refinement of the structure: i) an original $R\bar{3}m$ model, and ii) a disordered $R\bar{3}m$ model. Fig. S4 of the ESI† shows [ρ_{dij} : (x, y, z)] residual electron density maps for the KEMO structure after the refinement in the $R\bar{3}m$ model in (001) and (010) planes through O1 and M1 atoms. Details of the KEMO structure refinement in

both models are listed in annex 1 of the ESI† and results are summarized in Table S3 of the ESI.†

As can be concluded from Table S3 of the ESI,† the disordered $R\bar{3}m$ model with displacement of the M1 and O1 atoms from special positions with site symmetry 3a (M1) and 6c(O1) to a special position (x, \bar{x}, z ; symmetry 18m) is characterized by significantly lower values of structural *R*-factors, atomic displacement parameters and max/min residual density peaks. However, the refinement of the disordered $R\bar{3}m$ model results in a strong distortion of $MOO_4^{2^-}$ tetrahedra (O1–Mo–O2 angles in Table S3 of the ESI†).

It should be noted that residual electron density for the KEMO structure after the refinement around majority of atoms also shows the possibility of lowering the real structure symmetry from $R\bar{3}m$. Therefore, we will clarify a correct SG using SAED.

3.4. SAED study

Fig. 2 shows ED patterns of the crushed crystal along some of the main zone axes. The ED patterns demonstrate reflections which are characteristic of the $R\bar{3}m$ palmierite-type structure (Fig. 2a). These reflections can be indexed using $R\bar{3}m$ unit cell with $a \approx 6.0$ Å, $c \approx 20.7$ Å. Weak extra reflections observed in $[001]_R$ and $[1\bar{1}0]_R$ ED patterns are satellite reflections due to an incommensurate modulation of the palmierite-type structure and can be indexed using a modulation vector $\mathbf{q} = 0.336\mathbf{a}^* + 0.336\mathbf{b}^*$. Deviation of the modulation vector \mathbf{q} from $\mathbf{q} = 1/3\mathbf{a}^* + 1/3\mathbf{b}^*$ is clearly visibly looking at the $[1\bar{1}0]_R$ zone, where extra reflections do not lie on a straight line, but shift up and down. The two components of the modulation vector require transformation of a rhombohedral subcell to a monoclinic supercell.

Thus SAED study has revealed that a real structure of KEMO requires a monoclinic distortion of the rhombohedral sublattice to Cm or C2/m space group. An insignificant value of SHG responses (<0.1) for KEMO indicated a centrosymmetric SG C2/m for the structure.

The link of the unit cells vectors of the rhombohedral (*R*) and the monoclinic structure is: $[001]_R = [103]$, $[1\bar{1}0]_R = [100]$ and $[110]_R = [010]$. ED patterns indexing was made with four *hklm* indices given by diffraction vector $H = ha^* + kb^* + lc^* + mq$, $q = 0.689b^*$ (Fig. 2b). Reflections with m = 0 correspond to main reflections. The ED patterns can be completely indexed in the (3 + 1)D superspace group $C2/m(0\beta 0)00$ with the unique axis *b* and unit cell parameters $a \approx 10.4$ Å, $b \approx 6.00$ Å, $c \approx 7.7$ Å and $\beta \approx 117^{\circ}$. The presence of weak satellite reflections specifies ordering between K and Eu cations in the M1 position of the palmierite-type structure. However, the absence of satellite reflections in the PXRD patterns and the presence of only several extra broad reflections with small intensity in the synchrotron XRD patterns means that the order is very local.

Fig. 3a shows a [103] ED pattern of KEMO which is a superposition of three [103] ED patterns of KEMO twinned domains rotated along the c axis of a *R*-subcell at 60° with





Fig. 2 ED patterns along the main zone axes for $K_5Eu(MoO_4)_4$: a) indexed in R3m space group (left column); b) indexing in the superspace group $C2/m(0\beta 0)00$ (right column).

respect to each other. These domains are formed due to the loss of a 3-fold axis as a result of monoclinic distortion of the rhombohedral sublattice. Schematic drawing is shown in Fig. 4.

