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Influence of annealing conditions on the structure and luminescence properties of $KGd_{1-x}Eu_x(MoO_4)_2$ ($0 \le x \le 1$)†

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This study describes the influence of annealing temperature on the structure and luminescence properties of KGd_{1-x}Eu_x(MoO₄)₂ (0 $\leq x \leq$ 1). Compounds with the general formula (A', A'')_n[(W, Mo)O₄]_m are investigated as luminescent materials for photonic applications such as phosphor-converted LEDs (light-emitting diodes). Herein, the KGd_{0.8}Eu_{0.2}(MoO₄)₂ light-rose crystal was grown by the Czochralski technique. Moreover, three polymorphs of $KGd_{1-x}Eu_x(MoO_4)_2$ were present in the 923–1223 K range of annealing temperatures under ambient pressure: a triclinic α -phase, a disproportionately modulated monoclinic β -phase and an orthorhombic γ -phase with a KY(MoO₄)₂-type structure. The different behaviors of KGd(MoO₄)₂ and $KEu(MoO_d)_2$ were revealed by DSC studies. The number and the character of phase transitions for KGd1-xEux(MoO4)2 depended on the elemental composition. The formation of a continuous range of solid solutions with the triclinic α -KEu(MoO₄)₂-type structure and ordering of K⁺ and Eu³⁺/Gd³⁺ cations were observed only for α -KGd_{1-x}Eu_x(MoO₄)₂ (0 \leq x \leq 1) prepared at 923 K. The structures of γ -KGd_{1-x}Eu_x(MoO₄)₂ (x = 0 and 0.2) were studied using electron diffraction and refined using the powder X-ray diffraction data. The luminescence properties of $KGd_{1-x}Eu_x(MoO_4)_2$ prepared at different annealing temperatures were studied and related to their different structures. The maxima of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ integral emission intensities were found under excitation at λ_{ex} = 300 nm and λ_{ex} = 395 nm for triclinic scheelitetype α -KGd_{0.6}Eu_{0.4}(MoO₄)₂ and monoclinic scheelite-type β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ prepared at 1173 K, respectively. The latter shows the brightest red light emission among the $KGd_{1-x}Eu_x(MOO_4)_2$ phosphors. The maximum and integral emission intensity of β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ in the ⁵D₀ \rightarrow ⁷F₂ transition region is ~20% higher than that of the commercially used red phosphor $Gd_2O_2S:Eu^{3+}$. Thus, β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ is very attractive for application as a near-UV convertible red-emitting phosphor for LEDs.

1. Introduction

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Light-emitting diodes (LEDs) are solid-state light (SSL) sources with the ability to efficiently and directly convert electricity into light. They are low-cost materials, have high

electro-optical conversion efficiencies, are stable and reliable,¹ and have transformed the lighting industry into a rapidly growing business sector.² White light-emitting diodes (WLEDs) have replaced incandescent and fluorescent lamps and are used as backlights for portable electronics and

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[†] Electronic supplementary information (ESI) available: The photos of the KGd_{0.8}Eu_{0.2}(MoO₄)₂ crystal grown by Czochralski technique under the daily light and under the excitation (~395 nm). EDX analysis results of KGd_{1-x}Eu_x(MoO₄)₂ (x = 0.2, 0.4, 0.5) (Table S1). SEM images of KEu(MoO₄)₂ prepared at 923 K (a) and KR(MoO₄)₂ (R = Eu (b), Gd (c)) prepared at 1223 K (Fig. S2). Unit cell parameters for KGd_{1-x}Eu_x(MoO₄)₂ ($0 \le x \le 1$) solid solutions prepared by heating at 923 K as determined from XRD patterns (S.G. $P\overline{1}, Z = 2$) (Table S2). Unit cell parameters for KGd_{1-x}Eu_x(MoO₄)₂ ($0 \le x \le 1$) prepared at 1073 K as determined from XRD patterns (Table S3). Parts of XRD patterns of KGd_{1-x}Eu_x(MoO₄)₂ ($0.7 \le x \le 1$) annealed at 1073 K (Fig. S1). Unit cell parameters for KGd_{1-x}Eu_x(MoO₄)₂ ($0 \le x \le 1$) main phases) prepared at 1173 K as determined from XRD patterns (Table S4). Parts of XRD patterns of KGd_{1-x}Eu_x(MoO₄)₂ ($0 \le x \le 1$, main phases) prepared at 1223 K as determined from XRD patterns (Table S5). Fractional atomic coordinates, site symmetry, isotropic displacement atomic parameters (U_{iso}) and site occupation for KGd_{1-x}Eu_x(MoO₄)₂ (x = 0, 0.2) (Table S6). Selected distances (Å) in KGd_{1-x}Eu_x(MoO₄)₂ (x = 0, 0.2) (Table S7). PLE ($\lambda_{em} = 610-625$ nm) spectra at room temperature of KGd_{1-x}Eu_x(MoO₄)₂ ($0.1 \le x \le 1$) prepared at 1173 K and 1223 K (Fig. S3). PL ($\lambda_{ex} = 395$ nm) spectra at room temperature of KGd_{1-x}Eu_x(MOO₄)₂ ($0.1 \le x \le 1$) prepared at 1173 K and 1223 K (Fig. S4). See DOI: 10.1039/c9ce01244c

medical and architectural lightings.⁶ In the current commercial WLEDs, (In,Ga)N double-heterostructure devices are used, whose development by Nakamura *et al.*³⁻⁵ was a landmark achievement in the field of SSL.

