# KTb(MoO<sub>4</sub>)<sub>2</sub> Green Phosphor with K<sup>+</sup>-Ion Conductivity: Derived from Different Synthesis Routes

Vladimir A. Morozov, Svetlana M. Posokhova, Sergey Ya. Istomin, Dina V. Deyneko,\* Aleksandra A. Savina, Boris S. Redkin, Nikolay V. Lyskov, Dmitry A. Spassky, Alexei A. Belik, and Bogdan I. Lazoryak



and luminescent properties of KTb(MoO<sub>4</sub>)<sub>2</sub> (KTMO) was studied. KTMO samples were prepared by solid-state, hydrothermal, and Czochralski techniques. These methods lead to the following different crystal structures: a triclinic scheelite-type  $\alpha$ -phase is the result for the solid-state method, and an orthorhombic KY(MoO<sub>4</sub>)<sub>2</sub>-type  $\gamma$ -phase is the result for the hydrothermal and Czochralski techniques. The triclinic  $\alpha$ -KTMO phase transforms into the orthorhombic  $\gamma$ -phase when heated at 1273 K above the melting point, while KTMO prepared by the hydrothermal method does not show phase transitions. The influence of treatment conditions on the average crystallite size of orthorhombic KTMO was revealed by X-ray diffraction line broadening measurements. The electrical conductivity was measured on KTMO single crystals. The orthorhombic structure of KTMO that was



Article

prepared by the hydrothermal method was refined using synchrotron powder X-ray diffraction data. K<sup>+</sup> cations are located in extensive two-dimensional channels along the *c*-axis and the *a*-axis. The possibility of K<sup>+</sup> migration inside these channels was confirmed by electrical conductivity measurements, where strong anisotropy was observed in different crystallographic directions. The evolution of luminescent properties as a result of synthesis routes and heating and cooling conditions was studied and compared with data for the average crystallite size calculation and the grain size determination. All samples' emission spectra exhibit a strong green emission at 545 nm due to the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  Tb<sup>3+</sup> transition. The maximum of the integral intensity emission for the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  emission under  $\lambda_{ex} = 380$  nm excitation was found for the KTMO crashed single crystal.

# 1. INTRODUCTION

A new generation of light sources has been integrated into a range of applications, such as efficient solid-state lighting, backlights and multicolor 3D displays, fluorescent sensors, etc.<sup>1–5</sup> In the area of white light solid-state lighting, phosphor-converted white light-emitting diodes (pc-WLEDs) are a new and now commonly used generation of light sources. The advantages of pc-WLEDs are long operation times, restricted energy consumption, nontoxicity, high luminous efficiency, ease of fabrication, and cost efficiency.<sup>6–12</sup> pc-WLEDs are used as backlights for electronic devices, including portative devices and medical and building light sources.<sup>13</sup> Modern WLEDs were invented, including the (In,Al)GaN heterostructure chip. The progress in the field of these semiconductor materials was an important achievement in the solid-state lighting field that was made by Nakamura et al.<sup>14–16</sup>

The Mo- and W-based phosphors doped with rare earth elements are potential materials for pc-WLED applications (and also for solid-state lasers) due to opportunity to tailor the luminescence spectral characteristics and their excellent thermal stability.<sup>17–23</sup> In the near-UV region, they show

strong absorption bands due to charge transfer from oxygen to Mo or W. Different methods can be used to produce Mo- and W-based phosphors doped by rare earth elements, including solid-state,<sup>24–27</sup> sol-combustion,<sup>27,28</sup> sol–gel,<sup>27,29–31</sup> and hydrothermal<sup>32–34</sup> methods. However, an important feature of these compounds is that bulk single crystals can be grown by the Czochralski technique.<sup>22–24,35–37</sup> This makes it possible to measure many physical properties of compounds directly on single crystals and compare them with properties in the powder or ceramic forms. The luminescent properties strongly depend on their crystal structure,<sup>24,25</sup> preparation method,<sup>27</sup> sintering temperature,<sup>28–31</sup> grain diameter,<sup>32,33,28,38</sup> crystal size,<sup>39</sup> and morphology.<sup>34,40</sup>

Received: February 27, 2021

In this work, we have made an effort to relate the influence of different synthesis routes on the structure and properties of  $KTb(MoO_4)_2$ . The magnetic susceptibility and electrical conductivity were measured on a  $KTb(MoO_4)_2$  single crystal.

# 2. EXPERIMENTAL SECTION

**2.1. Materials and Sample Preparation.** The  $\alpha$ -modification of KTb(MoO<sub>4</sub>)<sub>2</sub> ( $\alpha$ -KTMO) was synthesized from stoichiometric amounts of Tb<sub>4</sub>O<sub>7</sub> (99%, Rushim), K<sub>2</sub>CO<sub>3</sub> (99%, Rushim), and MoO<sub>3</sub> (99%, Rushim) by a solid-state reaction in an alumina crucible at 893 ± 10 K for 30 h in air, followed by slow cooling in the furnace from 893 K to room temperature ( $T_R$ ).  $\alpha$ -KTMO was annealed at 1273 K, followed by quenching from 1273 K to the temperature of liquid N<sub>2</sub>.

The synthesis of KTMO (ht-KTMO) was carried out by a hydrothermal method. Tb<sub>4</sub>O<sub>7</sub> (99%, Rushim) and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>. 4H<sub>2</sub>O (99%, Rushim) were used as the starting raw materials. A  $Tb(NO_3)_3$  solution was prepared by mixing  $Tb_4O_7$  in dilute HNO<sub>3</sub> under stirring and heating until the powder was completely dissolved.  $(NH_4)_6Mo_7O_{24}$ ·4H<sub>2</sub>O was dissolved in distilled water with magnetic stirring at 313 K for 30 min to form an aqueous solution. Stoichiometric amounts of Tb(NO<sub>3</sub>)<sub>3</sub> and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O solutions were mixed with magnetic stirring at  $T_{\rm R}$  for 10 min. The solution was adjusted to pH 7-8 by adding a desired amount of KOH (5 M) dropwise into the above solutions under vigorous stirring. A slurry-like white precipitate formed immediately after addition of KOH. After stirring for 1 h, this mother liquor was poured into a Teflon-lined autoclave until two-thirds of the volume of the autoclave was occupied. Finally, the autoclave was sealed into a stainless-steel tank and kept at 473 K for 12 h under constant magnetic stirring, then air-cooled to  $T_{\rm R}$ . Afterward, the residual was centrifuged, washed with deionized water and ethanol, and dried in air at 333 K for 8 h. ht-KTMO was successively annealed at different temperatures (773, 893, 1033, 1143, and 1273 K) for 12 h in air and then slowly cooled in the furnace from the high temperature (773, 893, 1033, and 1143 K) to  $T_{\rm R}$  or quenched from 1273 K to  $T_{\rm R}$  (Table S1 of the Supporting Information). The annealing temperatures were chosen based on the differential scanning calorimetry studies.

The polycrystalline materials used for the KTMO single-crystal growth were prepared by a solid-state reaction. A stoichiometric mixture of the raw materials (K<sub>2</sub>CO<sub>3</sub>, Tb<sub>4</sub>O<sub>7</sub> (spectroscopic purity  $\geq$ 99.995%), and MoO<sub>3</sub>) was placed in a Pt crucible and annealed at 773-823 K for 15 h to decompose the carbonate. Then the mixture was grinded, homogenized, and heated at 1173 K for 15 h in air. The synthesized polycrystalline samples of KTMO were melted in a 40  $\times$ 40 mm<sup>2</sup> diameter Pt crucible using a 17 kHz frequency induction furnace. A small nonoriented KTMO single-crystal bar was used as a seed. The growing temperature was accurately determined by repeated seeding trials. A KTMO colorless transparent crystal with up to a 10 mm diameter and 20 mm length was grown at 1373 K by the Czochralski (CZ) technique at a pulling rate of 0.5-1.5 mm/h and a rotating rate of 50 rpm in a slightly oxidizing atmosphere. The images of the KTMO crystal grown by the Czochralski technique under either daily light or excitation (~380 nm) are shown in Figure 1.

The slice, having a surface of 10 mm  $\times$  10 mm and a thickness of 2 mm, was cut perpendicular to the *b*-axis and then optically polished to obtain parallel faces. Impedance spectroscopy (IS) measurements were performed on a polished crystal plate with a size of 8.8 mm  $\times$  8.3 mm  $\times$  1.3 mm (Figure S1 of the Supporting Information).

**2.2. Characterization.** Scanning electron microscopy (SEM) observations were performed using a Tescan VEGA3 scanning electron microscope equipped with an Oxford Instruments X-Max 50 silicon drift energy-dispersive X-ray spectrometry (EDXs) system with AZtec and INCA software. Prior to the SEM examination, the specimens were coated with a thin layer of carbon. The elemental composition of KTMO prepared by different techniques was measured at 10 points of each sample. The EDX analysis results were based on the  $K_{\rm K}$ , Tb<sub>1</sub>, and Mo<sub>1</sub> lines. Figures S2 and S3 of the



Figure 1. Images of the  $KTb(MoO_4)_2$  single crystal under (a) daily light and (b) the excitation (~380 nm).

Supporting Information show representative SEM-EDX spectra and SEM images of the KTMO samples.

Particle sizes for KTMO prepared by solid-state and hydrothermal techniques were determined in an isopropyl alcohol/aqueous suspension (20:80) mixture using a CILAS 1180 laser diffraction particle size analyzer in the range from 0.04 to 2500  $\mu$ m. All analyses were performed five times.

Powder X-ray diffraction (XRD) patterns for the phase analysis were collected on a Thermo ARL X'TRA powder diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5418$  Å, Bragg–Brentano geometry, Peltier-cooled CCD detector). The XRD data were collected at  $T_{\rm R}$  over the 5°–70°  $2\theta$  range with steps of 0.02°. To determine the lattice parameters, the Le Bail decomposition<sup>41</sup> was applied using JANA2006 software.<sup>42</sup> The coherent scattering regions, which are usually considered to be equal to the crystallite sizes, were determined from the Scherrer equation.<sup>43</sup> LaB<sub>6</sub> (SRM 660c) was used as a line-shape standard to determine the instrumental broadening.