3.5. Refinement of crystal structure

In the synchrotron XRD patterns, reflections of a basic palmierite-type subcell and several extra broad reflections were present. However, a number, low intensity and large difference in width (~3-4 times) of broad reflections in comparison with the basic reflections did not allow the structure to be refined as incommensurately modulated with (3 + 1)D SSG $C2/m(0\beta 0)00.$

Based on the SAED data, the KEMO structure was finally refined in 3D monoclinic SG C2/m. It can be concluded that the distribution of the K and Eu cations in the M1 position is disordered. The unit cell parameters are: a = 10.37099(5) Å, b = 5.98542(3) Å, c = 7.72496(4) Å, $\beta = 116.58(5)^{\circ}$. The atom coordinates for the C2/m model have been obtained by transforming coordinates of corresponding sites in the $K_2Pb(SO_4)_2$ structure^{27,28} in accordance with a transformation matrix.



Fig. 3 (a) [103] ED patterns for three K₅Eu(MoO₄)₄ domains due to 60° rotation twins; schematic representation of the diffraction pattern for 1 (b), 2 (c) and 3 (d) twin domains and a superposition of ED patterns for three domains (e). Full circles are the main reflections. Black, red and blue rings are satellite reflections of the first, second, and third domains, respectively.

The transformation matrix from the $R\bar{3}m$ subcell (s) to the

monoclinic supercell (C2/m) is $T = \begin{pmatrix} 1 & 1 \\ -\frac{1}{3} & \frac{1}{3} \end{pmatrix}_{3}$ 0 in

the matrix equation $A_{C2/m} = A_s \times T$. The details of the KEMO structure refinement in the primary C2/m model are summarized in Table S3 of the ESI.†

After the refinement of the KEMO structure in the primary C2/m model, an isotropic atomic displacement parameter for the K and Eu cations in the M1 position (0, 0, 0; site



Fig. 4 Parts of the observed, calculated and difference synchrotron XRD patterns for $K_5Eu(MoO_4)_4$. Tick marks denote the peak positions of possible Bragg reflections.

symmetry 2*a*) was $U_{iso.} = 0.059(1)$ (Table S3 of the ESI†). The displacement of the M1 atoms from special positions with 2*a* site symmetry (M1) to a special position (*x*, 0, *z*; site symmetry 4*i*) leads to essentially lower values of structural *R*-factors, atomic displacement parameters and max/min residual density peaks. Fig. 4 shows fragments of the synchrotron XRD patterns. The crystallographic information is shown in Table 1, Table S4 contains atomic parameters (ESI†). Main interatomic distances are given in Table S5 of the ESI.† The CCDC deposition number is 2114453.

3.6. Luminescence properties

PLE and PL spectra at $T_{\rm R}$ of KEMO synthesized by three methods are shown in Fig. 5. PL spectra of all samples measured at three excitation wavelengths 465, 395 and 220 nm and at temperatures 78 K, 300 K and 500 K are listed in Fig. S5 of the ESI.[†] PLE spectra over the 130-550 nm wavelength range for Eu³⁺ emission upon monitoring emission at 613 nm in KEMO samples are presented in Fig. 5a together with an absorbance spectrum of the KEMO crystal grown by the CZ technique. The PLE spectra of all phosphors show a broad excitation band in the range of 170-310 nm as well as a group of sharp lines in the range of 310-500 nm. The absorbance demonstrates a set of narrow peaks in the range of 350–550 nm while the crystal becomes opaque at $\lambda < 300$ nm. Temperature dependencies of luminescence intensity excited in two narrow peaks at 465 and 395 nm and in a broad peak at 220 nm are shown in Fig. 6.

The PL spectra of KEMO under excitation of the Eu³⁺ (⁵L₆) level at λ_{ex} =395 nm show typical red emission features of Eu³⁺, including ⁵D₀ \rightarrow ⁷F_{*J*</sup> (*J* = 0, 1, 2, 3 and 4) transitions (Fig. 5b). The most intense peak in the region from 602 nm to 640 nm is due to the electric dipole transition ⁵D₀ \rightarrow ⁷F₂. A transition at 582–602 nm is the ⁵D₀ \rightarrow ⁷F₁ magnetic dipole transition. Decay curves of the Eu³⁺ emission of KEMO samples are presented in Fig. 7.}

Table 1	Crystallog	raphic data	a for	K₅Eu(MoO ₄)	1
Table T	Crystallog		101	115601	11004	14