Many Eu³⁺-containing luminescent materials with various crystal structures have been investigated for their potential application as red luminescent materials in WLEDs.⁷ Eu³⁺-Doped compounds with the scheelite-type ($CaWO_4$) structure are often proposed as potential red-phosphors for WLEDs.⁸⁻¹³ The scheelite-type ABO₄ structures consist of [...-AO₈-BO₄- \dots] columns parallel to the *c*-axis. The AO₈ polyhedra and BO₄ tetrahedra share vertices and combine into a 3D framework. A partial substitution is possible for the A and/or B cations to achieve the composition $(A', A'')_n [(B', B'')O_4]_m (A', A'' =$ alkali, alkaline-earth or rare-earth elements; B', B" = Mo, W). Many of the resulting compounds have good optical properties and stability and are relatively simple to prepare. $KR(MoO_4)_2$ compounds can be divided into two groups: the scheelite-type modifications¹⁴⁻²⁴ and the non-scheelite modifications with the KY(MoO₄)₂-type structure (SG Pbcn).^{25,26} There are three groups of scheelite-type modifications: 1) tetragonal or monoclinic distortion phases with a random distribution of K^+ and R^{3+} cations;^{14–18} 2) triclinic α -phases^{19–22} with the α -KEu(MoO₄)₂ structure (space group P1) and ordered K^+ and R^{3+} up to $R = Dy;^{21}$ and 3) monoclinic, disproportionately modulated β -phases (superspace group I2/ $b(\alpha\beta 0)00)$ with complete^{22,23} or partial²⁴ ordering of the K⁺ and R³⁺ cations.

We have provided a summary of the crystal structures of all $(A',A'')_{1-x}BO_4$ (B = Mo, W) scheelites in a previous study and demonstrated that the A-site cation ordering depends on the difference r(A') - r(A'') between the ionic radii of the A-cations.²⁷ In the case of KR(MoO₄)₂ (R = La (ref. 14)–Ce (ref. 15 and 16)), there is a random distribution of K⁺ and R³⁺. An increase in $\Delta r = r(K) - r(R)$ from 0.367 Å (R = Ce) to 0.401 Å (R = Nd) results in an ordered distribution of K⁺ and R³⁺ and disproportionately modulated structures for R = Nd–Eu. For even higher Δr , from 0.483 Å (Dy) to 0.491 Å (Y), the resulting structures are of the non-scheelite KY(MoO₄)₂-type.^{25,26} Thus, it appears that the scheelite-type structure occurs only for r(A') - r(A'') < 0.49 Å.

The schematic of the KR(MoO₄)₂ structure types was first reported in ref. 28. However, it is already outdated and requires revision and addition. Previously, we have confirmed the data about the α - and β -phases of KEu(MoO₄)₂ (ref. 21) and revealed the influence of different orderings of the K⁺ and Eu³⁺ cations on the luminescence properties of KEu(MoO₄)₂. Contrary to the study reported by Klevtsov *et al.*, the formation of the orthorhombic γ -KEu(MoO₄)₂ phase with the KY(MoO₄)₂-type structure was not observed.²⁹ For KGd(MoO₄)₂, we have revealed a triclinic α -phase with the α -KEu(MoO₄)₂ structure and a non-scheelite orthorhombic γ -phase with the KY(MoO₄)₂-type structure.^{29,30}

In this study, we revealed the influence of annealing temperature on the structure and luminescence properties of $KGd_{1-x}Eu_x(MoO_4)_2$ ($0 \le x \le 1$).

2. Experimental

2.1. Materials and sample preparation

The low-temperature (LT) α -modifications of KGd_{1-x}Eu_x-(MoO₄)₂ ($0 \le x \le 1$) solid solutions were conducted using Gd₂O₃ (99.99%), Eu₂O₃ (99.99%), K₂CO₃ (99.99%) and MoO₃ (99.99%) in stoichiometric amounts by a routine ceramic technique in an alumina crucible at 923 ± 10 K for 30 h in air followed by slow cooling in a furnace from 923 K to room temperature ($T_{\rm R} = 300$ K). The α -KGd_{1-x}Eu_x(MoO₄)₂ (KGEMO) solid solutions were successively annealed at different temperatures (1073 K, 1173 K and 1223 K) for 12 h in air followed by slow cooling in the furnace to $T_{\rm R}$. The annealing temperatures were chosen based on the differential scanning calorimetry studies.

The polycrystalline materials used for the KGd_{0.8}Eu_{0.2}- $(MoO_4)_2$ single crystal growth were prepared by a solid-state reaction. A stoichiometric mixture of raw materials (K₂CO₃, Gd_2O_3 (spectroscopically pure \geq 99.995%), Eu_2O_3 (spectroscopically pure \geq 99.995%) and MoO₃) was placed in a Pt crucible and annealed at 773-823 K for 15 h to decompose the carbonate. Then, the annealed mixture was ground, mixed again and heated at 1173 K for 15 h in air. The synthesized polycrystalline material $KGd_{0.8}Eu_{0.2}(MoO_4)_2$ was melted in a $40 \times 40 \text{ mm}^2$ diameter platinum crucible using a 17 kHz frequency induction furnace. A small non-oriented KGd_{0.8}Eu_{0.2}(MoO₄)₂ single crystal bar was used as a seed. The growth temperature was accurately determined by repeated seeding trials. A $KGd_{0.8}Eu_{0.2}(MoO_4)_2$ light-rose crystal of up to 10 mm diameter and 10 mm length was grown at 1373 K by the Czochralski (CZ) technique at the pulling rate of 1 mm h⁻¹ and rotating rate of 50-100 rpm under a slightly oxidizing atmosphere. The images of the KGd_{0.8}Eu_{0.2}(MoO₄)₂ crystal grown by the Czochralski technique under daylight and under excitation (~395 nm) are shown in the ESI† Fig. S1.

2.2. Characterization

The cation composition of the KGEMO (x = 0.2, 0.4, and 0.5) samples was determined by energy-dispersive X-ray spectrometry (EDX) using the Jeol JSM-6490LV scanning electron microscope (SEM) equipped with an EDX spectrometer (Oxford Instruments). The ESI† Fig. S2 shows the SEM images of some KGEMO samples.

Powder X-ray diffraction (XRD) patterns for phase determination were obtained using the Thermo ARL X'TRA powder diffractometer (CuK α radiation, $\lambda = 1.5418$ Å, Bragg–Brentano geometry, and the Peltier-cooled CCD detector). The XRD data were obtained at $T_{\rm R}$ over the 2θ range of 5–70° with the steps of 0.02°. To determine lattice parameters, the Le Bail decomposition³¹ was applied using the JANA2006 software.³²

Powder XRD patterns for KGEMO (x = 0 and 0.2) crystal structure determination were obtained using the STADI-P diffractometer (CoK_{α 1} radiation, curved Ge monochromator, transmission mode, and linear PSD). The XRD data were obtained at $T_{\rm R}$ over the 2θ range of 5–100° with a step of

0.01°. Moreover, Rietveld refinements were performed using the JANA2006 software. $^{\rm 32}$

Selected area electron diffraction (ED) patterns were obtained using the Tecnai G^2 transmission electron microscope operating at 200 kV. For the electron diffraction samples, the powder was crushed in an agate mortar and dispersed in methanol. The crystallites were dispersed using an ultrasonic bath, and a few drops of the solution were dropcast on a copper grid with a holey carbon film.