Synchrotron XRD data for KTMO prepared by hydrothermal technique were measured with a large Debye–Scherrer camera at the BL15XU beamline of SPring-8.<sup>44,45</sup> The intensity data were collected between 1.048° and 60.842° at 0.003° intervals in 2 $\theta$ , and the incident beam was monochromated at  $\lambda = 0.65298$  Å. The sample was packed into a Lindemann glass capillary (inner diameter 0.1 mm), which was rotated during the measurement. The Rietveld analysis was performed using JANA2006 software.<sup>42</sup>

**2.3. Physical and Chemical Properties.** A NETZSCH STA Jupiter 449 thermal analyzer operated in air was used to study the temperature dependence of the weight and the thermal behavior of samples prepared by the solid-state and hydrothermal techniques. The thermal analysis was performed on powdered KTMO samples placed in Pt crucibles with lids at 303–1273 K at a rate of 3 K/min in a heating and cooling cycles. The typical sample weight was about 30 mg.

The magnetic susceptibility,  $\chi = \mathbf{M/H}$ , of *ht*-KTMO was measured on a dc SQUID magnetometer (Quantum Design, MPMS XL) between 2 and 350 K in applied fields of 100 Oe and 5 kOe (1 Oe =  $10^{3}/4\pi$  Am<sup>-1</sup>) under both zero-field-cooled (ZFC) and field-cooled on cooling (FCC) conditions. Isothermal magnetization curves were recorded at 2 and 300 K in applied fields from 0 to 70 kOe.

Photoluminescence excitation (PLE) and emission (PL) spectra were recorded using a LOT-Oriel MS-257 spectrograph equipped with a Marconi CCD detector and a 150 W Xe arc as an excitation source. The powder samples were placed into an optical cryostat Cryotrade LN-120. Photoluminescence spectra of all samples were recorded in similar experimental conditions to compare the relative emission intensity and reduce the error. The initial *ht*-KTMO was used as a reference. The integral emission intensities of *ht*-KTMO in the region of the  ${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{5}$  Tb<sup>3+</sup> transition were taken as 100%, and the luminescence intensities of the other samples were normalized to the former.

Electrical conductivity ( $\sigma$ ) was measured alternately in different crystallographic directions by a P-5X impedancemeter (OOO, Electrochemical Instruments, Russia) using the double-contact method in a frequency range from 1 Hz to 500 kHz with an applied oscillation voltage of 10 mV in the temperature range of 773-1073 K in air. A Pt paste was put alternately on the flat parallel surfaces of the crystal plate. After applying the paste, the sample was kept in a drying oven at 400 K for 20 min to dry it. Additional annealing was accomplished at 1073 K for 60 min in air to ensure the good electrical contact between sample and the metal electrodes. The measurements were performed during cooling, with isothermal holding at each temperature for at least 30 min. The temperature was controlled by a Pt/Pt-10% Rh thermocouple inside the cell, which was placed close to the sample. After measurements along one of the crystallographic directions, the Pt electrodes were cleaned using a diamond=coated needle file, and a similar deposition procedure was carried out in a different crystallographic direction.

## 3. RESULTS

**3.1. Element Composition and Grain Size Distributions.** The compositions were found to be close for all samples and were in the range of 23.30-24.61, 23.82-24.68, and 51.44-52.47 at. % for K, Tb, and Mo, respectively. Results of the EDX analysis are summarized in Table S2 of the Supporting Information and prove that composition of samples corresponds to the target stoichiometry  $\text{KTb}(\text{MoO}_4)_2$ . Figure S4 of the Supporting Information shows the particle size distributions of KTMO prepared by solid state and hydrothermal methods.

**3.2. DSC Study.** Figures 2 and 3 show fragments of the DSC curves for KTMO prepared by the solid-state reaction ( $\alpha$ -KTMO) and the hydrothermal technique (ht-KTMO) obtained at a 3 K/min rate in a heating-cooling cycle. The DSC curves for  $\alpha$ -KTMO reveal a single peak at 1260 K (heating mode) and another at 1213.5 K (cooling mode) (Figure 2). The former is most likely associated with melting, while the latter is most likely associated with the crystallization of KTMO.

Similarly peaks at ~1254 (heating) and 1212 K (cooling) at the DSC curve for the *ht*-KTMO sample correspond to the melting and crystallization of the  $\gamma$ -KTMO phase (Figure 3). However, additional peaks were also observed, such as a wide peak at  $T_{\rm min} \sim 1033$  K on the heating cycle and two narrow ones at  $T_{\rm min} \sim 1238$  and 1131 K on the heating cooling cycle, respectively.

**3.3. XRD Characterization.** Parts of the powder XRD patterns of KTMO prepared by different methods, followed by annealing at different temperatures and cooling conditions, are shown in Figure 4. The unit cell parameters of the KTMO samples that were calculated using Le Bail decomposition are listed in Table S1 of the Supporting Information.

In accordance with the XRD data, triclinic  $\alpha$ -KTMO transforms into the orthorhombic  $\gamma$ -phase via quenching from 1273 K (above the melting point) to the temperature of liquid N<sub>2</sub> (Figure 2). The conversion from the scheelite-type  $\alpha$ -KTMO to the orthorhombic  $\gamma$ -phase results in an increase (~8%) in the unit cell volume (V/Z) for KTMO (Table S1 of the Supporting Information). The annealing of *ht*-KTMO ( $\gamma$ -phase) at 773 K and a further increase in the treatment temperature up to 1273 K do not lead to the transformation of the orthorhombic  $\gamma$ -phase into the triclinic  $\alpha$ -phase or the monoclinic  $\beta$ -form. Nevertheless, the annealing of *ht*-KTMO at 773 K leads to an insignificant decrease in the unit cell volume (~0.4%) due to the reduction of the *b*-parameter.



**Figure 2.** Fragments of DSC curves for  $\alpha$ -KTb(MoO<sub>4</sub>)<sub>2</sub> obtained by a solid-state reaction at 893 K in the temperature ranges of (a) 400–1273 K and (b) 1073–1273 K in successive heating (1) and cooling (2) cycles.

When changing the annealing temperature from 773 to 1143 K, the *a*, *c*, and *V* unit cell parameters slightly increase, while the *b* parameter remains almost unchanged (Figure S5 of the Supporting Information). The overall change in the cooling conditions from slow cooling in the furnace to quenching from a high temperature to the temperature of liquid N<sub>2</sub> also does not lead to a phase transformation of the  $\gamma$ -phase.

It should be noted that the use of the Bragg–Brentano geometry for X-ray diffraction experiments led to the observation of a strong preferred orientation along the *b*-axis. This feature of the powder XRD patterns was observed when the  $\alpha$ -phase was quenched from *T* above the melting point, when, *ht*-KTMO was annealed above 1033 K, and when a single crystal was grown by the Czochralski method (Figure 4).

Crystallite sizes of  $\gamma$ -KTMO samples were estimated from the observed line broadening on the XRD patterns by Debye– Scherrer's equation (neglecting the microstrain in the crystal).<sup>43</sup> The Scherrer equation is

$$D_{hkl} = K\lambda/(B_{hkl}\cos\theta)$$

where  $D_{hkl}$  is the crystallite size, hkl are the Miller indices, K is the crystallite-shape factor (K is usually equal to 0.9),  $\lambda$  is the wavelength,  $B_{hkl}$  is the full-width at half-maximum (FWHM) of the X-ray diffraction peak, and  $\theta$  is the Bragg angle. The 130, 112, 042, and 150 reflections were used for the peak broadening measurements. The FWHM was corrected for instrumental broadening. Figure 5 displaces parts of the



**Figure 3.** Fragments of TG and DSC curves for ht-KTb(MoO<sub>4</sub>) in the temperature ranges of (a) 400–1273 K and (b) 1073–1273 K in successive heating (1) and cooling (2) cycles. Dotted lines show the annealing temperatures of the samples studied by XRD.

powder XRD patterns in the  $2\theta$  range of  $21-31^{\circ}$  for the orthorhombic  $\gamma$ -KTMO prepared at different conditions, and the dependence of the average crystallite size was calculated by the Scherrer equation from 130, 112, 042, and 150 reflections of  $\gamma$ -KTMO samples from the treatment temperature and cooling conditions. The influence of annealing and cooling conditions on the crystallite size was calculated using the Debye–Scherrer equation for 130, 112, 042, and 150 reflections and is separately shown in Figure S6 of the Supporting Information.

**3.4.** *ht*-**KTb**(**MoO**<sub>4</sub>)<sub>2</sub> **Crystal Structure.** The *ht*-KTMO ( $\gamma$ -phase) crystal structure was refined using the Rietveld method from synchrotron powder XRD data. The data for the KY(MoO<sub>4</sub>)<sub>2</sub> structure were used as a start model for the refinement.<sup>46</sup> The refinement results of the *ht*-KTMO structure are given in Table 1. Tables S3 and S4 of the Supporting Information include atom coordinates and selected interatomic distances. Figure 6 shows the fragments of the synchrotron XRD patterns. The CCDC deposition number is 2065395.

**3.5.** Physical Properties. Figure 7 presents plots of  $\chi$  and  $\chi^{-1}$  (ZFC and FCC curves) against temperature for *ht*-KTMO. No noticeable difference was found between the curves measured under the ZFC and FCC conditions. Between 200 and 350 K, the  $\chi^{-1}$  vs *T* curve shows an almost linear behavior and can be fitted by the Curie–Weiss equation. The



**Figure 4.** Parts of the powder XRD patterns of  $\text{KTb}(\text{MOO}_4)_2$  samples that were prepared by a solid-state reaction at 893 K (1), followed by annealing at 1273 K and quenching with liquid N<sub>2</sub> (2); prepared by the hydrothermal method (3), followed by annealing at 773 K (4), 893 K (5), 1033 K (6), or 1143 K (7) and slow cooling in the furnace to room temperature; prepared by hydrothermal method, followed by annealing at 1273 K and quenching to room temperature (8); and grown by the Czochralski technique (9).

experimental effective magnetic moment of 9.625(3)  $\mu_{\rm B}$  corresponds to the expected value for Tb<sup>3+</sup> (9.50–9.72  $\mu_{\rm B}$ ).<sup>47</sup> Isothermal magnetization curves recorded at 2 and 300 K in applied fields from 0 to 70 kOe are shown in Figure 8.