Crystal data			
Sample preparationCzoCrystal systemMorSpace groupC2/r	Czochralski techniques at 1073 K Monoclinic <i>C2/m</i>		
Lattice parameters			
$a (\mathring{A})$ $b (\mathring{A})$ $c (\mathring{A})$ $\beta (deg.)$ $V (\mathring{A}^{3})$ Formula units, Z Color Density, g cm ⁻³	10.37099(5) 5.98542(3) 7.72496(4) 116.5836(5) 428.831(4) 1 White 3.82266(1)		
Data collection			
Diffractometer Radiation/wavelength $(\lambda, \text{ Å})$ 2θ range (°) Step scan (2θ) I_{max} Number of points	BL15XU beamline of SPring-8 Synchrotron/0.65298 2.041–61.831 0.003 439 989 19 916		
Refinement			
Refinement Background function	Rietveld Legendre polynomials,		
No. reflections (all/obs.) No. of refined parameters/refined atomic parameters	452/436 c 45/19		
R and $R_{\rm w}$ (%) for Bragg reflections $(R_{\rm all}/R_{\rm obs})$	9.83/9.27 and 12.93/12.84		
$R_{\rm P}; R_{\rm wp}; R_{\rm exp}$ Goodness of fit (ChiQ) Max./min. residual density (e Å ⁻³) CSD deposition number	3.30, 6.08, 1.14 5.32 3.09/-2.65 2114453		

4. Discussion

We prepared the KEMO by three methods (solid state, sol-gel and Czochralski techniques) and studied the influence of synthesis conditions on luminescence properties. The XRD powder study revealed that the KEMO structure is similar to that of other high temperature α -K₅R(MoO₄)₄ palmierite-type phases (SG $R\bar{3}m$).^{45–48}

Palmierite related compounds can be described with the general formula $M2^2M1^{[6+6]}(AO_4)_2$. The M1 and M2 cations in the palmierite-type structure are ordered in separate M2-layers and $[M1A_2O_8]$ -layers alternating along the *c*-axis of the rhombohedral cell (Fig. 8). Earlier, nine varieties of the palmierite-type structure were picked out for $M_5R(MOQ_4)_4$ (M = Rb, K, Tl; R = RE, Y, Bi, Fe, In) compounds.⁴⁵ However, this scheme was revised during the study of the $K_5Yb(MOQ_4)_4$ polymorph modification and an incommensurately modulated structure of β -phase was refined.^{46,49}

The majority of $M_5R(MOO_4)_4$ crystallize in the $R\bar{3}m$ symmetry similar to $K_2Pb(SO_4)_2$. R^{3+} and M^+ cations occupy the M1 sites in either an ordered or a statistical manner, while the M2 sites are occupied by M^+ cations only.^{46–51} Depending on elemental



Fig. 5 (a) Photoluminescence excitation ($\lambda_{em} = 613$ nm) spectra and an absorbance spectrum of K₅Eu(MoO₄)₄ crystal grown by the CZ technique as well as (b) photoluminescence emission ($\lambda_{ex} = 395$ nm) spectra of K₅Eu(MoO₄)₄ at T_R: sg893-KEMO (1), ss-KEMO (2) and the crushed crystal (3). All intensities of PLE spectra are normalized to the ⁷F₀ \rightarrow ⁵L₆ transition intensity of Eu³⁺. An inset shows a comparative integrated intensity of emission from the ⁵D₀ term. Electronic transitions for the main excitation and emission peaks are specified. Measurement conditions are observed the same for all samples.

content, the crystal structure is subjected to different distortions, which are mainly associated with the rotation of MoO_4^{2-} tetrahedra and R³⁺ and M⁺ cations ordering in the M1 sites. To formulate coordination polyhedra characteristic of each R³⁺ cation is possible due to flexibility of the tetrahedra in the palmierite-type structure. For example, ordering Yb³⁺ and K⁺ cations in the M1 sites decreases the symmetry of the palmieritetype structure from rhombohedral $R\bar{3}m$ for α -K₅Yb(MoO₄)₄ (KYbMO) to monoclinic C2/c for the γ -phase and to incommensurately modulated monoclinic $X2/m(0\beta0)00$ for the β -phase.^{46,49} In addition, a question of the real palmierite-type structure of some compounds and atoms ordering therein remains unanswered.47-48 Weak superstructure reflections with intensities from 1σ to 3σ were found in single crystal data. However, their small number did not allow to determine the true structure and atom coordinates in the structure were determined in the approximate $R\bar{3}m$ subcell.