Differential scanning calorimetry (DSC) and thermogravimetry (TG) studies for KR(MoO₄)₂ (R = Gd and Eu) were performed using the NETZSCH STA Jupiter 449 simultaneous thermal analyzer at 303–1273 and 1273–673 K (heating/cooling at the rate of 3 K min⁻¹) in air. The sample weight was ~30 mg. The samples were placed in Pt crucibles with lids.

Photoluminescence emission and photoluminescence excitation spectra were obtained using the Lot-Oriel MS-257 spectrograph equipped with the Marconi CCD detector and a 150 W Xe arc lamp as an excitation source. The powder samples were placed in an optical cryostat, Cryotrade LM-120. The photoluminescence spectra of all samples were obtained under similar experimental conditions to compare the relative emission intensities and reduce the error. All measurements were performed at 80 K and 300 K, and the obtained spectra were corrected for the sensitivity of the spectrometer. Polycrystalline α -KEu(MoO₄)₂ was used as a reference. The luminescence intensity maximum (I_{max}) and integral emission intensities (I_{int}) of α -KEu(MoO₄)₂ in the region of the ⁵D₀ \rightarrow $^{7}F_{2}$ transition were taken as 100%, and the luminescence intensities of the other samples were normalized to the former.

3. Results and discussion

3.1. Elemental composition

EDX analysis of the KGEMO (x = 0.2, 0.4, and 0.5) samples was performed at 15 points for each sample. Using SEM-EDX, the Gd:Eu ratios in the KGEMO (x = 0.2, 0.4, and 0.5) samples were found to be 0.82(1):0.18(1), 0.61(1):0.39(1) and 0.51(2):0.49(2), respectively, close to the expected composition. The results of the EDX analysis are summarized in Table S1 of the ESL[†]

3.2. XRD characterization

The XRD patterns of KGEMO ($0 \le x \le 1$) prepared at different annealing temperatures are shown in Fig. 1 and 2 and the ESI† Fig. S3 and S4. The results of the XRD phase analysis of KGEMO prepared at different temperatures are listed in Table 1. The XRD patterns of the solid solutions of KGEMO prepared at 923 K are similar to those of triclinic $P\bar{1}$ α -KEu(MoO₄)₂.²¹ The unit cell parameters of the α -KGEMO phases were determined using the Le Bail decomposition of the XRD patterns in the $P\bar{1}$ space group (ESI† Table S2). The substitution of Gd³⁺ ($r_{VIII} = 1.053$ Å (ref. 33)) by Eu³⁺ ($r_{VIII} =$ 1.066 Å (ref. 33)) increased the unit cell volume.



Fig. 1 Parts of the powder XRD patterns of $KGd_{1-x}Eu_x(MoO_4)_2$ solid solutions prepared at 923 K.

An increase in the calcination temperature from 923 to 1073 K did not completely transform α -KGEMO ($0 \le x \le 0.9$) into the monoclinic β -form with a disproportionately modulated structure, contrary to the case of pure KEu(MoO₄)₂ (Fig. S3 of ESI†). A mixture of KGEMO solid solutions with the α -triclinic and β -monoclinic *12/b*($\alpha\beta$ 0)00 structures was formed in the case of x = 0.8–0.9, whereas the XRD patterns for $0 \le x \le 0.7$ practically did not change (Table 1 and Fig. S3



Fig. 2 Parts of the powder XRD patterns of $\mathsf{KGd}_{1-x}\mathsf{Eu}_x(\mathsf{MoO}_4)_2$ annealed at 1223 K.

Table 1 Results of the XRD phase analysis of $KGd_{1-x}Eu_x(MoO_4)_2$ ($0 \le x \le 1$) solid solutions prepared at different temperatures followed by slow cooling

x	923 K	1073 K	1173 K	1223 K
0	α-Phase	α-Phase	γ-Phase ^c	γ-Phase
			$+\alpha$ -Phase (t)	$+\alpha$ -Phase (t)
0.1	α-Phase	α-Phase	γ-Phase	γ-Phase
			$+\alpha$ -Phase (t)	$+\alpha$ -Phase (t)
0.2	α-Phase	α-Phase	γ-Phase	γ-Phase
			$+\alpha$ -Phase (t)	$+\alpha$ -Phase (t)
			+ β -Phase (t)	
0.30	α-Phase	α-Phase	γ-Phase	γ-Phase
			+β-Phase	+ α -Phase (t)
			$+\alpha$ -Phase (t)	
0.40	α-Phase	α-Phase	β-Phase	γ-Phase
			+α-Phase (t)	$+\alpha$ -Phase (t)
			$+\gamma$ -Phase (t)	+ β -Phase (t)
0.50	α-Phase	α-Phase	β-Phase	α-Phase
			+α-Phase (t)	+y-Phase (t)
			+γ-Phase (t)	, ()
0.60	α-Phase	α-Phase	β-Phase	α-Phase
			,	+β-Phase (t)
0.70	α-Phase	α-Phase	β-Phase	α-Phase
			,	+B-Phase (t)
0.80	α-Phase	α-Phase	β-Phase	β-Phase
		+β-Phase (t)	,	1
0.90	α-Phase	α-Phase	β-Phase	β-Phase
		+β-Phase	P	I
1	α -Phase ^a	β-Phase ^b	β-Phase	β-Phase
		1	1	1

^{*a*} Triclinic α-phase (SG $P\overline{1}$). ^{*b*} β-Phase with the disproportionately modulated structure (SSG *I2/b*(αβ0)00). ^{*c*} Orthorhombic γ-phase (SG *Pbcn*). The main phase in the mixture is shown first in bold. (t) means traces.

of the ESI[†]). The phase transition from the triclinic 3D structure of $\text{KEu}(\text{MoO}_4)_2$ to a monoclinic (3 + 1)D structure decreased the unit cell volume (Table S3 of ESI[†]).