To study the electrical conductivity anisotropy of the KTMO single crystal, the conductivity of the sample was measured in different crystallographic directions. Figure S7 of the Supporting Information shows typical impedance responses for the KTMO single crystal at 973 K depending on the crystallographic direction. The impedance spectra consist of high-frequency (~100 Hz to 500 kHz) and low-frequency parts. The high-frequency part looks like a semicircle arc and corresponds to the bulk conductivity properties of the crystal, whereas the low-frequency impedance response (frequencies lower than 100 Hz) characterizes charge transfer processes through the electrode-electrolyte interface.<sup>48</sup> To provide a better fit of the semicircle arc in the whole temperature range under study, an equivalent electrical circuit consisting of resistance (R) connected in parallel with a constant-phase element (CPE) was used. The CPE admittance in the Boukamp notations<sup>49</sup> can be represented as  $Q = Q_0 (j\omega)^n$ , where  $Q_0$  is a proportionality factor and the *n* index is related to the phase angle. The n-value changes slightly from 0.86 to ~1, demonstrating a weak dispersion in the distribution of the relaxation times. The  $Q_0$  (~10<sup>-10</sup> F/cm) value corresponds to an apparent geometric capacitance of the sample. The bulk resistance  $(R_{\rm h})$  was obtained as a right-end extrapolation of the high-frequency arc on the real axis, as shown in Figure S7 of

D



**Figure 5.** (a) Parts of the XRD patterns in the  $2\theta$  range of  $21-31^{\circ}$  for orthorhombic  $\gamma$ -KTb(MoO<sub>4</sub>)<sub>2</sub> prepared by the following different methods: a solid-state reaction at 893 K, followed by annealing at 1273 K and quenching to liquid N<sub>2</sub> (1); the hydrothermal method (2), followed by annealing at 773 K (3), 893 K (4), 1033 K (5), or 1143 K (6) and slow cooling in the furnace to room temperature; and the hydrothermal method, followed by annealing at 1273 K and quenching to room temperature (7). (b) dependence of the average crystallite size of  $\gamma$ -KTb(MoO<sub>4</sub>)<sub>2</sub> samples from the treatment temperature and cooling conditions.

the Supporting Information. The obtained  $R_b$  value was used to calculate of the specific conductivity of the sample according to the following equation:

$$\sigma = \frac{1}{R_{\rm b}} \frac{l}{S}$$

where l is the thickness of the sample and S the area of the sample.

The conductivity  $\sigma$  was calculated from the impedance spectra for the KTMO different crystallographic directions, and the results are shown in Figure 9 as an Arrhenius plot. Linear dependences of log  $\sigma T$  vs 1000/T were observed for all directions. The conductivity demonstrates a strong anisotropy  $\sigma_{[a]}/\sigma_{[b]}/\sigma_{[c]} \approx 1500-3000/1/70-100$  (depending on temperature) in different crystallographic directions over the whole temperature range. The activation energy ( $E_a$ ) also depends on the measurement direction (Figure 9). Table 1. Crystallographic Data for  $\gamma$ -KTb(MoO<sub>4</sub>)<sub>2</sub>

crystal data		
sample preparation	hydrothermal technique at 473 K	
crystal system	orthorhombic	
space group	Pbcn	
lattice parameters:		
a (Å)	5.09318(3)	
b (Å)	18.2552(2)	
c (Å)	8.00765(4)	
V (Å <sup>3</sup> )	744.529(8)	
formula units, Z	4	
color	white	
density (g/cm <sup>3</sup> )	4.62029(5)	
data collection		
diffractometer	BL1	5XU beamline of SPring-8
radiation/wavelength ( $\lambda$ , Å)	Synchrotron/0.65298	
$2\theta$ range (deg)	2.889-60.842	
Step scan $(2\theta)$	0.003	
I <sub>max</sub>	5179	963
no. of points	19318	
refinement		
refinement		Rietveld
background function		Legendre polynomials, 15 terms
preferred orientation function, hkl direction		March–Dollase, 0k0
no. of reflections (All/Obs.)		610/609
no. of refined parameters/refined atomic parameters		50/24
<i>R</i> and $R_{\rm w}$ (%) for Bragg reflections $(R_{\rm all}/R_{\rm obs})$		2.60/2.59 and 4.35/4.35
$R_{\rm P}$ , $R_{\rm wP}$ ; $R_{\rm exp}$		2.29, 3.53, 0.62
goodness of fit (ChiQ)		5.71
maximum/minimum residual density $(e \times Å^{-3})$		1.07/-1.20
CSD deposition number		2065395



**Figure 6.** Parts of the experimental, calculated, and difference synchrotron XRD patterns for ht-KTb $(MoO_4)_2$  prepared by the hydrothermal technique. The peak positions of possible Bragg reflections are shown by tick marks.

Figures 10-12 show the photoluminescence excitation (PLE) and emission (PL) spectra for KTMO. The PL



**Figure** 7. (a) Magnetic susceptibility,  $\chi$ , and (b) inverse magnetic susceptibility,  $\chi$ , curves for *ht*-KTb(MoO<sub>4</sub>)<sub>2</sub> ( $\gamma$ -phase) measured in the ZFC mode at 100 Oe and the FCC mode at 100 Oe and 5 kOe. The fit to the Curie–Weiss law is given on the  $\chi^{-1}(T)$  curve by the solid red line with  $\mu_{\text{eff}} = 9.625(3)\mu_{\text{B}}$  and  $\theta = +0.8(2)$  K.



**Figure 8.** Isothermal magnetization curves, M vs H, at T = 2 (1) and 300 K (2).

spectrum of *ht*-KTMO annealed at 1143 K and that of the KTMO crashed single crystal at 300 K under excitation at the  ${}^{7}F_{6} \rightarrow {}^{5}D_{3}$  transition of Tb<sup>3+</sup> (~380 nm) are shown in Figure 10. The PLE spectra of KTMO samples with an orthorhombic structure that were recorded by monitoring the 545 nm emission of Tb<sup>3+</sup> are shown in Figure 11a. A broad excitation band at the 200–350 nm range and a group of sharp lines at



Figure 9. Temperature dependence of the conductivity in different crystallographic directions of the  $KTb(MoO_4)_2$  single crystal.



**Figure 10.** Photoluminescence emission ( $\lambda_{ex} = 380$  nm) spectra of  $\gamma$ -KTb(MoO<sub>4</sub>)<sub>2</sub> at room temperature for *ht*-KTb(MoO<sub>4</sub>)<sub>2</sub> annealed at 1143 K (1) and the KTb(MoO<sub>4</sub>)<sub>2</sub> crashed single crystal (2). The electronic transitions for the main emission peaks are indicated. All PL spectra were normalized on the initial *ht*-KTb(MoO<sub>4</sub>)<sub>2</sub> intensity value. Both samples are measured under the same conditions.

310–500 nm are visible on the PLE spectra. The influence of the treatment temperature on the PL spectra of *ht*-KTMO under excitation at the  ${}^{7}F_{6} \rightarrow {}^{5}D_{3}$  transition of Tb<sup>3+</sup> (~380 nm) is shown in Figure 11b.

PL spectra of  $\alpha$ -KTMO that was prepared by the solid-state reaction and those of KTMO with an orthorhombic KY(MoO<sub>4</sub>)<sub>2</sub>-type structure ( $\gamma$ -phase) that was prepared from  $\alpha$ -KTMO by annealing at 1273 K are presented in Figure 12a. Figure 12b summarizes the influence of synthesis routes, the structure, and annealing temperatures on the integral emission intensity of the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  Tb<sup>3+</sup> transition for KTMO.

# 4. DISCUSSION

We have investigated the influence of different synthesis routes and treatment conditions on the structure and luminescent properties of KTMO. Three methods used for KTMO preparation led to the following different results: the triclinic scheelite-type  $\alpha$ -phase was the result for the solid-state method, and the orthorhombic KY(MoO<sub>4</sub>)<sub>2</sub>-type  $\gamma$ -phase was obtained by using hydrothermal and Czochralski techniques.



**Figure 11.** (a) Photoluminescence spectra of  $\gamma$ -KTb $(MoO_4)_2$  with an orthorhombic KY $(MoO_4)_2$ -type structure at room temperature showing the excitation  $(\lambda_{em} = 545 \text{ nm})$  spectra of initial *ht*-KTb $(MoO_4)_2$  (1); *ht*-KTb $(MoO_4)_2$  annealed at 893 K (2), 1033 K (3), and 1143 K (4) and the crashed single crystal (5). (b) Emission  $(\lambda_{ex} = 380 \text{ nm})$  spectra of initial *ht*-KTb $(MoO_4)_2$  (1) and *ht*-KTb $(MoO_4)_2$  annealed at 893 K (2), 1033 K (3), and 1143 K (4). All intensities of the PLE spectra were normalized on the <sup>7</sup>F<sub>6</sub>  $\rightarrow$ <sup>5</sup>D<sub>4</sub> transition intensity of Tb<sup>3+</sup>. The inset shows the enlarged region of the  $f \rightarrow f$  transitions of Eu<sup>3+</sup>. All samples were measured under the same conditions.