Fig. 6 Temperature dependence of Eu³⁺ luminescence intensity (λ_{em} = 613 nm) of K₅Eu(MoO₄)₄ measured at λ_{ex} =220 nm (1), 395 nm (2) and 465 nm (3) for sg893-KEMO (a), ss-KEMO (b) and the crushed crystal grown by the CZ technique (c).

ac projections and [M1A₂O₈]-layers in the rhombohedral α -KYbMO and monoclinic C2/c γ -phase are presented in Fig. 8. The most pronounced difference between these two structures appears when cations ordering in the M1 positions are viewed in [M1A2O8]-layers along directions marked with lines I, II, and III in Fig. 8c and d. Being viewed along these directions, the M1 positions statistically occupied by K⁺ and Yb^{3+} (M1 = 0.5 K⁺ + 0.5Yb^{3+}) in the α -KYbMO structure appear to be uniformly spaced by \sim 6.04 Å as shown in Fig. 8c. In contrast to that, M1 alternation of columns along the I and II directions is different from the III direction due to cations ordering in the M1 positions in the γ -phase structure (Fig. 8d). Two K⁺ columns and two Yb³⁺ columns alternate along the I and II directions of $[M1A_2O_8]$ -layers in the γ -phase structure. There are pairs of the Yb³⁺ columns with the intercolumn distance of ~6.00 Å and pairs of the K⁺ columns separated by ~5.93 Å. The greatest intercolumn M1-M1 distance of \sim 6.18 Å is observed between the K⁺ and Yb³⁺ columns along the I and II directions. Unlike the I and II directions the K⁺ and Yb³⁺ columns with the intercolumn distances of \sim 5.99 Å and \sim 6.3 Å alternate along the III direction. This difference in K⁺ and Yb³⁺ cations ordering in the I, II, and III directions leads to the loss of a 3-fold axis.

Cation ordering in the $[M1A_2O_8]$ -layers leads to deformation of zig-zag M2-layers occupied by K⁺ cations in γ -KYbMO



Fig. 7 Decay curves of $K_5Eu(MoO_4)_4$ (λ_{ex} = 395 nm and λ_{em} = 620 nm) at room temperature for sg893-KEMO (a), ss-KEMO (b) and the crushed crystal grown by the CZ technique (c).

as compared to α -KYbMO. In the α -phase, six K⁺ cations form six-membered rings with K⁺–K⁺ distances of 3.65 Å. The K2layer can be represented as constructed from these rings (Fig. S6a of the ESI[†]). Similar K⁺-rings can be selected in the γ -phase with K⁺–K⁺ distances in the range from 3.54 Å to 3.99 Å (Fig. S6b of the ESI[†]). K1 and Yb1 ordering in the [M1A₂O₈]layers and the rotation of MoO₄²⁻ tetrahedral in the γ -phase lead to a change of M1O₁₂ polyhedra in the palmierite-type structure from (K,Yb)O₁₂ for the α -phase (Fig. S6c of the ESI[†]) to K1O₁₀ and Yb1O₆ (Fig. S6d of the ESI[†]).

Aperiodic ordering of K1 and Yb1 in M1 positions in the β -KYbMO structure along *ab* direction results in different oxygen environments for K1 (the first coordination sphere) and induces rotation and displacement of the MoO₄ tetrahedra. The second coordination sphere for K1 and Yb1 in the β -phase structure can be represented as two types of cubic clusters [K1Mo₆K2₂] and [Yb1Mo₆K2₂].^{49,52} An oxygen polyhedron for K1 depends on a ratio between surrounding [K1Mo₆K2₂] and [Yb1Mo₆K2₂] clusters (the third coordination sphere) and a coordination number for K1 varies from 8 to 12.

A superspace approach based method was presented in order to create a family of modular structures from a single incommensurately modulated structure.⁵² Established on the incommensurately modulated structure of the β -KYbMO and on a variation of the modulation vector **q** they predicted for K₅R(MoO₄)₄ compounds the generation of the palmierite-type phases with a superspace group $C2/m(0\beta 0)00$ and a modulation vector **q** = 2/3**b***. Contrary to the powder XRD (Fig. S1b of the ESI†), the electron diffraction study has revealed that the KEMO crystal grown by the CZ technique had a (3 + 1)D incommensurately modulated structure with (3 + 1)D SSG $C2/m(0\beta0)00$ and a modulation vector $\mathbf{q} = 0.689\mathbf{b}^*$ (Fig. 2). Thus, this confirmed a prediction made earlier by Arakcheeva and Chapuis.⁵² Moreover, a detailed analysis of satellite reflections located on the [103] ED pattern has shown the formation of three twinned domains rotated along the *c* axis of the *R*-subcell at 60° with respect to each other.