A further increase in the treatment temperature did not lead to the formation of a continuous range of solid solutions with the same structure as observed for the α -phases prepared at 923 K (Table 1). An increase in the annealing temperature from 1073 to 1173 K resulted in monoclinic β -KGEMO for x = 0.4-1, and the transformation of α -KGEMO to the orthorhombic γ -phase occurred for $0 \le x \le 0.3$ (Fig. S4 of ESI[†]). The transformation from the triclinic scheelite-type α -phase to the orthorhombic KY(MoO₄)₂-type γ -phase resulted in an increase (~8%) in the unit cell volume (V/Z) for $KGd(MoO_4)_2$ (Table S2–S5 of ESI[†]). When the annealing temperature was increased from 1173 to 1223 K, the interval of the existence of pure β -phase decreased from $0.6 \le x \le 1$ to $0.8 \le x \le 1$, whereas the range of the γ -phase increased from $0 \le x \le 0.3$ to $0 \le x \le 0.4$ (Fig. 2). In addition, the α -phase was the main phase in the range of $0.5 \le x \le 0.7$.

Thus, the following four intervals of *x* can be selected for the annealing of KGEMO phases in the temperature range from 923 K to 1223 K followed by slow cooling to room temperature: 1) $0 \le x \le 0.3$ with the reversible $\alpha \leftrightarrow \gamma$ phase transition; 2) x = 0.4 with two non-reversible $\alpha \rightarrow \beta \rightarrow \gamma$ phase transitions; 3) $0.5 \le x \le 0.7$ with the $\alpha \rightarrow \beta \rightarrow \alpha$ transformations; and 4) $0.8 \le x \le 1$ with the irreversible $\alpha \to \beta$ phase transition. The $\alpha \to \beta \to \alpha$ transformation for $0.4 \le x \le 0.7$ apparently occurs through the formation of the γ -phase, which transforms to the α -phase upon slow cooling. Perhaps, the γ -phases for $0.4 \le x \le 0.7$ can be synthesized *via* quenching from high temperature to room or liquid nitrogen temperatures.

3.3. DSC study

Fig. 3 shows the fragments of the DSC curves for KGd(MoO₄)₂ and KEu(MoO₄)₂ in a heating-cooling cycle obtained at the heating/cooling rate of 3 K min⁻¹. The heating/cooling DSC curves for KEu(MoO₄)₂ indicate the presence of only one peak at the temperatures of 1250 and 1230 K (Fig. 3a). The peak of the heating DSC *versus T* curve indicates an endothermic first-order phase transition and corresponds to melting (T_{mel} . = 1273 ± 10 K (ref. 19)), whereas the exothermic effect with $T_{max} \sim 1230$ K can be associated with the crystallization of KEu(MoO₄)₂ at 1073 K followed by slow cooling transforms the triclinic α -phase into the monoclinic β -phase with a disproportionately modulated structure (Fig. S3 of the ESI†). Thus, the $\alpha \rightarrow \beta$ phase transition is a second-order phase transition and not reversible.

Compared with the case of KEu(MoO₄)₂, the DSC heating curve of KGd(MoO₄)₂ exhibits three peaks: 1) a wide peak at $T_{\rm min} \sim 1073$ K, 2) a peak at $T_{\rm min} \sim 1259$ K and 3) a peak at $T_{\rm min} \sim 1271$ K (Fig. 3b). The three minima on the DSC



Fig. 3 Fragments of DSC curves for $KEu(MoO_4)_2$ (a) and $KGd(MoO_4)_2$ (b) in a successive cycle: (1) heating and (2) cooling.

heating curve indicate endothermic first-order phase transitions in KGd(MoO₄)₂. The last minimum at ~1271 K can be associated with the melting of KGd(MoO₄)₂. According to the XRD study, the wide peak at $T_{\rm min} \sim 1073$ K corresponds to the transition from the triclinic α -phase to the orthorhombic γ -phase. The cooling curve also shows only two maxima, characterizing the exothermic first-order phase transitions. The first maximum at 1230 K corresponds to the crystallization of $KGd(MoO_4)_2$, whereas that at 1090 K corresponds to the partial transition from the γ -phase to the α -phase. Compared with the $\alpha \rightarrow \beta$ phase transition, the $\alpha \leftrightarrow \gamma$ phase transition is reversible. In literature, the triclinic α -KGd(MoO₄)₂ single crystal has been grown by heating at 1173 K followed by a very complex step-by-step cooling process: slow cooling from 1173 K to 973 K at the rate of 4 K h^{-1} ; heating at 973 K for 20 h; slow cooling from 973 K to 873 K at the rate 2 K h^{-1} , followed by quenching to $T_{\rm R}$.²⁰ Thus, the transformation from the orthorhombic γ -phase to the triclinic α -KGd(MoO₄)₂ phase is kinetic in nature. The γ : α ratio in the mixture depends on the elemental composition (x) and annealing temperatures (Table 1 and Fig. S3 and S4 of the ESI[†]).

3.4. Electron diffraction study

Fig. 4 shows the representative [100], [010], [001] and [$\overline{1}$ 10] ED patterns of orthorhombic γ -KGd(MoO₄)₂. The ED patterns can be indexed using the unit cell parameters determined from PXRD and the space group *Pbcn* (Table S5 of ESI†). The [100], [010] and [$\overline{1}$ 10] ED patterns show the reflections h00:h = 2n + 1 and 00l:l = 2n + 1, which should be extinct according to the *Pbcn* symmetry. However, these reflections vanished upon sufficiently tilting the sample out-of-zone around the h00 or 00l reciprocal rows. Therefore, these reflections were due to multiple diffractions. This was also confirmed for the h00:h = 2n + 1 reflections by their absence in the [001] zone.