The crystal structures of  $KR(MOO_4)_2$  (R = rare earth elements) can be separated into two extensive groups: a scheelite-type group and a nonscheelite  $KY(MOO_4)_2$ -type group.<sup>24,46,50</sup> Such a scheme was shown for the first time in ref 51. However, it was revised later.<sup>24,25,52,53</sup> The following three groups of scheelite-type modifications can be distinguished: (1) tetragonal or monoclinic phases with random distribution of K<sup>+</sup> and R<sup>3+</sup> cations,<sup>21,54–57</sup> (2) triclinic  $\alpha$ -phases (SG  $P\overline{1}$ ) with a  $\alpha$ -KEu(MoO<sub>4</sub>)<sub>2</sub>-type structure and ordered K<sup>+</sup> and R<sup>3+</sup> up to R = Dy,<sup>25,58–60</sup> and (3) monoclinic incommensurately modulated  $\beta$ -phases with complete<sup>25,52</sup> or partial<sup>53</sup> ordering of K<sup>+</sup> and R<sup>3+</sup> cations.

Earlier,<sup>61</sup> it was shown that *A*-site cation ordering in  $(A', A'')_{1-x}BO_4$  (B = Mo, W) scheelites depends on the ionic radii difference r(A') - r(A''). In KR(MoO<sub>4</sub>)<sub>2</sub> phases, the triclinic  $\alpha$ -phase with the scheelite-type structure appears for  $\Delta r = r(K) - r(R) < 0.49$  Å ( $\alpha$ -phase), while the incommensurately modulated  $\beta$ -phases appears to occur only for  $\Delta r \leq 0.45$  Å.<sup>24</sup> The formation of a  $\gamma$ -phase with the



**Figure 12.** (a) Photoluminescence emission spectra ( $\lambda_{ex} = 380 \text{ nm}$ ) of KTb(MoO<sub>4</sub>)<sub>2</sub> for  $\alpha$ -KTb(MoO<sub>4</sub>)<sub>2</sub> prepared by a solid state-reaction and annealed at 893 K (1), followed by quenching from 1273 K (2). The insets show the enlarged region normalized on the intensity emission spectra in the regions of the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition of Tb<sup>3+</sup> and the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of Eu<sup>3+</sup>. (b) Comparative intensity of the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  Tb<sup>3+</sup> emission integrated in the spectral region 540–555 nm of KTb(MoO<sub>4</sub>)<sub>2</sub> for the following: KTb(MoO<sub>4</sub>)<sub>2</sub> prepared by a solid-state reaction at 893 K (1), followed by annealing at 1273 K and quenching from 1273 (2); initial *ht*-KTb(MoO<sub>4</sub>)<sub>2</sub> (3); *ht*-KTb(MoO<sub>4</sub>)<sub>2</sub> annealed at 893 K (4), 1033 K (5), and 1143 K (6), followed by slow cooling to *T<sub>R</sub>*; *ht*-KTb(MoO<sub>4</sub>)<sub>2</sub> annealed at 1273 (7); and the KTb(MoO<sub>4</sub>)<sub>2</sub> crashed single crystal (8). All emission intensities were normalized on the *ht*-KTb(MoO<sub>4</sub>)<sub>2</sub> intensity value.

KY(MoO<sub>4</sub>)<sub>2</sub>-type structure starts from  $\Delta r = 0.457$  Å (R = Gd) and from 0.483 Å (Dy) to 0.491 Å (Y) for even higher  $\Delta r$  values.

The orthorhombic  $\gamma$ -KTMO structure is like other KY- $(MoO_4)_2$ -type phases.<sup>24,46,50</sup> The  $\gamma$ -phase KY $(MoO_4)_2$ -type structures are layered. They contain  $[TbMo_2O_8]$  layers from  $MoO_4$  tetrahedra and TbO<sub>8</sub> polyhedra, which are perpendicular to the *b*-axis (Figure 13). Two neighboring  $[TbMo_2O_8]$  layers are detached by a zigzag K<sup>+</sup>-layer. The distance between neighboring  $[TbMo_2O_8]$  layers varies from ~2.7 to ~5.6 Å. The Tb-O distances in the TbO<sub>8</sub> polyhedra vary from 2.192 to 2.550 Å (Table S4 of the Supporting Information).

The structure contains extensive 2D channels along the *c*-axis (~4.8 Å × ~4 Å) and along the *a*-axis (~5.6 Å × ~4 Å). The first six-membered channels are formed by the edge of the TbO<sub>8</sub> polyhedron and the O atoms of four MoO<sub>4</sub> tetrahedra (Figure 13a), while other eight-membered ones are formed by the edges of two TbO<sub>8</sub> polyhedra and four MoO<sub>4</sub> tetrahedra (Figure 13*b*). K<sup>+</sup> cations are located in these channels, and K<sup>+</sup> transport is possible in them.

pubs.acs.org/IC



**Figure 13.** (a) *ab*- and (b) *bc*-projection of the ht-KTb(MoO<sub>4</sub>)<sub>2</sub> structure. The O atoms are shown as small red spheres.

Two TbO<sub>8</sub> polyhedra share an O–O edge and form infinite  $[Tb_2O_{14}]_n$  chains, where the Tb–Tb distance in the chains is 4.009 Å. The distance between the chains is 5.093 Å (Figure 14a). The MoO<sub>4</sub> tetrahedra separate neighboring  $[Tb_2O_{14}]_n$  chains. So, the Tb<sup>3+</sup> ordering in the  $\gamma$ -phase is 1D. In the zigzag K<sup>+</sup>-layer, each K<sup>+</sup> ion is surrounded by six other K<sup>+</sup> ions. The K<sup>+</sup>-K<sup>+</sup> distances range from 4 × 4.802 Å to 2 × 5.093 Å (Figure 14b).

The difference between the  $\alpha$ - and *ht*-KTMO ( $\gamma$ -KTMO) structures can be better understood by considering the surrounding of Tb<sup>3+</sup> by neighboring Tb<sup>3+</sup> cations (Figure 15). Six Tb<sup>3+</sup> cations form six-membered rings in the  $\alpha$ -KTMO structure with Tb<sup>3+</sup>-Tb<sup>3+</sup> distances in the range of 3.84–3.96 Å. The Tb<sup>3+</sup> layer can be represented as being constructed from these rings, and a 2D Tb<sup>3+</sup> network forms as a result (Figure 15a).

The possible assumption of K<sup>+</sup> ionic transport along the K<sup>+</sup> layers was confirmed by electrical conductivity measurements. The conductivity demonstrates strong anisotropy in different crystallographic directions over the temperature range from 773 to 1073 K, and linear dependences of  $\log \sigma(T)$  vs 1000/T



pubs.acs.org/IC

Article

Figure 14. (a)  $[TbMo_2O_8]$  and (b) K layers in the *ht*-KTb $(MoO_4)_2$  structure. The O atoms are shown as small red spheres.



Figure 15. Tb-layers in (a)  $\alpha$ - and (b) ht-KTb(MoO<sub>4</sub>)<sub>2</sub> structures.

were observed for all directions (Figure 9). The conductivity of KTMO increases with the increasing temperature from 773 to 1073 K along the *a*-direction from  $6.6 \times 10^{-4}$  S/cm to  $0.88 \times 10^{-2}$  S/cm, along the *b*-direction from  $3.7 \times 10^{-7}$  S/cm to  $2.5 \times 10^{-5}$  S/cm, and along the *c*-direction from  $2.5 \times 10^{-5}$  S/cm to  $2.7 \times 10^{-4}$  S/cm. Thus, the value of the conductivity along one of the directions is several orders of magnitude higher in comparison with that one along the other directions, and one

should speak rather of the 1D character of the K<sup>+</sup> ionic transport. A similar strong anisotropy of conductivity was observed for the single crystal of the K<sub>2</sub>Fe<sub>4</sub>O<sub>7</sub> superionic conductor in which the conductivity that along *a*-axis was two orders of magnitude higher than that along the *c*-axis, reaching  $3.5 \times 10^2$  S/cm at 298 K and  $5.0 \times 10^2$  S/cm at 773 K, respectively.<sup>62</sup>

Information about the transport properties of KR(MoO<sub>4</sub>)<sub>2</sub> (R = lanthanides), including the orthorhombic KY(MoO<sub>4</sub>)<sub>2</sub>type phases, is missing in the literature. The maximum conductivity of KTMO equals to  $\sigma = 0.88 \times 10^{-2}$  S/cm at T = 1073 K and is close to the K<sup>+</sup> ion conductivity of the polycrystalline K<sub>2</sub>Fe<sub>4</sub>O<sub>7</sub> sample (5.0 × 10<sup>-2</sup> S/cm at 298 K)<sup>62</sup> and K<sub>5</sub>Sb<sub>5</sub>P<sub>2</sub>O<sub>20</sub> (~10<sup>-3</sup> S/cm at 773 K).<sup>63</sup>

**4.1. Thermal Behavior.** The DSC study revealed that the thermal behavior of KTMO samples in the heating–cooling cycle depends on the synthesis routes (Figure 2 and 3). On the one hand, the melting and crystallization temperatures for the *ht*-KTMO sample are close to the same for those for  $\alpha$ -KTMO. The peaks at  $T_{\min} \sim 1254$  K (heating) and  $T_{\max} \sim 1212$  K (cooling) in the DSC curves for *ht*-KTMO correspond to the melting and crystallization of *ht*-KTMO, respectively, as well as that for  $\alpha$ -KTMO ( $T_{\min} \sim 1260$  K and  $T_{\max} \sim 1213.5$  K).

On the other hand the DSC heating—cooling curves of *ht*-KTMO exhibit additional peaks in comparison with those of  $\alpha$ -KTMO, including three effects at  $T_{\rm max} \sim 745$  K,  $T_{\rm min} \sim 1033$  K, and  $T_{\rm min} \sim 1238$  K on the heating curve and at  $T_{\rm min} \sim 1131$  K on the cooling one. At first sight, the  $\alpha \rightarrow \gamma$  phase transition (PT) is irreversible. However, the XRD investigation shows that the quenching of *ht*-KTMO from the temperature above the melting point to  $T_{\rm R}$  leads to the appearance of low-intensity reflections of the  $\alpha$ -phase on the XRD patterns (Figure 4). Thus, the endothermic first-order PT ( $T_{\rm min} \sim 1131$  K) observed on the DSC cooling curve is apparently due to the  $\gamma \rightarrow \alpha$  partial transition. This PT is reversible and kinetic in nature, similar to that for KGd(MoO<sub>4</sub>)<sub>2</sub>.<sup>24</sup>

The nature of other additional peaks is unknown, but the orthorhombic structure does not change under different treatment temperatures and cooling conditions (Table S1 of the Supporting Information). The sample mass decreases insignificantly (~0.5%) with the increasing annealing temperature up to 1273 K.

