Synthesis and Luminescence Properties of a Li₃BaCaY₃(MoO₄)₈:Er³⁺ Phosphor with a Layered Scheelite-Like Structure

N. M. Kozhevnikova

Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, ul. Sakh'yanovoi 6, Ulan-Ude, 670047 Buryat Republic, Russia

> *e-mail: nicas@binm.bscnet.ru* Received July 22, 2016

Abstract—A Li₃BaCaY₃(MoO₄)₈: Er^{3+} phosphor with a scheelite-like structure (sp. gr. *C*2/*c*) has been synthesized and its luminescence properties have been studied. The phosphor has been characterized by X-ray diffraction, differential thermal analysis, and IR spectroscopy.

Keywords: phosphor, X-ray diffraction analysis **DOI:** 10.1134/S0020168517040082

INTRODUCTION

Oxide compounds having layered scheelite-like crystal structures and activated with rare-earth ions are potentially attractive as laser materials, phosphors, and solid electrolytes [1-3]. In recent years, there has been an intensive search for multifunctional phosphors offering bright luminescence under UV excitation and anti-Stokes luminescence under IR excitation. One efficient way of modifying luminescence properties of materials is by activating them with Er^{3+} ions, which are capable of absorbing IR radiation and converting it to visible anti-Stokes luminescence [4-6]. In scheelite-like molvbdates and tungstates, one can stabilize a combination of different cations, atypical coordination polyhedra, and metastable polymorphs of three-dimensional structures in the form of layers [3]. Which structural variety will be realized depends on the nature of the cations present in the composition of the compound, their combination, their distribution over structural sites, and site occupancies. A wide isomorphism of cations differing in nature leads to charge disbalance in the structure as a consequence of specific geometric features in the arrangement of nearest neighbor polyhedra and to local and cooperative distortions and makes it possible to control the spectroscopic properties of compounds with layered structures [3, 7–10].

The objectives of this work were to synthesize a $Li_3BaCaY_3(MoO_4)_8$: Er^{3+} phosphor with a layered scheelite-like structure and investigate its spectroscopic and physicochemical characteristics.

EXPERIMENTAL

The starting chemicals used to study phase rela-Li₂MoO₄-BaMoO₄-CaMoO₄tions in the $Y_2(MoO_4)_3$ system were Li_2MoO_4 , $BaMoO_4$, $CaMoO_4$, and $Y_2(MoO_4)_3$ presynthesized by solidstate reactions in mixtures of the Li₂CO₃, BaCO₃, and $CaCO_3$ carbonates; molybdenum trioxide, MoO_3 (analytical grade); and yttrium and erbium oxides (99.99+% purity). The Li₂CO₃, BaCO₃, CaCO₃, and MoO₃ compounds were calcined for 10 h at 400°C, and the rare-earth oxides were calcined in the temperature range 400-700°C. Li₃BaCaY₃(MoO₄)₈ was synthesized using a reaction mixture of the lithium, barium, calcium, and yttrium molybdates, 3Li₂MoO₄ + $2BaMoO_4 + 2CaMoO_4 + 3Y_2(MoO_4)_3$, which was calcined in the temperature range 500-750°C with repeated intermediate grindings every 20-30 h. The calcination time at each temperature was 100-120 h. To obtain different activator concentrations, erbium oxide $(3-5 \mod \%)$ was substituted for an equimolar amount of yttrium molybdate. After firing, the samples were slowly furnace-cooled. Nonequilibrium samples were annealed further. Equilibrium was thought to be reached if the phase composition of the samples remained unchanged after two sequential anneals. The synthesis products were identified by X-ray diffraction on a Bruker D8 Advance diffractometer (Cu K_{α} radiation). X-ray diffraction data were analyzed using Rentgen software.

