Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

K₅Eu_{1-x}Ho_x(MoO₄)₄: Structures and luminescence properties

Svetlana M. Posokhova^{a,*}, Vladimir A. Morozov^a, Kirill N. Boldyrev^b, Dina V. Deyneko^a, Erzhena T. Pavlova^c, Bogdan I. Lazoryak^a

^a Chemistry Department, Moscow State University, Moscow 119991 Russia

^b Institute of Spectroscopy of the Russian Academy of Sciences, Fizicheskaya Str. 5, Troitsk, Moscow, 108840 Russia

^c Buryat State University, Smolin St. 24a, Ulan-Ude, 670000 Buryat Republic, Russia

A R T I C L E I N F O Keywords: Molybdates Solid-state methods Structure Luminescence	A B S T R A C T	
	The palmierite-type matrix with lanthanides is capable of producing customizable multicolored emission, and has characteristics such as long service life and high energy efficiency. This research explored the impact of synthesis method and composition on structural and luminescence properties of $K_5Eu_{1-x}Ho_x(MoO_4)_4$ with the palmierite-type structure. Two modifications with space group (SG) <i>R</i> $\overline{3}m$ (α - phase) and $C2/m$ (β -phase) were observed and characterized. This study underscores the critical role of co-doping of Eu^{3+} and Ho^{3+} cations in manipulating charge transfer and luminescence efficiency in visible and IR region. The existence of ${}^5D_0 \rightarrow {}^7F_0$ transition in the PL spectra indicates stable local environment of Eu^{3+} cations regardless of synthesis conditions.	

1. Introduction

Double molybdates $K_5R(MOO_4)_4$ with palmierite-related structure (R = rare earth elements (*REE*)) are effective phosphors characterized by high luminescence intensity, a small half-width of lines in the spectrum and a long lifetime. The great flexibility and stability of the palmierite-type structure adapting to different cations, define effective use of these matrices to create phosphors. The possibility of MOO_4^2 tetrahedra rotation in palmierite-type structures, the lability of oxygen atoms, and the possibility of both statistical and ordered *M*1 cite occupation with K^+ and R^{3+} determines the presence several polymorphic modifications. Besides, formation of phases with an incommensurately modulated structure were established for some compounds [1–4].

 $K_5R(MoO_4)_4$ compounds are host systems where R^{3+} ions are embedded in *M*1 cite of inorganic host lattice. *REE* provide luminescent centers determining the efficiency of radiation by certain distances between ions, coordination numbers and spatial location in threedimensional space. Eu³⁺ and Ho³⁺ are widely used to create red phosphors and phosphors with radiation in the IR range, respectively. The joint doping of cations into one matrix aims to study processes of concentration quenching and energy transfer between ions to create multifunctional materials such as IR sensors and light emitting diodes.

In this paper the influence of conditions of preparation and elemental composition on structure and luminescent properties of $K_5Eu_{1-x}Ho_x(-MoO_4)_4$ has been studied.

2. Materials and methods

K₂CO₃ (99.99 %), MoO₃ (99.99 %), Eu₂O₃ (99.99 %), Ho₂O₃ (99.99 %) were used for the synthesis of LT-K₅Eu_{1-x}Ho_x(MoO₄)₄ (LT-KEHM, 0 $\leq x \leq 1$, step 0.1) at 620 °C. High-temperature (HT) phases were obtained from LT-KEHM by melting in a Pt crucible at 840 °C followed by quenching into liquid N₂.

materials letters

The refinement of unit cells parameters was carried out by the Le Bail method [5] (Jana2006 software [6]) using powder X-ray (XRD) data obtained on Huber G670 powder diffractometer (CuK_{α}) and Thermo ARL X'TRA (CuK_{α}). Structures of K₅Ho(MoO₄)₄ (KHM) modifications were refined by Rietveld method (Jana2006) using XRD data obtained on Siemens D500 (CuK_{α 1}- radiation, $\lambda = 1.5406$ Å).

Luminescence excitation spectra (PLE) and photoluminescence emission spectra (PL) were captured using the Agilent Cary Eclipse luminescence spectroscopy facility and the Bruker IFS 125HR FTIR spectrometer.