**4.2. Element Composition and Grain and Crystallite Sizes.** The element composition for our samples prepared by different synthesis routes is close to that of the nominal  $\text{KTb}(\text{MoO}_4)_2$  (Table S2 of the Supporting Information). The experimental effective magnetic moment of 9.625(3)  $\mu_B$  that was calculated from magnetic susceptibility measurements indicates Tb<sup>3+</sup> (Figure 7).

Granulometric curves characterize a different grain size distribution for samples prepared by the solid-state reaction and those prepared by hydrothermal methods (Figure S4 of the Supporting Information). The bimodal particle size distribution was found for  $\alpha$ -KTMO (14 ± 2 (major peak) and 1 ± 0.4  $\mu$ m;  $D_{10}:D_{50}:D_{90} = <1 \,\mu$ m:<9  $\mu$ m:<22  $\mu$ m), while *ht*-KTMO was characterized by a trimodal one (8.5 ± 1.5 (major peak), 1 ± 0.4, and 50 ± 12  $\mu$ m;  $D_{10}:D_{50}:D_{90} = <0.7 \,\mu$ m:<6.5  $\mu$ m:<25  $\mu$ m). Thus, the solid-state method results in more large particles in the main fraction of the sample (65% more) compared to the hydrothermal method.

XRD line broadening measurements revealed the influence of heating and cooling conditions on the average crystallite size of orthorhombic KTMO. The crystallite size value increased with the increase in treatment temperature and slow cooling (Figure 5b, Figure S6 of the Supporting Information). The average crystallite size increased almost three times with the increased treatment temperature from 473 to 1143 K. In contrast, heating to the melting at 1273 K and quenching to  $T_{\rm R}$  or the temperature of liquid N<sub>2</sub> leads to a decrease in the crystallite size.

4.3. Luminescent Properties. The PLE spectra of KTMO samples with an orthorhombic  $KY(MoO_4)_2$ -type structure at  $\lambda_{\rm em}$  = 545 nm exhibit a broad band at 200–350 nm and a group of narrow lines at 350–500 nm (Figure 11a). The broad band is attributed to O  $2p \rightarrow Mo$  4d charge transfer from a ligand to metal transition within the  $MoO_4^{2-}$  groups.<sup>64</sup> The excitation spectrum of the initial *ht*-KTMO exhibits a large contribution of the charge transfer band (CT band) due to the high efficiency of the energy transfer mechanism between the host and the emitting  ${\rm Tb}^{3+}$  ions in comparison with that of direct excitation. However, the CT band intensity dramatically decreases with the increase in the ht-KTMO treatment temperature, and it is the lowest for the crashed single crystal. Apparently, the annealing temperature influences the relative intensity of the  $f \rightarrow f$  and CT transitions (Figure 11a). The particles size increases as the annealing temperature increases (Figure 5b). It is reasonable to suppose that the absorption rate of incident radiation rises accordingly with the increase in crystallite size that is more essential for forbidden  $f \rightarrow f \text{ Tb}^{3+}$ transitions than for fundamental absorption in the CT band, which is usually characterized by high absorption coefficients up to  $10^6$  cm<sup>-1</sup>. However, there are also other effects, influencing luminescence intensity, as will be shown below.

At the 360-500 nm wavelength, the group of excitation bands on the PLE spectra at 351, 359, 370, 379, and 488 nm are ascribed to transitions from <sup>7</sup>F<sub>6</sub> to different excited terms within Tb<sup>3+</sup>. The presence of a low-intensity excitation band at 395 nm, which corresponds to  ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$  transitions in Eu<sup>3+</sup> ions in the excitation spectrum of the Tb<sup>3+</sup> emission, points out the energy transfer (ET) from Eu<sup>3+</sup> to Tb<sup>3+</sup> (Figure 11a, inset). PL spectra under an excitation of 380 nm show several groups of sharp lines that are ascribed to the respective  ${}^{5}D_{4} \rightarrow {}^{7}F_{I}$  (J = 3-6) transitions of Tb<sup>3+</sup> ions, with the most prominent peak at 545 nm in the spectral region of 480-720 nm (Figure 12a). The band at  $\sim$ 613 nm can be associated with the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  electric dipole transition of Eu<sup>3+</sup>. It indicates Eu<sup>3+</sup> ion traces in nominally Eu-free samples. The absence of the excitation peak at 395 nm and the much lower intensity of the emission peak at 613 nm in a crashed single crystal indicates a lower concentration of Eu<sup>3+</sup> contaminating impurities in this sample.

It should be noted that the intensive emission of Eu<sup>3+</sup> was observed under excitation at 380 nm that corresponds to  ${}^{7}F_{6} \rightarrow {}^{5}D_{3}$  transitions in Tb<sup>3+</sup>. Therefore, we can suppose the existence of ET between Tb<sup>3+</sup> and Eu<sup>3+</sup> ions as well as the O–Mo CT transition. Thus, Tb<sup>3+</sup> ions can be an excitation energy donor in the KTMO host. Further, Tb<sup>3+</sup> transferred energy to acceptor Eu<sup>3+</sup> ions.

The energy of the  ${}^{7}F_{6} \rightarrow {}^{5}D_{3}$  Tb<sup>3+</sup> transition is higher than those of the  ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$  and  ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$  Eu<sup>3+</sup> transitions. As a result, the ET from Tb<sup>3+</sup> to Eu<sup>3+</sup> through nonradiative processes is possible. Moreover, the energy of the  ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 3-6) emission of Tb<sup>3+</sup> ions corresponds to the energy of the  ${}^{7}F_{0,1} \rightarrow {}^{5}D_{J}$  (J = 0-2) absorption of Eu<sup>3+</sup>. Therefore, the Tb<sup>3+</sup>  $\rightarrow$  Eu<sup>3+</sup> ET is efficient in general. Earlier, the efficient ET from Tb<sup>3+</sup> to Eu<sup>3+</sup> based on a dipole-dipole mechanism was The influence of the thermal treatment on the PL spectra of *ht*-KTMO under excitation at the  ${}^{7}F_{6} \rightarrow {}^{5}D_{3}$  transition of Tb<sup>3+</sup> (~380 nm) was studied (Figure 11b). PL spectra of  $\alpha$ -KTMO and KTMO with an orthorhombic KY(MoO<sub>4</sub>)<sub>2</sub>-type structure ( $\gamma$ -phase), which was prepared from  $\alpha$ -KTMO by annealing at 1273 K, are presented in Figure 12a. Figure 12b summarizes the influence of preparation conditions, the structure, and annealing temperatures on the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition band integral intensity for Tb<sup>3+</sup> emission in KTMO ( $\lambda_{ex} = 380$  nm). The maximum was found for the KTMO crashed single crystal.

As it can be seen in Figure 5b, increasing the treatment temperature of ht-KTMO from 473 to 1143 K, followed by slow cooling, leads to an increase of the average crystallite size from 50  $\pm$  10 to 130  $\pm$  5 nm. As a result, the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  Tb<sup>3+</sup> emission intensity increases ~15 times (Figure 12b). However, heating above the melting point (Figures 2 and 3) at 1273 K and changing the cooling conditions from slow cooling to quenching to  $T_{\rm R}$  leads to an insignificant increase in the  ${}^{\rm 5}D_4 \rightarrow$  ${}^{7}F_{5}$  Tb<sup>3+</sup> emission intensity (Figure 12b), while the crystallite size decreases to almost half from 130 to  $60 \pm 5$  nm (Figure 5b). Moreover, the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  Tb<sup>3+</sup> emission intensity of  $\gamma$ phases prepared from different precursors ( $\alpha$ -phase and ht-KTMO) by melting at 1273 K, followed by quenching to  $T_{\rm R}$  or the temperature of liquid N<sub>2</sub>, was almost the same despite the fact that differences in the crystallite size were observed (Figure 5b). The average crystallite sizes of the samples melted at 1273 K (60  $\pm$  5 and 80  $\pm$  10 nm) are close to those of *ht*-KTMO annealed at 773 K (70  $\pm$  10 nm) and 893 K (85  $\pm$  5 nm), but the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5} Tb^{3+}$  emission intensity differs significantly (Figure 12b). As it can be seen in Figure 12b, the intensity of the brightest sample (treatment temperature of 1273 K) is approximately four times lower than of the crashed single crystal sample. The higher emission intensity of the latter sample most likely results from the lower concentration of structural defects. Thus, despite the fact that an increase of the annealing temperature leads concomitantly to an increase of the crystallite size and, as a consequence, an increase in the luminescence intensity, it is more correct to say that a higher temperature leads to a decrease in the number of structural defects, especially during melting. It also manifests in the white color of the crashed single crystal sample (colorless transparent crystal), while samples synthesized by hydrothermal and solidstate methods have a beige color (Table S2 of the Supporting Information). Nevertheless, the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5} Tb^{3+}$  emission integral intensity for the  $\alpha$ -phase is ~12 times higher than for the *ht*-KTMO, although the color of the samples is almost the same. The conditions of the hydrothermal experiment are much softer than those for the solid-state synthesis, which apparently leads to a larger number of structural defects in the ht-KTMO.