Vibrational spectra of the $Li_3BaCaY_3(MoO_4)_8:Er^{3+}$ phosphor were measured on a Varian 3100 Fourier



Fig. 1. X-ray diffraction patterns of (1) $Li_3Ba_2Y_3(MoO_4)_8$, (2) $Li_3BaCaY_3(MoO_4)_8$, and (3) $Li_3BaCaY_3(MoO_4)_8$: Er^{3+} .

transform IR (FTIR) spectrometer (equipped with a multiple frustrated total internal reflection auxiliary). The samples were prepared by pressing with KBr. Differential thermal analysis scans were performed with an MOM OD-103 thermoanalytical system (Hungary) at a heating rate of 10°C/min (sample weight, 0.3–0.4 g). Luminescence spectra of Li₃Ba-CaY₃(MoO₄)₈:Er³⁺ under UV excitation ($\lambda_{ex} = 365$ nm) were obtained on an SM 2203 spectrofluorometer (Solar, Belarus). The excitation was provided by a DKsSh 150-1M high-pressure xenon arc lamp. In the IR spectral region, luminescence was excited by an InGaAs laser diode ($\lambda_{ex} = 977$ nm), and luminescence spectra were measured on an Ocean Optics QE 65000 spectrometer.

RESULTS AND DISCUSSION

X-ray diffraction characterization showed that the samples annealed at 700°C contained no unreacted lithium, alkaline-earth, or rare-earth molybdates. The X-ray diffraction pattern of $Li_3BaCaY_3(MoO_4)_8$: Er³⁺ was similar in peak positions and intensities to those of the $Li_3Ba_2R_3(MoO_4)_8$ (R = La-Lu) lithium barium rare-earth molybdates, confirming that they had a monoclinically distorted scheelite structure (sp. gr. C2/c, Z = 2) (Fig. 1). The structure of Li₃Ba-CaY₃(MoO₄)₈ contains honeycomb layers of eightvertex Y polyhedra. Each layer shares oxygen corners with Mo tetrahedra on both sides. The lithium atoms occupy different crystallographic sites. One-third of the lithium atoms are located at random on the rareearth site (coordination number CN = 8). The other two-thirds of the lithium atoms occupy a special position on the twofold axis and have an octahedral oxygen coordination [3, 9]. The Ba and Ca atoms are in ten coordination and reside between the layers formed by the Mo and rare-earth polyhedra.

The X-ray diffraction pattern of Li₃Ba-CaY₃(MoO₄)₈:Er³⁺ could be indexed in monoclinic symmetry using the unit-cell parameters of a Li₃Ba₂-Gd₃(MoO₄)₈ single crystal: a = 5.171(5) Å, b = 12.532(3) Å, c = 19.114(3) Å, and $\beta = 91.59(1)^{\circ}$. The Li₃BaCaY₃(MoO₄)₈:Er³⁺ phosphor melts incongruently at 950°C.

The structure of the Li₃Ba₂Gd₃(MoO₄)₈ single crystal was solved by the heavy atom method using a three-dimensional Patterson function. The lighter atoms O and Li were located using $\rho(xyz)$ electron density map calculations. Anisotropic structure refinement, involving gadolinium site occupancy refinement, converged to R = 0.044. We evaluated the local valence force balance, taking into account site occupancies. The data thus obtained are well consistent with the stoichiometric composition of the Li₃Ba₂-Gd₃(MoO₄)₈ compound. The valence balance quality D_0 is 2.10% [3, 9].

The measured vibrational frequencies in the longwavelength part of the IR spectra of $Li_3BaCaY_3(MoO_4)_8$, Li₃BaCaY₃(MoO₄)₈:Er³⁺ and Li₃Ba₂Y₃(MoO₄)₈ are listed in the table. The effect of the nature of their constituent cations on the key structural features of $Li_3BaCaR_3(MoO_4)_8$ was studied by comparing their IR spectra to those of the $Li_3Ba_2R_3(MoO_4)_8$ isostructural compounds, which are very similar in the spectral region in question (Fig. 2) [11]. In group-theoretical analysis of the vibrational modes of $Li_3BaCaR_3(MoO_4)_8$, we used analogies with previously studied double and triple molybdates crystallizing in a monoclinically distorted layered scheelite structure (sp. gr. C2/c) [3]. Group-theoretical analysis of the vibrational modes of $Li_3BaCaR_3(MoO_4)_8$ suggests the following distribution over irreducible representations:

 $\Gamma(\text{Li}) = 1A_{\text{g}} + 2B_{\text{g}} + 1A_{\text{u}} + 2B_{\text{u}}$ for the lithium cations residing on the twofold axes (in octahedra);

 $\Gamma(M1) = 1A_g + 2B_g + 1A_u + 2B_u$ for the barium, calcium, and rare-earth cations on the twofold axes (M1 site); and

 $\Gamma(M2) = 3A_g + 3B_g + 3A_u + 3B_u$ for the lithium, barium, calcium, and rare-earth cations in general position (M2 site in the eight-vertex polyhedra).

These modes are active in IR absorption spectra and should have frequencies under 500 cm⁻¹. The IR spectra have large bandwidths, and their bands overlap, being a combination of several closely spaced lines

Wavenumber, cm ⁻¹			Assignment
Li ₃ Ba ₂ Y ₃ (MoO ₄) ₈	Li ₃ BaCaY ₃ (MoO ₄) ₈	Li ₃ BaCaY ₃ (MoO ₄) ₈ :Er ³⁺	Assignment
456	454	452	δ(MoO4)
417	416	417	δ(MoO4)
382	382	382	δ(MoO4)
324	319	319	TLi
290	287	288	TLi
265	265	265	TMo + T Y
263	257	258	TLi
232	227	230	TLi
186	186	186	TMo + T Y

Vibrational frequencies in the long-wavelength part of the IR absorption spectra of $Li_3Ba_2Y_3(MoO_4)_8$, $Li_3BaCaR_3(MoO_4)_8$, and $Li_3BaCaY_3(MoO_4)_8$: Er^3

[3, 11]. Moreover, this part of the spectrum should also contain bands arising from bending, librational, and translational modes of the MoO_4 groups.

The measured spectra of the compounds studied here have no marked differences in their high-frequency part (660–990 cm⁻¹). The absorption bands in this spectral region, due to the valence modes of the MoO₄ groups, are poorly resolved. This is a consequence of the described cation distribution over the crystallographic sites of the crystals and the associated statistics of distortions of the tetrahedral anion groups. In the bending region of the MoO₄ groups and the region of vibrational modes of the cation sublattices (below 500 cm⁻¹), up to 14 absorption bands were detected in the spectrum of Li₃BaCaY₃(MoO₄)₈:Er³⁺. At the same time, in this region the spectra of the compounds under consideration are very similar to those of $Li_3Ba_2R_3(MoO_4)_8$. This indicates that the vibrational modes of the cation sublattices are similar to each other and to the bending modes of the MoO₄ tetrahedra.

The frequencies of the external vibrational modes of the MoO₄ groups and the vibrational modes of the heavy cation sublattices are roughly the same as in $Li_3Ba_2Y_3(MoO_4)_8$.

The librational modes of the MoO_4 groups are responsible for the bands in the range 156–164 cm⁻¹, and vibrations of atoms in the Sr and Ba sublattices are responsible for the bands at 102–103 and 90–91 cm⁻¹, respectively. The translational modes of the molybdenum are intermixed with vibrations of atoms in the rare-earth sublattice and have frequencies of 265 and 186 cm⁻¹. In the long-wavelength part of the spectra of the compounds under study, we detected two bands, at 227–232 and 257–263 cm⁻¹, attributable to vibrations of the lithium cations [5]. Doping of the luminescent material Li₃Ba-CaY₃(MoO₄)₈ with erbium ions is an efficient way of raising the luminescence brightness of IR and visible phosphors with a scheelite-like structure. Activation of phosphors with Er³⁺ ions, which are capable of absorbing IR light and converting it to visible anti-Stokes luminescence, makes it possible to raise the efficiency of lasers. The spectral composition of steady-state Li₃BaCaY₃(MoO₄)₈:Er³⁺ luminescence at $\lambda_{ex} = 365$ nm is determined by bands corresponding to optical transitions of the Er³⁺ ion. As the Er³⁺ content is raised to 5 mol %, several groups of erbium-related narrow emission bands emerge in the green (535–610 nm)



Fig. 2. IR spectra of (1) $Li_3Ba_2Y_3(MoO_4)_8$, (2) $Li_3Ba-CaY_3(MoO_4)_8$, and (3) $Li_3BaCaY_3(MoO_4)_8$: Er^{3+} .