3.5. $KGd_{1-x}Eu_x(MoO_4)_2$ (x = 0 and 0.2) crystal structures

The γ -KGd(MoO₄)₂ (prepared by the ceramic technique at 1223 K) and γ -KGd_{0.8}Eu_{0.2}(MoO₄)₂ (grown by the CZ technique) structures were refined using the Rietveld method from the XRD data. Using the Bragg–Brentano geometry for the XRD experiments, a strong preferred orientation along the *b* direction was revealed for γ -KGd_{1-x}Eu_x(MoO₄)₂. For this reason, transmission geometry was used for obtaining the XRD patterns for crystal structure refinements. The fractional coordinates of KY(MoO₄)₂ were used as initial parameters for the refinements.²⁵

The crystallographic parameters of γ -KGEMO (x = 0 and 0.2) are presented in Table 2. Atom coordinates and interatomic distances are presented in Table S6 and S7 of the ESI.† The fragments of the experimental, calculated and difference XRD patterns are shown in Fig. 5.

The γ-KGEMO (x = 0 and 0.2) structures are similar to those of other orthorhombic KY(MoO₄)₂-type phases.^{25,26} Unlike the scheelite-type α- and β-KR(MoO₄)₂ phases with the 3D frame-



Fig. 4 ED patterns along the main zone axes for the orthorhombic γ -KGd(MoO₄)₂.

work, the $KY(MOO_4)_2$ -type structures of the γ -phase are layered. The γ -KGd(MoO_4)₂ structure contains [GdMo₂O₈] layers perpendicular to the *b*-direction formed by the MoO₄ tetrahedra and GdO₈ polyhedra (Fig. 6). Moreover, two neighboring [GdMo₂O₈] layers are separated by a zigzag K⁺-layer.

The Gd–O distances in the GdO₈ polyhedra vary from 2.288 to 2.539 Å (Table S7 of the ESI[†]). Moreover, two GdO₈ polyhedra share a common O₃–O₃ edge and form infinite $[Gd_2O_{14}]_n$ chains with the Gd–Gd distances of 4.03 Å within the chains and 5.11 Å between chains (Fig. 7a). In addition, the two neighboring $[Gd_2O_{14}]_n$ chains are separated by the MoO₄ tetrahedra. Thus, the cation ordering in the γ -phase results in 1D Gd³⁺ ordering as compared to the 2D and 3D ordering in the scheelite-type α - and β -phases, respectively.

In the α -phase, the ordering of the R^{3+} and K^+ cations leads to zigzag R^{3+} and K^+ -layers, respectively, parallel to the (101) plane and alternating along the [100] direction of the scheelite-type unit cell.²² The R^{3+} -layers can be represented as constructed from the six-membered rings of the R^{3+} cations, with each R^{3+} cation surrounded by three other R^{3+} cations, resulting in a 2D R^{3+} network. In the β -phase, similar sixmembered R^{3+} -rings are present, but they form a 3D R^{3+} framework.

The zigzag K⁺-layer in the γ -phase is also different from the similar layer in the α -phase. Similar to the case of the R³⁺-layer, six K⁺ cations form six-membered rings in the zigzag K⁺-layer of the α -phase, whereas in the zigzag K⁺-layer of the γ -phase, each K⁺ cation is surrounded by six other K⁺ cations with the K⁺-K⁺ distances ranging from 4 × 4.82 Å to 2 × 5.11 Å (Fig. 7b).

3.6. Luminescence properties of KGd_{1-x}Eu_x(MoO₄)₂

Photoluminescence excitation (PLE) and emission (PL) spectra of α -KGd_{0.7}Eu_{0.3}(MoO₄)₂ prepared at 923 K are shown in

Table 2 Crystallographic data for $KGd_{1-x}Eu_x(MoO_4)_2$ (x = 0 and 0.2)

	x = 0	<i>x</i> = 0.200
Phase content	0.9425(5) γ-phase + 0.0575(6) α-phase	0.9646(6) γ-phase + 0.0354(7) α-phase
Formula γ-phase	γ -KGd(MoO ₄) ₂	γ-KGd _{0.8} Eu _{0.2} (MoO ₄) ₂
Sample preparation	Ceramic technique at 1223 K	Crashed crystal grown by the CZ technique
Crystal system	Orthorhombic	
Superspace group	Pbcn	
Lattice parameters:		
a (Å)	5.11465(4)	5.11590(4)
$b(\mathbf{A})$	18.0858(2)	18.0907(6)
c (Å)	8.04600(5)	8.05104(7)
$V(\dot{A}^3)$	744.27(1)	745.13(2)
Formula units, Z	4	
Color	White	
Density, g cm ⁻³	4.60691(6)	4.5922(1)
Data collection		
Diffractometer	STADI-P	
Radiation/ λ (Å)	$CoK_{\alpha 1}/1.78892$	
2θ range (°)	5.0-100.0	5.0-100.0
Step scan (2θ)	0.01	0.01
I _{max}	34 264	48 473
Number of points	9520	9520
Refinement		
No. reflections (all/Obs.)	250/250	251/250
No. of refined parameters/refined atomic parameters	49/21	49/21
R and $R_{\rm w}$ (%) for Bragg reflections	3.49 and 4.91	4.41 and 5.92
$R_{\rm P}; R_{\rm wP}; R_{\rm exp}$	5.72; 8.36; 4.23	4.31; 6.45; 3.03
Goodness of fit (ChiQ)	1.98	2.13
Max./min. residual density ($e \times Å^{-3}$)	1.21/-0.75	1.07/-1.21

Fig. 8. The PLE spectrum (Fig. 8a) consists of bands corresponding to the intraconfigurational $4f^6-4f^6$ transitions of Eu^{3+} in the host lattice in the 350–500 nm region and a broad non-elementary band in the region from 230 to 350 nm. The most intense Eu^{3+} 4f-4f excitations could be attributed to the $^7F_0 \rightarrow {}^5L_6$ (~395 nm) transition. The corresponding PL spectra of α -KGd_{0.7} $Eu_{0.3}$ (MoO₄)₂ under excitations at 395 nm and 300 nm are shown in Fig. 8b; typical red emissions of Eu^{3+} have been observed, consisting of different ${}^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions.