Earlier, the effect of the treatment temperature and the Eu<sup>3+</sup> concentration on the luminescent properties was found for the NaBi(MoO<sub>4</sub>)<sub>2</sub>:Eu<sup>3+</sup> phosphors.<sup>28</sup> It was shown that grain diameters of the samples increase with the calcination temperature from 973 to 1073 K in the following way: ~7  $\mu$ m at 973 K, 12  $\mu$ m at 1023 K, and 15  $\mu$ m at 1073 K. Simultaneously, the maximum of the red emission intensity (618 nm) was obtained after heating at 1023 K, while higher calcination temperatures led to an insignificant intensity reduction. The relative emission intensity of AEu(MoO<sub>4</sub>)<sub>2</sub>:

(A = Li, Na, and Ag) phosphors increased continuously with increasing of annealing temperatures from 773 to 1173 K, while the red emission line (616 nm) intensity from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition for KEu(MoO<sub>4</sub>)<sub>2</sub> reached a maximum at 1073 K.<sup>29</sup> The calcination temperature slightly influences the position of the peaks and the profile of the NaLa(MoO<sub>4</sub>)<sub>2</sub>:Tb<sup>3+</sup> PL spectra. However, it greatly influences the intensity of the main emission peak at 544 nm, which increases with increasing treatment temperature from 973 to 1173 K.<sup>31</sup> The higher calcination temperature yields better crystallization and a larger particle size.<sup>31</sup>

As demonstrated in Figure 12a, the  $\alpha \rightarrow \gamma$  phase transition practically does not change the intensity of the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  Tb<sup>3+</sup> transition. Thus, the difference in the ordering of the Tb<sup>3+</sup> cations in the triclinic  $\alpha$ -phase and the orthorhombic  $\gamma$ -phase (Figure 15) structures does not practically affect the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ luminescence intensity. Nevertheless, the  $\alpha \rightarrow \gamma$  phase transformation results in the band number changing in the PL spectra. Sharp lines in the region of 610–625 nm are connected with the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions in Eu<sup>3+</sup>, which was accidently incorporated into the KTMO samples (Figure 12a). PL spectra at the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition range for KTMO:Eu samples are similar to the PL spectra for KGd<sub>1-x</sub>Eu<sub>x</sub>(MoO<sub>4</sub>)<sub>2</sub> with triclinic scheelite-type and orthorhombic structures.<sup>24</sup>

Previously, we have shown the relation between the structure and photoluminescent properties of the  $\alpha$ - and  $\beta$ -modifications in KEu(MoO<sub>4</sub>)<sub>2</sub>.<sup>25</sup> It was revealed that a layered network of Eu<sup>3+</sup> ions in the  $\alpha$ -phase demonstrates a better luminescence intensity in comparison with 3D Eu<sup>3+</sup> ion framework in the  $\beta$ -phase. The  $\alpha \rightarrow \beta$  PT causes modifications in the splitting of the <sup>7</sup>F<sub>2</sub> multiplet.<sup>25</sup> However, the study of the Eu<sup>3+</sup> concentration dependence and tempering conditions on the KGd<sub>1-x</sub>Eu<sub>x</sub>(MoO<sub>4</sub>)<sub>2</sub> structure allows us to conclude that the  $\beta$ -KGd<sub>0.4</sub>Eu<sub>0.6</sub>(MoO<sub>4</sub>)<sub>2</sub> phosphor (synthesized at 1173 K) shows the most intensive red emission in the KGd<sub>1-x</sub>Eu<sub>x</sub>(MoO<sub>4</sub>)<sub>2</sub> series.<sup>24</sup>

#### 5. CONCLUSION

The influence of synthesis routes and treatment conditions on the structure and luminescent properties of KTMO is revealed. The following three different synthesis methods were used for the KTMO preparation: the solid-state method, the hydrothermal method, and the Czochralski (CZ) technique. These methods led to different results. The triclinic scheelite-type  $\alpha$ phase is the result for the solid-state method, and the orthorhombic  $KY(MoO_4)_2$ -type  $\gamma$ -phase is the result for the hydrothermal and Czochralski techniques. Triclinic  $\alpha$ -KTMO transforms into the orthorhombic  $\gamma$ -phase by heating at 1273 K above the melting point, while KTMO prepared by the hydrothermal method does not show any phase transitions. Differences between the thermal behavior of KTMO prepared by the solid-state and hydrothermal methods was shown by the DSC study. The influence of heating and cooling conditions on the average crystallite size of orthorhombic KTMO was revealed from XRD line broadening measurements using a Debye-Scherrer equation. The magnetic susceptibility and the electrical conductivity were measured on a  $KTb(MoO_4)_2$ single crystal. The experimental effective magnetic moment of 9.625(3)  $\mu_{\rm B}$  corresponds to the expected value for Tb<sup>3+</sup>  $(9.50 - 9.72 \ \mu_{\rm B}).$ 

The orthorhombic structure of KTMO prepared by the hydrothermal method was refined using synchrotron powder X-ray diffraction data. The structure is layered and contains  $[TbMo_2O_8]$  layers perpendicular to the *b*-direction, and two adjacent  $[TbMo_2O_8]$  layers are divided by a zigzag K<sup>+</sup> layer. K<sup>+</sup> cations are located in the extensive 2D channels along the *c*-axis. The possibility of K<sup>+</sup> ionic transport along the K<sup>+</sup> layers was confirmed by electrical conductivity measurements. Strong anisotropy in different crystallographic directions over the temperature range from 773 to 1073 K was revealed, and the conductivity value along one of the directions in the crystal was one or two times higher than those along the other directions. Luminescent properties as a result of synthesis routes and heating and cooling conditions were studied and compared with the data for the average crystallite size calculation and the grain size determination.

The photoluminescence emission spectra of all samples exhibit an intense green emission at 545 nm due to the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  Tb<sup>3+</sup> transition. The emission intensity maximum of the  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition ( $\lambda_{ex} = 380$  nm) was found for the KTMO crashed single crystal. The presence of an emission band at ~613 nm on the PL spectrum is associated with the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  Eu<sup>3+</sup> transition. It indicates the presence of Eu<sup>3+</sup> ion traces in nominally Eu-free samples that were obtained by the solid-state and hydrothermal methods. Thus, the effective Tb<sup>3+</sup>  $\rightarrow$  Eu<sup>3+</sup> energy transfer was found, and terbium ions can be an excitation energy donor in the KTMO host. Further, Tb<sup>3+</sup> transferred energy to an acceptor Eu<sup>3+</sup> ion.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00597.

Unit cell parameters for different preparations of  $KTb(MoO_4)_2$ ; image of the  $KTb(MoO_4)_2$  crystal plate; EDX spectra and analysis results of different preparations of  $KTb(MoO_4)_2$ ; SEM images of  $KTb(MoO_4)_2$ ; particle size distributions of  $KTb(MoO_4)_2$ ; unit cell parameters of *ht*-KTb(MoO\_4)\_2 versus the annealing temperature; depence of the crystallite size on the XRD patters, fraction atomic coordinates, isotropic atomic displacement parameters, and selected distances for  $\gamma$ -KTb(MoO<sub>4</sub>)<sub>2</sub>; and impedance spectra of KTb-(MoO<sub>4</sub>)<sub>2</sub> (PDF)

### **Accession Codes**

CCDC 2065395 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

### **Corresponding Author**

Dina V. Deyneko – Chemistry Department, Moscow State University, 119991 Moscow, Russia; O orcid.org/0000-0002-9422-1925; Phone: +74959392138; Email: deynekomsu@gmail.ru

#### Authors

Vladimir A. Morozov – Chemistry Department, Moscow State University, 119991 Moscow, Russia; © orcid.org/0000-0002-0674-2449

Svetlana M. Posokhova – Chemistry Department, Moscow State University, 119991 Moscow, Russia

- Sergey Ya. Istomin Chemistry Department, Moscow State University, 119991 Moscow, Russia
- Aleksandra A. Savina Skolkovo Institute of Science and Technology, 121205 Moscow, Russia; Orcid.org/0000-0002-7108-8535
- Boris S. Redkin Institute of Solid State Physics of the Russian Academy of Sciences (ISSP RAS), 142432 Chernogolovka, Russia
- Nikolay V. Lyskov Institute of Problems of Chemical Physics of the Russian Academy of Sciences (IPCP RAS), 142432 Chernogolovka, Russia
- Dmitry A. Spassky Skobeltsyn Institute of Nuclear Physics, Moscow State University, 119991 Moscow, Russia; Institute of Physics, University of Tartu, 50411 Tartu, Estonia
- Alexei A. Belik International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan;
  orcid.org/0000-0001-9031-2355
- Bogdan I. Lazoryak Chemistry Department, Moscow State University, 119991 Moscow, Russia; © orcid.org/0000-0003-1952-5555

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.1c00597

#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We acknowledge the support of the Russian Foundation for Basic Research through Grant 18-03-00611. This research was performed according to the Development program of the Interdisciplinary Scientific and Educational School of Lomonosov Moscow State University "The future of the planet and global environmental change". The research was carried out within the task of ISSP RAS. The synchrotron radiation experiments were performed at SPring-8 with the approval of the NIMS Synchrotron X-ray Station (proposal no. 2020A4501). We thank Dr. M. Tanaka and Dr. Y. Katsuya for their help at SPring-8. D.S. is grateful for financial support of the Estonian Research Council, project PUT PRG111.

#### REFERENCES

(1) Evans, R. C.; Carlos, L. D.; Douglas, P.; Rocha, J. Tuning the emission color in mixed lanthanide microporous silicates: energy transfer, composition and chromaticity. *J. Mater. Chem.* **2008**, *18*, 1100–1107.

(2) Evans, R. C.; Douglas, P.; Winscom, C. J. Coordination complexes exhibiting room-temperature phosphorescence: Evaluation of their suitability as triplet emitters in organic light emitting diodes. *Coord. Chem. Rev.* **2006**, *250*, 2093–2126.

(3) He, G.; Guo, D.; He, C.; Zhang, X.; Zhao, X.; Duan, C. A colortunable europium complex emitting three primary colors and white light. *Angew. Chem., Int. Ed.* **2009**, *48*, 6132–6135.