3. Results and discussion

XRD study was revealed that the substitution of Eu^{3+} by Ho^{3+} in HTphases leads to formation of KEHM solid solutions with a *R* $\overline{3}m$ space group (SG) for all *x* (Fig. 1). Substitution of the larger Eu^{3+} ($r_{\text{VIII}} = 1.066$ Å) cation by Ho^{3+} ($r_{\text{VIII}} = 1.015$ Å) leads to a decrease in unit cell

https://doi.org/10.1016/j.matlet.2023.135625

Received 10 October 2023; Received in revised form 17 November 2023; Accepted 22 November 2023 Available online 23 November 2023 0167-577X/© 2023 Elsevier B.V. All rights reserved.



^{*} Corresponding author at: Chemistry Department, Lomonosov Moscow State University, 119991 Moscow, Russia. *E-mail address*: posohovasm@gmail.ru (S.M. Posokhova).



Fig. 1. Parts of XRD patterns for LT- (*a*) and HT- K₅Eu_{1-x}Ho_x(MoO₄)₄ (*b*) phases in 2θ ranges of 25-33° and 39-43°. Dependencies of unit cell parameters on *x* for HT-phase (*c*).

parameters *V/Z* and *a*, while a parameter "*c*" increases. For LT- KEHM ($0 \le x \le 1$) at *x* in the range from 0 to 0.5, the structure of the compounds does not differ from the structure of the high-temperature α -phase, however, an increase in the Ho³⁺ content leads to a transition to the monoclinic β -phase with a SG C2/*m* (Fig. 1).

Coordinates of atoms in the structures α -K₅Yb(MoO₄)₄ (SG R $\overline{3}m$ [1]) and β -K₅Tb(MoO₄)₄ (SG C2/m [2]) were used to refine the structures α and β -K₅Ho(MoO₄)₄ (KHM), respectively. In both KHM modifications K⁺ occupy a M2 position of the palmierite-type structure, whereas a M1 position is statistically occupied by K⁺ and Ho³⁺ (M1 = 0.5 K⁺+0.5Ho³⁺).

After refining the structure of α-KHM large values of isotropic atomic displacement parameters (Uiso.) 0.188(6) and 0.135(9) were observed in the R $\overline{3}m$ odel for O1 (site symmetry 6c) and O2 (site symmetry 18h) atoms, respectively. In this structure oxygen atoms O1 and O2 are located on a 3-fold axis and in a plane perpendicular to this axis, respectively. High values of Uiso for O atoms can be associated with displacement of O1 from the 3-fold axis and the displacement of O2 from a 18-fold position (x, \overline{x}, z) to a 36-fold position (x, y, z), as in the palmierite-type structure α -K₅Y(MoO₄)₄ [7]. Fig. 2a,b shows [$\rho_{dif.} x, y, z$)] residual electron density $(e \times Å^{-3})$ maps for the α -KHMO structure in the plane (001) in the region of O1 (Fig. 2a) and O2 (Fig. 2b). The residual electron density for the α-KHMO structure after the refinement around majority of atoms also shows that the real structure can have lower symmetry than R $\overline{3}m$. Earlier similar problems were discovered when refining the structure of α -K₅Eu(MoO₄)₄, and only electron diffraction studies showed a slight monoclinic distortion of the structure [4].

Additional reflexes were observed on XRD patterns of the β -phase after refinement the *C*2/*m* (Fig. 2d). Based on the data for other palmierite-type structure [2–4] these reflexes can be indexed in a superspace group *C*2/*m*(0 β 0)00 with a modulation vector $q = 0.704857b^*$. Results of Le Bail decomposition are shown in Fig. 2e. Thus, the additional reflexes are satellite, and the real structure of the β -phase requires the application of a (3 + *n*)-dimensional formalism to refine the structure.

Refinement of the structures of α - and β -KHM led to a satisfactory correspondence of calculated and experimental profiles (Fig. 2c,d). The refinement results are given in Table 1. *ab* projections of α - and β -KHM show Mo-O distances (Fig. 2f,g). For the β -phase the displacement of an apical O_{ap} (O1) atom from the 3-*fold* axis is observed that does not contradict the data for structures with the SG *C*2/*m*.