Fig. 3a shows a [103] ED pattern of KEMO which is a superposition of three [103] ED patterns of KEMO twinned domains rotated along the *c* axis of the *R*-subcell at 60° with respect to each other. These domains are formed due to the loss of the 3-fold axis as a result of monoclinic distortion of the rhombohedral sublattice. An insignificant deviation of the monoclinic supercell from the *R*-subcell, positions of the main reflections are not different for the domains after rotation by 60° (within limited resolution on the ED patterns). The schematic drawing is shown in Fig. 3.

It should be noted, that only satellite reflections allow to detect the monoclinic distortion of the rhombohedral sublattice and formation of twins in the crystal. As a consequence of an insignificant difference in the a/c ratio of the unit cell parameters (Table 1) from $\sqrt{3}$ (*a*/*c* = 1.73271; $\sqrt{3}$ = 1.73205), positions of the main reflections on the [103] ED pattern are (within limited resolution on the SAED patterns) not different from those for the domains after rotation by 60° (Fig. 3). The black rectangles in Fig. 3a based on the main reflections for the three domains clearly show rotation of the domains by 60°. These domains are formed due to the loss of the 3-fold axis as а result of the monoclinic distortion of the R-sublattice.

The KEMO average structure was refined in the SG C2/m with random distribution of K1 and Eu1 in the [M1A₂O₈]layers due to an insufficient number of additional reflections, their low intensity and large width in the synchrotron X-ray diffraction patterns. Fig. 9 shows *ac* projection, K-layer and (K,Eu)O₈ polyhedron in the KEMO structure. Six-membered rings in K2-layers in the KEMO structure are significantly less distorted than the ones in the γ -KYbMO structure and K⁺-K⁺ distances vary from 3.25 Å to 3.86 Å (Fig. 9b). The coordination number for K1 and Eu1 is 8 (Fig. 9c).

PLE spectra of Eu³⁺ emission show a set of narrow peaks in the 310–550 nm region, which arise due to intraconfigurational 4f⁶–4f⁶ transitions in Eu³⁺, and a broad nonelementary band in the region from 170 to 310 nm (Fig. 5a). The most intense Eu³⁺ 4f–4f excitation peak is attributed to $a^7F_0 \rightarrow {}^5L_6$ transition (Fig. 5a). Corresponding PL spectra of KEMO under excitations at 395 nm are shown in Fig. 5b. They demonstrate typical red emissions of Eu³⁺, caused by different ${}^5D_0 \rightarrow {}^7F_J (J = 0-4)$ transitions.

Based on an optical absorption spectrum measured for a KEMO crystal grown by the CZ technique, an optical band gap of the compound is estimated as low as 3.88 eV (320 nm). Therefore, a broad excitation band in the region of



Fig. 8 ac projections (a and b) and [M1A₂O₈]-layers (c and d) in the rhombohedral α -K₅Yb(MoO₄)₄ (a and c) and monoclinic γ -phase (b and d).

170-300 nm and a less intensive separated peak at ~155 nm correspond to the region of fundamental absorption of KEMO. The broad excitation band consists of at least three sub-bands with maxima approximately at 260, 220 and 185 nm. These bands are tentatively attributed to electron transitions within the MoO₄²⁻ groups from 2p O²⁻ states forming the top of a valence band to 4d Mo⁶⁺ states in a conduction band. The observation of the 2p O \rightarrow 4f Eu charge transfer bands is supposed to be less probable due to enveloping 4f Eu states by the conduction band. The excitation at wavelengths shorter than 330 nm is essentially related to the region of the fundamental absorption, where processes of energy relaxation are different from the case of intracenter 4f-4f excitation of Eu³⁺ ions. An intensity ratio of the bands related to the intracenter Eu³⁺ excitation and the fundamental excitation band depended on the synthesis technique (Fig. 5a).