(4) Peng, H.; Stich, M. I. J.; Yu, J. B.; Sun, L.-N.; Fischer, L. H.; Wolfbeis, O. S. Luminescent europium(III) nanoparticles for sensing and imaging of temperature in the physiological range. *Adv. Mater.* **2010**, *22*, 716–719.

(5) Sun, L.-N.; Yu, J.; Peng, H.; Zhang, J. Z.; Shi, L.-Y.; Wolfbeis, O. S. Temperature-sensitive luminescent nanoparticles and films based on a terbium (III) complex probe. *J. Phys. Chem. C* **2010**, *114*, 12642–12648.

(6) Jüstel, T.; Nikol, H.; Ronda, C. New developments in the field of luminescent materials for lighting and displays. *Angew. Chem., Int. Ed.* **1998**, *37*, 3084–3103.

(7) Feldmann, C.; Jüstel, T.; Ronda, C. R.; Schmidt, P. J. Inorganic luminescent materials: 100 years of research and application. *Adv. Funct. Mater.* **2003**, *13*, 511–516.

(8) Xie, R. J.; Hirosaki, N. Silicon-based oxynitride and nitride phosphors for white LEDs—A review. *Sci. Technol. Adv. Mater.* **2007**, *8*, 588–600.

(9) Wang, J. W.; Tanner, P. A. Upconversion for white light generation by a single compound. *J. Am. Chem. Soc.* **2010**, *132*, 947–949.

(10) Smet, P. F.; Parmentier, A. B.; Poelman, D. Selecting conversion phosphors for white light-emitting diodes. *J. Electrochem. Soc.* **2011**, *158*, R37–R54.

(11) George, N. C.; Denault, K. A.; Seshadri, R. Phosphors for solidstate white lighting. *Annu. Rev. Mater. Res.* **2013**, *43*, 481–501.

(12) Pust, P.; Schmidt, P. J.; Schnick, W. A revolution in lighting. *Nat. Mater.* **2015**, *14*, 454–458. Xia, Z.; Liu, Q. Progress in discovery and structural design of color conversion phosphors for LEDs. *Prog. Mater. Sci.* **2016**, *84*, 59–117.

(13) Yam, F. K.; Hassan, Z. Innovative advances in LED technology. *Microelectron. J.* **2005**, *36*, 129–137.

(14) Nakamura, S.; Senoh, M.; Mukai, T. High-power lnGaN/GaN double-heterostructure violet light emitting diodes. *Appl. Phys. Lett.* **1993**, *62*, 2390–2392.

(15) Nakamura, S.; Mukai, T.; Senoh, M. Candela-class highbrightness InGaN/AIGaN double-heterostructure blue-light-emitting diodes. *Appl. Phys. Lett.* **1994**, *64*, 1687–1689.

(16) Nakamura, S.; Fasol, G. The Blue Laser Diodes: GaN Based Blue Light Emitters and Lasers. Springer, Berlin, Germany, 1997; p 216.

(17) Kim, T.; Kang, S. Potential red phosphor for UV-white LED device. J. Lumin. 2007, 122–123, 964–966.

(18) Haque, M. M.; Lee, H.-I.; Kim, D.-K. Luminescent properties of Eu<sup>3+</sup>-activated molybdate-based novel red-emitting phosphors for LEDs. *J. Alloys Compd.* **2009**, *481*, 792–796.

(19) Thangaraju, D.; Durairajan, A.; Balaji, D.; Moorthy Babu, S.; Hayakawa, Y. Novel  $KGd_{1-(x+y)}Eu_xBi_y(W_{1-z}Mo_zO_4)_2$  nanocrystalline red phosphors for tricolor white LEDs. *J. Lumin.* **2013**, *134*, 244–250.

(20) Wang, H.; Yang, T.; Feng, L.; Ning, Z.; Liu, M.; Lai, X.; Gao, D.; Bi, J. Energy transfer and multicolor tunable luminescence properties of  $NaGd_{0.5}Tb_{0.5-x}Eu_x(MoO_4)_2$  phosphors for UV-LED. J. Electron. Mater. **2018**, 47, 6494–6505.

(21) Cavalli, E.; Zannoni, E.; Mucchino, C.; Carozzo, V.; Toncelli, A.; Tonelli, M.; Bettinelli, M. Optical spectroscopy of Nd<sup>3+</sup> in KLa(MoO<sub>4</sub>)<sub>2</sub> crystals. *J. Opt. Soc. Am. B* **1999**, *16*, 1958–1965.

(22) Feng, J.; Xu, J.; Zhu, Z.; Wang, Y.; You, Z.; Li, J.; Wang, H.; Tu, C. Spectroscopic properties and orthogonally polarized dual-wavelength laser of  $Yb^{3+}:NaY(WO_4)_2$  crystals with high  $Yb^{3+}$  concentrations. *J. Alloys Compd.* **2013**, *566*, 229–234.

(23) Zhang, L.; Sun, S.; Lin, Z.; Lin, H.; Zhang, G.; Mateos, X.; Serres, J. M.; Aguilo, M.; Diaz, F.; Loiko, P.; Wang, Y.; Griebner, U.; Petrov, V.; Vilejshikova, E.; Chen, W. Crystal growth, spectroscopy and first laser operation of a novel disordered tetragonal Tm:Na<sub>2</sub>La<sub>4</sub>(WO<sub>4</sub>)<sub>7</sub> tungstate crystal. *J. Lumin.* **2018**, 203, 676–682. (24) Morozov, V. A.; Posokhova, S. M.; Deyneko, D. V.; Savina, A. A.; Morozov, A. V.; Tyablikov, O. A.; Redkin, B. S.; Spassky, D. A.; Hadermann, J.; Lazoryak, B. I. Influence of annealing conditions on the structure and luminescent properties of KGd<sub>1-x</sub>Eu<sub>x</sub>(MoO<sub>4</sub>)<sub>2</sub> (0 ≤  $x \le 1$ ). *CrystEngComm* **2019**, 21, 6460–6471.

(25) Morozov, V. A.; Arakcheeva, A. V.; Pattison, P.; Meert, K. W.; Smet, P. F.; Poelman, D.; Gauquelin, N.; Verbeeck, J.; Abakumov, A. M.; Hadermann, J. KEu( $MoO_4$ )<sub>2</sub>: Polymorphism, Structures and Luminescent Properties. *Chem. Mater.* **2015**, *27*, 5519–5530.

(26) Xie, A.; Yuan, X.; Wang, F.; Shi, Y.; Li, J.; Liu, L.; Mu, Z. Synthesis and luminescent properties of Eu<sup>3+</sup>-activated molybdatebased novel red-emitting phosphors for white LEDs. *J. Alloys Compd.* **2010**, *501*, 124–129.

(27) Durairajan, A.; Suresh Kumar, J.; Thangaraju, D.; Valente, M. A.; Moorthy Babu, S. Photoluminescence properties of sub-micron  $NaGd_{1-x}Eu_x(WO_4)_2$  red phosphor for solid state lightings application:

Derived by different synthesis routes. *Superlattices Microstruct.* 2016, 93, 308-321.

(28) Gan, Y.; Liu, W.; Zhang, W.; Li, W.; Huang, Y.; Qiu, K. Effects of  $Gd^{3+}$  codoping on the enhancement of the luminescent properties of a NaBi(MoO<sub>4</sub>)<sub>2</sub>: Eu<sup>3+</sup> red-emitting phosphors. *J. Alloys Compd.* **2019**, 784, 1003–1010.

(29) Guo, C.; Wang, S.; Chen, T.; Luan, L.; Xu, Y. Preparation of phosphors  $AEu(MoO_4)_2$  (A = Li, Na, K and Ag) by sol-gel method. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *94*, 365–371.

(30) Li, T.; Guo, C.; Wu, Y.; Li, L.; Jeong, J. H. Green upconversion luminescence in  $Yb^{3+}/Er^{3+}$  co-doped  $ALn(MoO_4)_2$  (A = Li, Na and K; Ln = La, Gd and Y). J. Alloys Compd. **2012**, 540, 107–112.

(31) Zhai, Y.; Li, J.; Li, X.; Dong, Y.; Wang, Y.; Song, S. Synthesis and luminescent properties of NaLa $(MoO_4)_2$ : Eu<sup>3+</sup>, Tb<sup>3+</sup> phosphors by microwave-assisted sol-gel method. *J. Sol-Gel Sci. Technol.* **2015**, 74, 544–549.

(32) Gu, J.; Zhu, Y.; Li, H.; Zhang, X.; Qian, Y. Uniform  $Ln^{3+}$  (Eu<sup>3+</sup>,  $Tb^{3+}$ ) doped NaLa(WO<sub>4</sub>)<sub>2</sub> nanocrystals: Synthesis, characterization, and optical properties. *J. Solid State Chem.* **2010**, *183*, 497–503.

(33) Hou, L.; Cui, S.; Fu, Z.; Wu, Z.; Fu, X.; Jeong, J. H. Facile template free synthesis of  $KLa(MoO_4)_2:Eu^{3+}$ ,  $Tb^{3+}$  microspheres and their multicolor tunable luminescence. *Dalton Trans.* **2014**, *43*, 5382–5392.

(34) Liu, Y.; Ma, S.; Zuo, H.; Li, J.; Shi, X.; Zhao, M. DTA-assisted hydrothermal synthesis of  $KLa(MOO_4)_2$ :Eu<sup>3+</sup> microcrystals and their luminescence properties. *Ceram. Int.* **2016**, *42*, 16499–16504.

(35) Guo, W.; Chen, Y.; Lin, Y.; Gong, X.; Luo, Z.; Huang, Y. Spectroscopic analysis and laser performance of Tm<sup>3+</sup>:NaGd(MoO<sub>4</sub>)<sub>2</sub> crystal. *J. Phys. D: Appl. Phys.* **2008**, *41*, 115409.

(36) Chen, Y. J.; Lin, Y. F.; Guo, W. J.; Gong, X. H.; Huang, J. H.; Luo, Z. D.; Huang, Y. D. Efficient  $1.9\mu m$  monolithic  $Tm^{3+}$ :NaLa- $(MoO_4)_2$  micro-laser. Laser Phys. Lett. **2012**, 9, 141–144.