The photoluminescence spectra of HT-KEHM at $\lambda_{ex}=395$ nm shows five bands from the excited metastable state 5D_0 Eu $^{3+}$ to components of multiplets 7F_j (j = 0, 1, 2, 3, 4). The highest intensity peak, characterized by an electric dipole transition $^5D_0 \rightarrow ^7F_2$ at ~ 610 nm, determines the characteristic red glow of the samples. The maximum intensity of luminescence is observed at the highest concentration of europium. Even at a low concentration of Ho $^{3+}$ there is a sharp decrease in the radiation intensity (more than 20 times) (Fig. 3b). This may indicate presence of an energy transfer from Eu $^{3+}$ to Ho $^{3+}$ ions with further non-radiative relaxation [8]. A peak at 578 nm corresponding to the $^5D_0 \rightarrow ^7F_0$ transition is determined by oxygen environment of the Eu $^{3+}$ cation. The fact that all compositions of solid solutions have only one emission line



Fig. 2. Residual electron density distribution maps for the α -K₅Ho(MoO₄)₄ structure in the region of O1 (interval 0–0.73; step 0.1) (*a*) and O2 (interval 0–0.24; step 0.1) (*b*) atoms after refinement in the $R \ \overline{3}m$ model. Parts of experimental, calculated and difference XRD profiles: after the Rietveld refinement of the α -phase structure (*c*) and β -K₅Ho(MoO₄)₄ structure in the SG C2/m (*d*). Satellite reflections are indicated with red arrows. Results of Le Bail decomposition of XRD patterns for β -K₅Ho (MoO₄)₄ in the SSG C2/m(0 β 0)00 (*e*). Black bars mark the positions of main reflections. *ab* projections in monoclinic β -phase (*f*) and rhombohedral α -phase (*g*). Distances are indicated in Å. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in the region of this transition (Fig. 3a) indicates one Eu^{3+} ion unchanging type of environment in compounds.

Kinetics study of 5D_0 luminescence attenuation at room temperature for HT-KEHM showed that a calculated lifetime (τ) of Eu $^{3+}$ luminescence decreases by ~ 2.8 times at 10 % Ho $^{3+}$ content (Fig. 3c). This indicates confirmation of the energy transfer during doping of the system with Ho $^{3+}$.

In the luminescence spectrum of Ho^{3+} at $\lambda_{ex} = 462$ nm (Fig. 3d), the

most intense is a wide peak in the 1940–2060 nm range, corresponding to ${}^{5}I_{7} \rightarrow {}^{5}I_{8}$ transition. A less intense peak at 1995 nm (${}^{5}I_{6} \rightarrow {}^{5}I_{8}$) is also noticeable. The dependence of integral photoluminescence intensity on *x* demonstrates the strongest luminescent properties for sample with maximum Ho³⁺ content. Substitution of Ho³⁺ by Eu³⁺ leads to a sharp decrease in intensity of the glow of Ho³⁺, that indicates a Ho³⁺ \rightarrow Eu³⁺ energy transfer, followed by non-radiative relaxation. Thus, energy transfer from Eu³⁺ to Ho³⁺ is observed at $\lambda_{ex} = 395$ nm and a reverse

Table 1

Crystallographic data for α - and β -K₅Ho(MoO₄)₄.

	β-	α-
Refinement	Rietveld	
Space group	C2/m	R 3 m
Background function	Legendre polynomials, 15 terms	
Interval 20(°)	8–130	
Lattice parameters:		
a (Å),	10.4666(1)	6.02497(7)
b (Å),	6.0300 (1)	6.02497(7)
c (Å),	7.7266 (1)	20.5222(2)
β (deg.)	117.868 (1)	
V (Å ³),	431.1 (3)	645.2(1)
Formula units, Z	1	1.5
N ^o reflections	306	164
$R_{\rm WP}, R_{\rm P}, R_{\rm exp}$ (%)	7.62, 5.45, 2.73	9.49, 6.70, 2.9
R and R_w (%) R_{all}/R_{obs}	5.35/5.27 and 6.87/6.86	9.95/9.96 and 11.42/11.42
Goodness of fit (ChiQ)	2.74	3.27

process at $\lambda_{ex} = 462$ nm. Both processes lead to non-radiative relaxation with a sharp decrease in luminescence intensity.