The PLE spectra for the Eu^{3+} emission in the α -KGEMO $(0.1 \le x \le 1)$ solid solutions are shown in Fig. 9a upon monitoring the emission at ~615 nm. The broad excitation bands in the region of 200-350 nm consist of three elementary bands at ~310, ~265 and ~225 nm. The bands are attributed to a charge transfer (CT) transition from oxygen to molybdenum within the MoO₄²⁻ groups (see the discussion hereinafter). These broad features generally originate from the mechanisms related to the host, such as CT states, and indicate energy transfer between the host and luminescent ions. The excitation spectra exhibit a high contribution of the charge transfer band, indicating a highly efficient mechanism of energy transfer between the host matrix and the luminescent ions as compared to the case of direct excitation. Apparently, the Eu³⁺ concentration influences the efficiency of this energy transfer.

The influence of the Eu³⁺ concentration on the PL spectra of α -KGEMO (0.1 $\leq x \leq 1$) under excitation at the ⁷F₀ \rightarrow ⁵L₆ transition (~395 nm) and CT band (~300 nm) was investigated, and the results are shown in Fig. 9b and 10. For all samples, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ forced electric dipole transition at ~615 nm generated the majority of the emission. This indicates that there is no inversion center in the site symmetry of



Fig. 5 Fragments of the experimental, calculated and difference SXPD patterns for γ -KGd_{1-x}Eu_x(MoO₄)₂ (x = 0 (a), 0.2 (b)). Tick marks denote the peak positions of possible bragg reflections for α - and γ -phases.



Fig. 6 *ab* (a) and *bc* (b) projection of γ -KGd(MoO₄)₂ structure. The O atoms are shown as red spheres.

A and thus the Eu³⁺ ion position,³⁴ in agreement with the low site symmetry derived from the structural data.²²

By changing the Eu³⁺ concentration, the peak positions or peak shape did not significantly change, but the ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ (J = 0-2) emission intensities depended on x, reaching maxima for x = 0.5 under excitation at the CT band (300 nm) and excitation at the ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ transition (395 nm) (Fig. 10b). Moreover, the change in the excitation from 395 nm to 300 nm for KGEMO leads to a significant increase in the luminescence intensity of these solid solutions. For example, for α -KGd_{0.5}Eu_{0.5}(MoO₄)₂, the luminescence intensity in the range of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition increased by a factor of ~ 2 (Fig. 10b). Thus, the revealed change in the luminescence intensity in the range of the ${}^5D_0 \rightarrow {}^7F_2$ transition for α -KGEMO with a change of λ_{ex} from 395 nm to 300 nm shows that for $0.1 \le x < 1$, the luminescence excitation mechanism involving charge transfer to luminescent centers (Eu³⁺) is more efficient than the direct excitation of luminescent centers, as is the case for the α -KEu(MoO₄)₂ phase.²²

The effect of the Eu³⁺ doping concentration on the relative PL intensity at the highest ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition was studied by Yi *et al.* in the KGEMO phosphors annealed at 1073 K for *x* in the range $0.1 \le x \le 0.35$.³⁵ The maximal ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission intensity ($\lambda_{ex} = 393$ nm) was found for *x* = 0.25, and the



Fig. 7 [GdMo₂O₈] layer (a) and K layer (b) in γ -KGd(MoO₄)₂ structure. The O atoms are shown as red spheres.

 ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ intensity maximum for this compound was about 2.7 times higher than that of the commercially used red phosphor Y₂O₂S:0.05Eu³⁺. Thus, our data about the effect of the Eu³⁺ content on the PL spectra of α -KGEMO in the entire range of *x* from 0.1 to 1 allowed us to add and correct the previously obtained data.

In accordance with the XRD study, the annealing of $KGd(MoO_4)_2$ at 1173 K leads to the transformation of the triclinic α -phase to the orthorhombic γ -phase. Photoluminescence excitation (PLE) and emission (PL) spectra of γ -KGd(MoO₄)₂ are shown in Fig. 11. Due to the strong thermal quenching of intrinsic emission at 300 K, the PL spectrum was obtained at 80 K. As shown in Fig. 11a, the PL spectrum consists of two broad emission bands with maxima at \sim 600 and 745 nm. The emission line at \sim 618 nm on the PL spectrum can be associated with the $^5D_0 \rightarrow \ ^7F_2$ transition of Eu³⁺ ions and indicates the presence of traces of Eu³⁺ ions in a nominally Eu-free sample. The emission bands at ~600 nm and at 745 nm are attributed to the emission from regular MoO₄²⁻ groups and oxygen-deficient MoO₃VO complexes, respectively.^{36–39} The excitation spectrum of the band at 600 nm was measured at $\lambda_{\rm em}$ = 570 nm to get rid of the contribution of the Eu³⁺ emission. The onset of the spectrum was observed at the fundamental absorption edge, and a peak at

intensity (a.u.)

200





Fig. 8 a) Photoluminescence excitation (λ_{em} = 615 nm) and (b) photoluminescence emission (λ_{ex} = 300 nm (1) and 395 nm (2)) spectra of α -KGd_{0.7}Eu_{0.3}(MoO₄)₂ at room temperature.

305 nm was obtained. This band corresponds to the electronic transitions from the top of the O2p valence band to the lower part of the conduction band formed mainly by the 4d states of Mo. The excitation peak of the defect-related band at $\lambda_{\rm em}$ = 745 nm shifted to a long wavelength region (to 318 nm) as compared to that of the intrinsic emission from the regular MoO₄²⁻ groups (305 nm). The peak at 318 nm is related to electronic transitions involving defect-related energy levels located in the bandgap (Fig. 11b).

Unlike the PLE of the ~600 and 745 nm bands, the PLE of the Eu³⁺ emission at λ_{em} = 618 nm demonstrated narrow excitation bands in the 350-500 nm region related to the intraconfigurational 4f⁶-4f⁶ transitions of Eu³⁺ ions in the host lattice (Fig. 11b). The onset of the PLE spectrum of the ~ 600 nm band coincides with that of the CT band of Eu³⁺. Therefore, the CT band on the PLE spectrum of Eu³⁺ is also connected to the O2p-Mo4d electronic transitions with consequent energy transfer to the Eu³⁺ ions. The PLE spectrum at λ_{em} = 618 nm does not change with an increase in temperature from 80 K to 300 K when the intrinsic emission is quenched. The slight long-wavelength shift of the CT band onset is connected to the increase in the electron-phonon interaction with the increasing temperature. The absence of the Eu³⁺-related PLE spectrum distortion with an increase in temperature indicates the absence of significant contribution of the PLE spectrum of the overlapping intrinsic emission and confirms our conclusion about the Eu³⁺ excitation via the host.