(37) Morozov, V.; Arakcheeva, A.; Redkin, B.; Sinitsyn, V.; Khasanov, S.; Kudrenko, E.; Raskina, M.; Lebedev, O.; Van Tendeloo, G.  $Na_{2/7}Gd_{4/7}MoO_4$ : a Modulated Scheelite-Type Structure and Conductivity Properties. *Inorg. Chem.* **2012**, *51*, 5313–5324.

(38) Tian, Y.; Chen, B.; Hua, R.; Sun, J.; Cheng, L.; Zhong, H.; Li, X.; Zhang, J.; Zheng, Y.; Yu, T.; Huang, L.; Yu, H. Optical transition, electron-phonon coupling and fluorescent quenching of  $La_2(MoO_4)_3$ :Eu<sup>3+</sup> phosphor. J. Appl. Phys. **2011**, 109, 053511.

(39) Dillip, G. R.; Deva Prasad Raju, B. A study of the luminescence in near UV-pumped red-emitting novel  $Eu^{3+}$ -doped  $Ba_3Ca_3(PO_4)_4$ phosphors for white light emitting diodes. *J. Alloys Compd.* **2012**, 540, 67–74.

(40) Huang, J.; Li, Q.; Wang, J.; Jin, L.; Tian, B.; Li, C.; Shi, Y.; Wang, Z.; Hao, J. Controllable synthesis of lanthanide  $Yb^{3+}$  and  $Er^{3+}$  co-doped AWO<sub>4</sub> (A = Ca, Sr, Ba) micro-structured materials: phase, morphology and up-conversion luminescence enhancement. *Dalton Trans.* **2018**, *47*, 8611–8618.

(41) Le Bail, A.; Duroy, H.; Fourquet, J. L. Ab-initio structure determination of LiSbWO<sub>6</sub> by X-ray powder diffraction. *Mater. Res. Bull.* **1988**, 23, 447–452.

(42) Petricek, V.; Dusek, M.; Palatinus, L. Crystallographic Computing System JANA2006: General features. Z. Kristallogr. - Cryst. Mater. 2014, 229, 345–352.

(43) Scherrer, P. Bestimmung der größe und der inneren struktur von kolloidteilchen mittels Röntgenstrahlen. *Göttinger Nachrichten Math. Phys.* **1912**, *2*, 387–409.

(44) Tanaka, M.; Katsuya, Y.; Yamamoto, A. A new large radius imaging plate camera for high-resolution and high-throughput synchrotron X-ray powder diffraction by multiexposure method. *Rev. Sci. Instrum.* **2008**, *79*, 075106.

(45) Tanaka, M.; Katsuya, Y.; Matsushita, Y.; Sakata, O. Development of a synchrotron powder diffractometer with a one-dimensional X-ray detector for analysis of advanced materials. *J. Ceram. Soc. Jpn.* **2013**, *121*, 287–290. (46) Klevtsova, R. F.; Borisov, S. V. X-ray diffraction studies of  $KY(MoO_4)_2$  double molybdate. *Dokl. Acad. Nauk SSSR* **1967**, 177, 1333–1336. This article is in Russian.

(47) Taira, N.; Hinatsu, Y. Magnetic properties of silver lanthanide molybdates AgLnMo<sub>2</sub>O<sub>8</sub> (Ln ~ lanthanide). *J. Mater. Chem.* **2002**, *12*, 148–152.

(48) Impedance Spectroscopy, Theory, Experiment and Applications, 2nd ed.; Barsoukov, E., Macdonald, J. R., Eds.; Wiley Interscience, New York, NY, 2005.

(49) Boukamp, B. A. A Nonlinear Least Squares Fit procedure for analysis of immittance data of electrochemical systems. *Solid State Ionics* **1986**, *20*, 31–44.

(50) Volokitina, A.; Loiko, P.; Vilejshikova, E.; Mateos, X.; Dunina, D.; Kornienko, A.; Kuleshov, N.; Pavlyuk, A.  $Eu^{3+}$ :KY(MoO<sub>4</sub>)<sub>2</sub>: A novel anisotropic red-emitting material with a layered structure. *J. Alloys Compd.* **2018**, *762*, 786–796.

(51) Klevtsov, P. V.; Klevtsova, R. F. Polymorphism of the double molybdates and tungstates of mono- and trivalent metals with the composition  $M^+R^{3+}(EO_4)_2$ . J. Struct. Chem. **1977**, 18, 339–355.

(52) Morozov, V. A.; Arakcheeva, A. V.; Chapuis, G.; Guiblin, N.; Rossell, M. D.; Van Tendeloo, G.  $KNd(MoO_4)_2$ : A New Incommensurate Modulated Structure in the Scheelite Family. *Chem. Mater.* **2006**, *18*, 4075–4082.

(53) Arakcheeva, A.; Pattison, P.; Chapuis, G.; Rossell, M.; Filaretov, A.; Morozov, V.; Van Tendeloo, G.  $KSm(MoO_4)_2$ , an incommensurately modulated and partially disordered scheelite-like structure. *Acta Crystallogr., Sect. B: Struct. Sci.* **2008**, *64*, 160–171.

(54) Klevtsov, P. V.; Kozeeva, L. P.; Pavlyuk, A. A. Polymorphism and crystallization of potassium-rare earth element molybdates  $KLn(MoO_4)_2$  (Ln = La, Ce, Pr and Nd). *Crystallog. Rep.* **1975**, 20, 1216–1220. This article is in Russian.

(55) Cavalli, E.; Meschini, C.; Toncelli, A.; Tonelli, M.; Bettinelli, M. Optical spectroscopy of  $Tm^{3+}$  doped in KLa(MoO<sub>4</sub>)<sub>2</sub> crystals. *J. Phys. Chem. Solids* **1997**, *58*, 587–595.

(56) Zhang, H. J.; Fu, L.; Wang, C.-P.; Fu, H.-F.; Xie, W.-G. Crystal structure of Scheelite-type potassium cerium bis(tetraoxomolybdate-(VI)),  $KCe(MoO_4)_2$ . Z. Kristallogr. - New Cryst. Struct. **2014**, 229, 191–192.

(57) Terebilenko, K. V.; Bychkov, K. L.; Klymyshyna, K. E.; Baumer, V. N.; Slobodyanik, M. S.; Khomenko, E. V.; Dotsenko, V. P. Single crystals of KRE( $MoO_4$ )<sub>2</sub>, (RE - Ce, Pr) obtained from fluorides: scheelite-related Structure and luminescence. *Cryst. Res. Technol.* **2017**, *52*, 1700222.

(58) Klevtsova, R. F.; Kozeeva, L. P.; Klevtsov, P. V. Preparation and structure of the crystals of potassium-europium molybdate KEu- $(MoO_4)_2$ . *Crystallog. Rep.* **1974**, *19*, 89–94. This article is in Russian. (59) Zhao, D.; Zhao, E.-X.; Xin, X.; Li, F.-F. Single-crystal structure and bond structure of scheelite-like KGd $(MoO_4)_2$ . *Chin. J. Inorg. Chem.* **2014**, *30*, 1143–1150.

(60) Basovich, O. M.; Khaikina, E. G.; Solodovnikov, S. F.; Tsyrenova, G. D. Phase formation in the systems  $Li_2MoO_4-K_2MoO_4-Ln_2(MoO_4)_3$  (Ln = La, Nd, Dy, Er) and properties of triple molybdates LiKLn<sub>2</sub>(MoO<sub>4</sub>)<sub>4</sub>. J. Solid State Chem. **2005**, 178, 1580–1588.

(61) Abakumov, A. M.; Morozov, V. A.; Tsirlin, A. A.; Verbeeck, J.; Hadermann, J. Cation ordering and flexibility of the  $BO_4^{2-}$  tetrahedra in incommensurately modulated  $CaEu_2(BO_4)_4$  (B = Mo, W) Scheelites. *Inorg. Chem.* **2014**, *53*, 9407–9415.

(62) Yuan, H.; Li, H.; Zhang, T.; Li, G.; He, T.; Du, F.; Feng, S. A  $K_2Fe_4O_7$  superionic conductor for all-solid-state potassium metal batteries. *J. Mater. Chem. A* 2018, *6*, 8413–8418.

(63) Wang, E.; Greenblatt, M. Ionic conductivity of potassium phosphatoantimonates and some of their ion-exchanged analogs. *Chem. Mater.* **1991**, *3*, 542–546.

(64) Groenink, J. A.; Hakfoort, C.; Blasse, G. The luminescence of calcium molybdate. *Phys. Status Solidi A* **1979**, *54*, 329–336.

(65) Tian, Y.; Chen, B.; Tian, B.; Yu, N.; Sun, J.; Li, X.; Zhang, J.; Cheng, L.; Zhong, H.; Meng, Q.; Hua, R. Hydrothermal synthesis and tunable luminescence of persimmon-like sodium lanthanum tungstate:Tb<sup>3+</sup>, Eu<sup>3+</sup> hierarchical microarchitectures. *J. Colloid Interface Sci.* **2013**, 393, 44–52.

(66) Qin, D.; Tang, W. Energy transfer and multicolor emission in single phase  $Na_5Ln(WO_4)_{4^2}(MoO_4)_{2^2}$ :  $Tb^{3^+}$ ,  $Eu^{3^+}$  (Ln = La, Y, Gd) phosphors. *RSC Adv.* **2016**, *6*, 45376–45385.

(67) Chen, H.; Ai, S.; Dong, C.; Wang, H.; Ning, Z.; Liu, M.; Bi, J.; Zhao, Y.; Lai, X.; Gao, D. Eu<sup>3+</sup>-induced multicolor luminescence properties and enhanced thermal stability in the novel phosphors of  $Li_{0.1}Na_{0.9}Gd_{0.5}Tb_{0.5-x}Eu_x(MoO_4)_2$ . J. Lumin. 2020, 222, 117116.