Direct excitation of Eu^{3+} is more efficient than the energy transfer from a matrix at T_R for ss-KEMO and especially for the KEMO crystal grown by the CZ technique. A similar phenomenon has also been observed in $KTb(MoO_4)_4$:Eu.³⁴ As it has been shown in ref. 34, the relative intensity under excitation in the fundamental region depends on particles size as well as on the concentration of structural defects in a sample, both defining non-radiative energy losses in the material. An intensity ratio between bands related to intracenter and inter band transitions is also temperature dependent (Fig. 6). The intensity of Eu³⁺ emission under intra center excitation at 395 nm (Eu^{3+ 7}F₀-⁵L₆ transitions) and 465 nm (Eu^{3+ 7}F₀-⁵D₂) transitions) remains at the same level up to 400 K for ss-KEMO and the crystal. At higher temperatures, a decrease of intensity is detected, which is related to an intracenter quenching process. A completely different behavior was observed under excitation at 220 nm. The Eu³⁺ emission intensity decreases exponentially in the whole temperature region. As a result, the intensity is by two orders of magnitude lower at 500 K in comparison to that at 80 K. Such behavior implies that energy transfer from the host to Eu³⁺ occurs via some intermediate state whose stability depends strongly on temperature. Self-trapped excitations created from separated electrons and holes may serve as such intermediate state. For the sg-KEMO sample (Fig. 6a) the emission intensity gradually decreases even at intracenter excitation in contrast to ss-KEMO and the crushed crystal. Such behavior reveals the worst quality of sg-KEMO compared to other samples and implies the presence of defects which intercept energy from Eu³⁺ centers.

Fig. 5b shows PL spectra of KEMO under excitation at 395 nm. Characteristic red emission of Eu³⁺ ion, caused by ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 0-4) transitions, is observed. The brightest emission was detected for KEMO crushed crystal, while the lowest



Fig. 9 A ac projection (a), a K-layer (b) and a (K,Eu)O_8 (c) polyhedron in the $K_5Eu(MoO_4)_4$ structure.

intensity was recorded for KEMO prepared by a sol-gel method. Integrated intensity of emission from the ⁵D₀ term for KEMO crushed crystal is twice that of sg893-KEMO. A quantum yield for the KEMO samples was measured and listed in Table S6 of the ESI.[†] For all studied KEMO samples, the shapes of emission spectra are almost identical. The number and positions of the peaks do not change, but there is a alternate in their relative intensity. The structure of the Eu³⁺ spectra responds to the symmetry of a site. Based on the data presented, there are no changes in the structure of the spectrum, which indicates that the synthesis method does not affect the local environment of luminescent ions. It is worth noting that the Eu³⁺ emission lines are rather broad though the spectra were measured with a relatively high spectral resolution 0.3 nm. The observed broadening is connected with the statistical distribution of K^{+} and Eu^{3+} ions in the M1 sites. The latter leads to a different surrounding of Eu³⁺ ions in the second coordination sphere, thus inducing a variety of Eu³⁺ centers with slightly different energies of ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 0-4) transitions and due to that slightly different positions of their spectral lines.

The palmierite-type structures with a trigonal symmetry (SG $R\bar{3}m$) have D_{3d} as 3D point group while monoclinic distortion leads to changing 3D point symmetry to C_{2h} . As a result, Eu³⁺ cations occupy a site with at most C_2 site symmetry. The ${}^5D_0 \rightarrow {}^7F_2$ transition is hypersensitive to the local environment of Eu³⁺ ions, and its efficiency depends crucially on the local symmetry of Eu³⁺ ions in the host. Emission bands in the range of 602–639 nm, which are related to the ${}^5D_0 \rightarrow {}^7F_2$ forced electric dipole transition are most intensive in KEMO (Fig. 5b). This indicates that there is no inversion center in the site symmetry of the Eu³⁺ position.⁵³ This also confirms a relatively low Eu³⁺ site symmetry established by structural data.

In contrast to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ magnetic dipole transition in the range of 582–602 nm is independent of the host and its intensity is hardly affected by the environment of Eu³⁺ ions. The crystal-field effect leads to the split of the ${}^{7}F_{J}$ energy levels into at most 2J + 1 sublevels (or Stark levels). As a consequence, the ${}^{5}D_{0} - {}^{7}F_{1}/{}^{5}D_{0} - {}^{7}F_{1}$ ratio is often referred to as the asymmetry ratio (R/O (red/orange)).⁵⁴ R/O characterizes a measure of environment disordering around Eu³⁺ ions and allows to assess the covalent nature and polarization of the Eu³⁺ surrounding. For KEMO samples, the values for this ratio vary from 4.03 to 4.34 (Table S6 of the ESI[†]) which is close to the previously found about 5 times.²⁹

The ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition accountable for the appearance of an emission line at 578 nm deserves special attention. Since this transition is forbidden both for electric and magnetic dipole interactions, the intensity of corresponding emission can be very low or even non-observable. Yet, for the C_2 symmetry, the transition is induced, so the emission line can be expected to appear. As splitting of excited and ground levels, both characterized by J = 0, is not possible, the observation of more than one transition could be an indication of the presence of more than one non-equivalent site for the luminescent Eu³⁺ ions. For all samples, only one peak related to the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transitions was observed in the PL spectra (Fig. S7 and Table S6 of the ESI[†]). Thus, the local environment of the Eu³⁺ ions remains the same and does not depend on the synthesis technique. Manifestation of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition in the PL spectra confirms a monoclinic distortion of the KEMO structure and the location of Eu³⁺ ions in sites with symmetry lower than D_{3d} (SG $R\bar{3}m$). Earlier, an assumption of symmetry lower than D_{3d} for Eu³⁺ ions sites was made in the study of the luminescent properties of K5Eu(MoO4)4 and K5Bi1-xEux(MoO4)4 crystals.^{29,31,32} In addition, the splitting of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition is clearly observed under excitation at 578 nm in the PL spectra for K₅Bi_{1-x}Eu_x(MoO₄)₄ crystals.^{31,32}

In order to verify the application of KEMO as near-UV converting phosphor applied as red-emitting components for LEDs a device was fabricated using 405 nm InGaN chip (Fig. 10a, switched off) with a KEMO crystal plate. Fig. 10b



Fig. 10 Images of LED devices using 404 nm UV LED chip combined with $K_5Eu(MoO_4)_4$ phosphor switched off (a) and switched on (b). EL spectra (c) and CIE coordinates (d) of the fabricated LED device.

shows an actual emission of corresponding red LEDs on a 404 nm chip (switched on). Fig. 10c exhibits that resulting EL spectra and a strong red emission can obviously be observed. CCT and CIE chromaticity coordinates are 2411 K and (0.6078, 0.3337), respectively (Fig. 10d). The obtained results show that KEMO phosphor is close to red standard (0.666, 0.333), and the LED device had a low CCT.

Decay profiles of ${}^{5}D_{0}$ – emission of all samples at T_{R} are shown in Fig. 7. The ss-KEMO and crushed crystal samples show a monoexponential decay, which can be fitted using the expression $I(t) = I_{0} \exp(-t/\tau)$ with decay constants of $\tau = 1.433$ ms and 1.473 ms, respectively (Table S6 of the ESI†). The calculated value of the lifetime of ${}^{5}D_{0}$ state is close to that previously obtained for the KEMO crystal grown by slow cooling (10 K h⁻¹) from 1073 K ($\tau = 1.4$ ms).³⁰ A light increase of ${}^{5}D_{0}$ lifetime from 1.1 to 1.4 µs with Eu³⁺ concentration together with a single exponential character of decays was found for K₅Bi_{1-x}Eu_x(MoO₄)₄ crystals grown by the Czochralski method.^{31,32} Lifetime behavior suggests the presence of a fast energy transfer between Eu³⁺ ions.

For the sg893-KEMO sample, decay time of the main component is shorter, $\tau = 1.282$ ms, and even a shorter component appears with $\tau = 0.099$ ms. The appearance of a fast component and shortening of decay time of the main component indicates a quenching process, which can be attributed to higher concentrations of structural defects in the sample grown by the sol-gel method.

5. Conclusion

We have synthesized $K_5Eu(MOO_4)_4$ by three methods and investigated the influence of preparation techniques on compound structure and luminescent properties. We have shown that additional structural features, namely (3 + 1)D incommensurate structural modulations, can be detected by electron diffraction using a crystal grown by the CZ technique. Powder X-ray diffraction techniques giving an average picture are not so sensitive even in the case of state-of-the-art synchrotron diffraction. Crystals grown by the CZ technique demonstrated maximum values of integrated emission intensities of the $Eu^{3+5}D_0 \rightarrow {}^7F_2$ transition among all studied samples, in addition to a very high quantum yield value reaching 66.5%. These facts confirm that $K_5Eu(MoO_4)_4$ crystals are entirely engaging as near-UV converting phosphors applied as red-emitting components for LEDs.

Conflicts of interest

There are no conflicts to declare.

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