Fig. 3. Luminescence spectra of Li₃BaCaY_{2.85}-Er_{0.15}(MoO₄)₈ at λ_{ex} = (a) 365 and (b) 977 nm.

and red (660–705 nm) regions of the visible spectrum. The emission bands in the range 590–610 nm, corresponding to the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition, have the simplest and best-resolved structure. To the left and right of these green bands, we observe weaker emission bands, in the ranges 535–538 and 556–560 nm, due to the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{2}H_{9/2} \rightarrow {}^{4}I_{13/2}$ transitions, respectively. The bands in the red spectral region are due to the ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{2}H_{9/2} \rightarrow {}^{4}I_{11/2}$ transitions, whose spectrum extends from 660 to 705 nm and has a more complex structure, because the ${}^{4}F_{9/2}$ excited state is split into five multiplets.

 $Li_3BaCaY_{2.85}Er_{0.15}(MoO_4)_8$ possesses efficient anti-Stokes luminescence in the visible range under IR excitation. The origin of the bands observed in its anti-Stokes luminescence spectra under excitation at $\lambda_{ex} =$ 977 nm can be understood as follows: According to a known energy diagram [5], after a sequential, two-step excitation of the Er^{3+} ion to the ${}^{4}F_{7/2}$ level, nonradiative relaxation processes lead to the filling of the ${}^{4}H_{11/2}$, ${}^{4}S_{3/2}$, ${}^{4}F_{9/2}$, and ${}^{4}I_{9/2}$ excited-state levels, giving rise to anti-Stokes luminescence in the range 530–850 nm. Figure 3 shows the anti-Stokes luminescence spectrum between 450 and 850 nm. There are four strong bands, located around 530, 550, 660, and 800 nm.

The 530- and 550-nm bands correspond to the $\mathrm{Er}^{3+\ 2}H_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions. The 660-nm emission is due to the ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition, and the 800-nm emission, to the ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$ transition. The weak blue band at 490 nm arises from the ${}^{4}F_{7/2} \rightarrow {}^{4}I_{15/2}$ transition. A characteristic feature of the Er³⁺ ion is a narrow luminescence bandwidth. The anti-Stokes luminescence excitation process typically involves a sequential absorption of two IR photons of the same energy, which leads to the following sequence of electronic transitions: ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$ and ${}^{4}I_{11/2} \rightarrow {}^{4}F_{7/2}$. Transitions from high energy levels may result in visible luminescence. The shape of the spectra can be understood in terms of the effect of the host crystal lattice on the Stark structure of the ground and excited-state levels of the activator ion.

CONCLUSIONS

A Li₃BaCaY₃(MoO₄)₈:Er³⁺ phosphor with a layered scheelite-like structure (sp. gr. C2/c) has been prepared by solid-state reaction. The luminescence data obtained in this study demonstrates that, as the Er³⁺ content is raised to 5 mol %, several groups of erbium-related narrow emission bands emerge in the green (535–610 nm) and red (660–705 nm) regions of the visible spectrum.

Li₃BaCaY₃(MoO₄)₈:Er³⁺ possesses efficient anti-Stokes luminescence in the visible range under IR excitation. The origin of the bands observed in its anti-Stokes luminescence spectra under excitation at $\lambda_{ex} =$ 977 nm can be understood in terms of the filling of the ⁴*H*_{11/2}, ⁴*S*_{3/2}, ⁴*F*_{9/2}, and ⁴*I*_{9/2} excited-state levels, giving rise to anti-Stokes luminescence in the range 530–850 nm. The Li₃BaCaY₃(MoO₄)₈:Er³⁺ phosphor may find application in lasers, converters of IR radiation to visible light, color displays, biomedical diagnostics, and optical communication systems.

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Translated by O. Tsarev