A comparison of a spectrum fragment for HT- and LT-K₅Eu_{0.5}Ho_{0.5}(MoO₄)₄ at $\lambda_{ex} = 462$ nm is shown in Fig. 3e. A peak corresponding to ${}^{5}I_{7} \rightarrow {}^{5}I_{8}$ transition has a more complex shape for the LTphase than for the HT- one. The luminescence intensity for the HT-phase is lower than for the LT-phase. Similar results were obtained in a study of other palmierite-type compounds [3].

4. Conclusion

HT- and LT-K₅Eu_{1-x}Ho_x(MoO₄)₄ were successfully prepared by the solid state synthesis method. Regions of α - (SG $R \ \overline{3}m$) and β - (SG C2/m) phase existence were found. Rietveld refinement allowed to process XRD patterns of α - and β -K₅Ho(MoO₄)₄. The presence of satellite reflections in the β -phase structure required the use of a (3 + n)-dimensional



Fig. 3. PL spectra of HT-K₅Eu_{1-x}Ho_x(MoO₄)₄ (x = 0 (1); 0.1 (2); 0.2 (3); 0.3 (4); 0.4 (5); 0.7 (8) 0.8 (9); 0.9 (10); 1 (11)) at $\lambda_{ex} = 395$ nm (a,b) and $\lambda_{ex} = 462$ nm (d,f). Inserts show integral intensities of the ${}^{5}D_{0} \rightarrow {}^{7}F_{j=0.4}$ (Eu³⁺) (b) and ${}^{5}I_{j=6,7} \rightarrow {}^{5}I_{8}$ (Ho³⁺) (d) emissions. Decay curves at the excitation of 395 nm (c). PL spectra of HT-, LT-K₅Eu_{0.5}Ho_{0.5}(MoO₄)₄ at $\lambda_{ex} = 462$ nm (e).

approach. HT-K₅Eu_{1-x}Ho_x(MoO₄)₄ exhibit significant energy transfer properties affecting the luminescence efficiency in both the visible and IR regions. The local environment of Eu³⁺ cation in HT-solid solutions is immutable and Eu³⁺ occupy only one site. Concentration quenching effect is not observed in both cases: both with intracenter excitation of Eu³⁺ and Ho³⁺ cations. The efficiency of LT-phase emission is higher than HT-phase that corresponds with previous data.

CRediT authorship contribution statement

Svetlana M. Posokhova: Investigation, Writing – original draft, Data curation. Vladimir A. Morozov: Conceptualization, Data curation, Supervision. Kirill N. Boldyrev: Investigation, Resources. Dina V. Deyneko: Methodology, Resources. Erzhena T. Pavlova: Writing – review & editing. Bogdan I. Lazoryak: Conceptualization, Resources, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Acknowledgements

This work was supported by the Russian Science Foundation (Grant: 21-13-00102), the Ministry of Science and Higher Education of the Russian Federation (Theme No. AAAA-A21-121011590086-0).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2023.135625.

References

- [1] V.A. Morozov, B.I. Lazoryak, O.I. Lebedev, et al., J. Solid State Chem. 176 (1) (2003) 76–87.
- [2] S.M. Posokhova, V.A. Morozov, D.V. Deyneko, et al., Inorg. Chem. 61 (20) (2022) 7910–7921.
- [3] S.M. Posokhova, V.A. Morozov, E.M. Zonov, et al., Cryst. Eng. Comm. 25 (2023) 4822–4833.
- [4] S.M. Posokhova, V.A. Morozov, D.V. Deyneko, et al., Cryst. Eng. Comm. 25 (2023) 835–847.
- [5] A. Le Bail, H. Duroy, J. L. Fourquet., Mater. Res. Bull. 23 (1988) 447-452.
- [6] V. Petříček, M. Dušek, L. Palatinus, Zeitschrift Für Krist., Cryst. Mater. 229 (2014) 345–352.
- [7] B.I. Lazoryak, V.A. Efremov, Crystallography 26 (1981) 3.
- [8] Q. Chen, J. Jiang, H. Zhang, et al., Crystals 13 (1) (2022) 13.