According to the XRD study (Table 1, Fig. S4 of ESI†), the increased Eu^{3+} concentration in the KGEMO sample prepared



Fig. 9 (a) PLE ($\lambda_{em} = 615 \text{ nm}$) and (b) PL ($\lambda_{ex} = 395 \text{ nm}$) spectra at room temperature of α -KGd_{1-x}Eu_x(MoO₄)₂ (0.1 $\leq x \leq 1$) solid solutions prepared at 923 K. The colors of ple spectra correspond to the color on the PL spectra.

at 1173 K changes the main phase from the orthorhombic γ -phase for $0 \le x \le 0.3$ to the monoclinic β -phase for $0.4 \le x \le 1$. A further increase in the annealing temperature up to 1223 K leads to the formation of three intervals with different main phases: orthorhombic γ -phase for $0 \le x \le 0.4$; triclinic α -phase in the range $0.5 \le x \le 0.7$ and monoclinic β -phase for $0.8 \le x \le 1$.

An increase in the annealing temperature from 923 to 1173 and 1223 K leads to strong changes in the PLE and PL spectra (Fig. 12 and 13 and S5 and S6 of the ESI†). As shown in Fig. S5 of the ESI,† the PLE spectra remain practically unchanged in the 350–500 nm region with the variation of x, whereas the CT band intensity decreases when compared with the case of α -KGd_{1-x}Eu_x(MoO₄)₂ (Fig. 9a). For example, the CT band intensity for γ -KGd_{0.8}Eu_{0.2}(MoO₄)₂ drastically decreases with the increasing annealing temperature, and thus, the direct excitation mechanism is more efficient than the charge transfer mechanism between the host matrix and the luminescent ion (Fig. 12a).

Earlier, we have revealed how the luminescence properties are related to the structure of the α - and β -modifications of KEu(MoO₄)₂.²² It was shown that the luminescence properties of the layered network of Eu³⁺ ions in the α -phase were better than those of the 3D framework of the Eu³⁺ ions in the β -phase synthesized by quenching from 1203 K to liquid nitrogen temperature.²¹ The ⁵D₀ \rightarrow ⁷F₀ transition is observed at



Fig. 10 (a) 10PL spectra at room temperature ($\lambda_{ex} = 300$ nm) of α -KGd_{1-x}Eu_x(MoO₄)₂ (0.1 $\leq x \leq$ 1) prepared at 923 K. (b) Concentration dependence of the Eu³⁺ (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) maximum emission intensity in α -KGd_{1-x}Eu_x(MoO₄)₂ (0.1 $\leq x \leq$ 1) prepared at 923 K after excitation at the ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ transition (395 nm) and CT band (300 nm). All spectra emission intensity are normalized on the intensity value of α -KEu(MoO₄)₂.

580 nm for the α-phase, but is shifted to higher energies for the β-phase. The $\alpha \rightarrow \beta$ phase transition also induces changes in the ⁷F₂ multiplet splitting, as reflected in the ⁵D₀ → ⁷F₂ transition.²²

PL ($\lambda_{ex} = 395 \text{ nm}$) spectra of KGEMO ($0.1 \le x \le 1$) prepared at 1173 K (a) and 1223 K (b) are shown in Fig. S6 of the ESI.[†] Parts of the PL spectra of KGEMO ($0.1 \le x \le 1$) prepared at 1173 K (a) and 1223 K (b) for the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions are shown in Fig. 13. The ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition in the region of 578–581 nm deserves special attention. Since this transition is forbidden for both electric and magnetic dipole interactions, the intensity can be very low or even non-observable. However, the transition is induced for the C_{1} symmetry of the Eu³⁺ ion polyhedron; thus, a peak is expected at this position. As the splitting of the initial and final level, both characterized by J = 0, is not possible, the observation of more than one peak for the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition would indicate the presence of more than one non-equivalent site for the luminescent Eu³⁺ ions.



Fig. 11 a) PL (λ_{ex} = 300 nm) spectrum at 80 K and (b) PLE spectra at λ_{em} = 570 nm (1), 760 nm (2) and 618 nm (3 and 4) at temperatures 80 K (1–3) and 300 (4) K of nominally undoped γ -KGd(MoO₄)₂ prepared at 1173 K.

As shown in Fig. 13, the number of bands depends on the cationic composition and annealing temperature. At least two emission bands (at ~579.2 and ~579.7 nm) were detected in the PL spectra for the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition of Eu³⁺ for pure β -KGEMO (0.6 $\leq x \leq 1$ for the annealing temperature T = 1173 K; 0.8 $\leq x \leq 1$ for the annealing temperature T = 1223 K), whereas only one band (at ~580 nm) was detected for the main α -phase in the range 0.5 $\leq x \leq 0.7$ for the annealing temperature T = 1223 K. However, these emission bands of Eu³⁺ appeared much earlier in the PL spectra (Fig. 13) when only traces of the α - and β -phases were found in the XRD patterns (Table 1). Unlike the α - and β -phases, no emission bands were observed in the PL spectra for the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition of Eu³⁺ for the orthorhombic γ -KGEMO phases with small Eu³⁺ concentrations (0.1 for the annealing temperature



Fig. 12 Arts of room temperature PLE (λ_{em} = 615 nm) (a) and PL (λ_{ex} = 395 nm) (b) spectra of γ-KGd_{0.8}Eu_{0.2}(MoO₄)₂: prepared at 1173 K (1) and 1223 K (2) and single crystal grown at 1373 K by the Czochralski technique (3). PLE spectra are normalized to the peak of the excitation of the ⁷F₀ → ⁵L₆ transition (~395 nm). All PL spectra are normalized on the intensity value of α-KEu(MoO₄)₂.



Fig. 13 Parts of room temperature PL (λ_{ex} = 395 nm) spectra of KGd_{1-x}Eu_x(MoO₄)₂ (0.1(1), 0.2(2), 0.3(3), 0.4(4), 0.5(5), 0.6(6), 0.7(7), 0.8(8), 0.9(9), 1 (a)) prepared at 1173 K (a and c) and 1223 K (b and d) for the ⁵D₀ \rightarrow ⁷F₀ (a and b) and ⁵D₀ \rightarrow ⁷F₂ (c and d) transitions. All PL spectra are normalized on the intensity value of α -KEu(MoO₄)₂.

T = 1173 K and 0.1 ≤ *x* ≤ 0.2 for the annealing temperature *T* = 1223 K) and small amounts of the α- and β-phases. The absence of bands in the PL spectra for the ⁵D₀ → ⁷F₀ transition of Eu³⁺ for the γ-phases indicates a higher symmetry of the Eu³⁺ oxygen environment in the orthorhombic phase as compared to the cases of the α- and β-phases. Compared with the cases of the α- and β-phases, in the PL spectra of the γ-phases, the ⁷F₂ multiplet splitting for the ⁵D₀ → ⁷F₂ transition was not observed, and only one band (at ~613.6 nm) was detected (Fig. 12b and 13). As shown in Fig. 12b, the



Fig. 14 Comparative integral intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission of different Eu^{3+} concentration for $KGd_{1-x}Eu_{x}(MOO_{4})_{2}$ phases prepared at different annealing temperatures and after different excitations.



Fig. 15 Parts of room-temperature PL (λ_{ex} = 395 nm) spectra of β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ prepared at 1173 K (1) and the commercially used red phosphor Gd₂O₂S:Eu³⁺ (2). All PL spectra are normalized on the intensity value of Gd₂O₂S:Eu³⁺. Both samples are measured under the same conditions.

annealing temperature and sample preparation method affect the emission intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition for samples with similar composition and structure. The maximum of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission intensities was found for orthorhombic γ -KGd_{0.8}Eu_{0.2}(MoO₄)₂ prepared at 1223 K.

Fig. 14 summarizes the influence of annealing temperature, the Eu³⁺ concentration and energy excitation on the integral intensity of the ${}^5D_0 \rightarrow \, {}^7F_2$ emission for KGEMO. The maximum of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ integral emission intensities after excitation at the charge transfer band (λ_{ex} = 300 nm) was found for the triclinic scheelite-type α-KGd_{0.6}Eu_{0.4}(MoO₄)₂ prepared at 923 K. Moreover, the change in the excitation from 300 nm to the excitation at the ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ transition of Eu^{3+} ions (λ_{ex} = 395 nm) for KGEMO leads to the maximum of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ intensities for the monoclinic scheelite-type $\beta\text{-}KGd_{0.4}Eu_{0.6}(MoO_4)_2$ prepared at 1173 K. Compared with the α - and β -modifications of KEu(MoO₄)₂,²² the revealed influence of the ${}^5D_0 \rightarrow {}^7F_2$ emission intensity for $KGd_{1-x}Eu_x(MoO_4)_2$ shows that a 3D framework of the $Eu^{3+}/$ Gd³⁺ ions in β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ is more preferable for red luminescence than a layered network of the Eu³⁺/Gd³⁺ ions in the triclinic α -phase and 1D Eu³⁺/Gd³⁺ ordering in the orthorhombic γ -phase.

Fig. 15 shows the comparison of the PL spectra of β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ (annealing T = 1173 K) and Gd₂O₂S: Eu³⁺. The maximum and integral emission intensity of β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ in the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition region is higher by ~20% than that of the commercially used red phosphor Gd₂O₂S:Eu³⁺. This confirms that β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ is exceptionally attractive as a near-UV convertible phosphor for application as a red-emitting phosphor in LEDs.

Conclusions

The study on the influence of annealing conditions and Eu^{3+} concentration on the structure of $KGd_{1-x}Eu_x(MoO_4)_2$ revealed that depending on the elemental composition and annealing temperature, three types of structures were found for

 $KGd_{1-x}Eu_x(MoO_4)_2$ (0 $\leq x \leq 1$): scheelite-type α - and β -modifications and an orthorhombic γ -phase with a $KY(MoO_4)_2$ -type structure. The number and the character of the phase transitions for $KGd_{1-x}Eu_x(MoO_4)_2$ depended on the elemental composition. The existence of the pure monoclinic disproportionately modulated β -KGd_{1-r}Eu_r(MoO₄)₂ phases was found only for $0.6 \le x \le 1$. Thus, the scheelite-type structure for the monoclinic β -phases appears to occur only for $r(K) - r(R) \le 0.45 \text{ Å} (r(R) = 0.4 \times r(Gd^{3+}) + 0.6 \times r(Eu^{3+}))$ when compared with the case of triclinic α -phases. The study of the luminescence properties indicated the influence of the structure of $KGd_{1-x}Eu_x(MoO_4)_2$ on the positions and intensities of the bands in the photoluminescence excitation and emission spectra. At 300 nm, the excitation spectra of α -KGd_{1-x}Eu_x(MoO₄)₂ indicated the highest charge transfer band contribution as compared to direct excitation and thus the most efficient energy transfer between the host matrix and the luminescent ion. The emission spectra of all the samples exhibited an intense red emission originating from the Eu^{3+ 5}D₀ \rightarrow ⁷F₂ transition. The maxima of the ⁵D₀ \rightarrow ⁷F₂ integral emission intensities was found for the triclinic scheelite-type α -KGd_{0.6}Eu_{0.4}(MoO₄)₂ ($\lambda_{ex} = 300$ nm) and the monoclinic scheelite-type β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ samples prepared at 1173 K (λ_{ex} = 395 nm). The phosphor β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ prepared at 1173 K showed the brightest red light emission among the $KGd_{1-x}Eu_x(MoO_4)_2$ phosphors after excitation at 395 nm. The maximum and integral emission intensities of β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ in the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition region are higher by ~20% than that of the commercially used red phosphor Gd₂O₂S:Eu³⁺. This confirms that β -KGd_{0.4}Eu_{0.6}(MoO₄)₂ is exceptionally attractive as a near-UV convertible phosphor for application as a redemitting phosphor in LEDs.

Conflicts of interest

There are no conflicts to declare.

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