Luminescence spectra of Ho^{3+} in distorted parity-breaking HoF_6^{3-} octahedra

A.S. Aleksandrovsky [a,b,*], A.S. Krylov [a], A.V. Malakhovskii [a], V.N. Voronov [a]

[a] L.V. Kirensky Institute of Physics, Krasnoyarsk, Russia
[b] Siberian Federal University, Krasnoyarsk, Russia

ABSTRACT

Low temperature luminescence spectrum of holmium ions in monoclinic Rb_2KHoF_6 crystal was found to be well analyzable by the comparison with earlier studied cubic Cs_2NaHoF_6. The manifestation of the local symmetry influence on the strength of individual lines is found to be distinctive. In the absence of structural data, the local symmetry of holmium in Rb_2KHoF_6 is proved to be a non-centrosymmetric one. The concentration quenching of holmium luminescence in Rb_2KHoF_6 is found to be rather modest.

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1. Introduction

Rare earth ions in crystalline hosts are under extensive studies as new materials for photonics. Fluorine-based crystalline lattices are presently of interest for photonics applications due to reduced radiativeless losses as compared to oxide lattices. They are under continuing extensive study as new hosts both for rare earth [1] and transition metals [2]. Among rare earth ions, holmium is of special interest, for instance, since it is extensively studied as lasing ion, and also it is considered as unavoidable constituent for producing high quality upconverted white light [3]. Recently Tanner et al. reported detailed investigation of holmium ions spectra in undistorted octahedra environment of cubic crystal Cs_2NaHoF_6 [4]. Quantum chemical calculations of the energy level structure were found to be in excellent agreement with measurements, and complete identification of the spectral structure was done, including details of phonon-assisted transitions. In undistorted octahedral environment of rare earth ions magnetic dipole allowed transitions are weak as compared to transitions involving excitation of odd phonons. If we consider low-symmetry crystal structure with, e.g., non-centrosymmetrically distorted octahedra in rare earth ion environment, then one would expect the appearance of crystal field induced electric dipole transitions as well as the complication of electron–phonon transitions spectra, in accordance with appearance of a number of new vibrational modes. These systems are expected to be much more difficult for the analysis of spectra. As a result, a number of studies of bialkaline rare earth fluorides and chlorides are almost exclusively concentrated on crystals of cubic symmetry [5–8].

In the present communication we study the luminescence spectra of monoclinic Rb_2KHoF_6 crystal and show that they are well interpretable on the basis of corresponding analysis made for cubic crystals.

2. Experimental

The monoclinic elpasolite Rb_2KHoF_6 crystal with stoichiometric rare earth ion content was obtained by Bridgeman–Stockbarger method at the hot zone temperature 900 °C. The starting materials were RbF, KF, and HoF_3 of spectral purity grade. The growth was performed in evacuated and sealed platinum ampoule. Temperature gradient inside the heater was 30 K/cm, and the pulling rate was 0.8 mm/hour.

At the temperature of synthesis the Rb_2KHoF_6 crystal has cubic symmetry $Fm\bar{3}m$ [9]. Cooling of the sample to the room temperature results in a triggered phase transition directly to monoclinic crystal structure that was reported suggestively belonging to the space group $P12_1/n1$. This transition is accompanied by the formation of microcrystalline domain structure. Due to this fact, completely resolved X-ray diffraction study of any of the crystals of related family was not reported up to date. Vibrational studies and lattice dynamics calculations are not available, too. For luminescence studies we used as-grown crystal sample. The excitation source was LaserCompact LCS-DTL-374QT diode-pumped laser at the wavelength 355 nm with the linear polarization of radiation and the power up to 30 mW. The luminescence
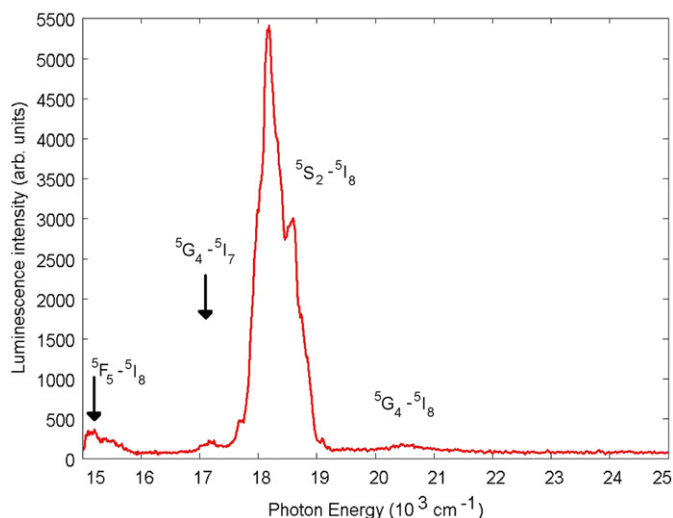
Fig. 1. Room-temperature luminescence spectrum of Rb_2KHoF_6 crystal excited at 355 nm.
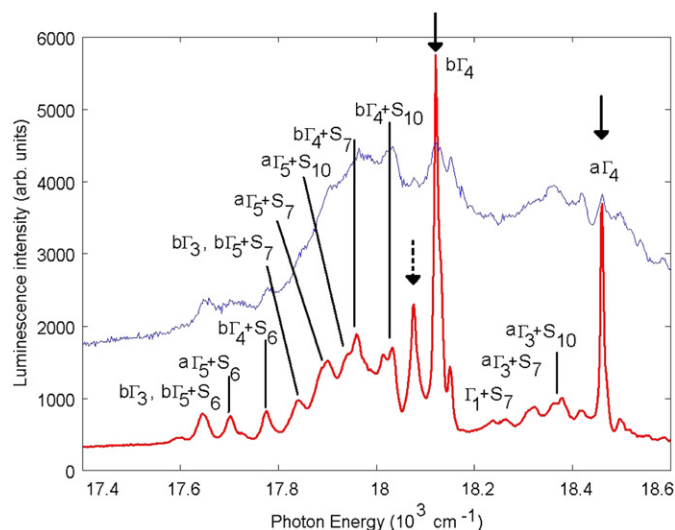

Fig. 2. The $^5S_2$–$^5I_8$ luminescence spectra of monoclinic Rb_2KHoF_6 at 100 K (thin line, multiplied by 7) and at 7 K (thick line). The notation of the lines corresponds to the terminal states in undistorted O_h local symmetry of Ho^{3+} ion, and S_N is the notation of vibrational modes [4].

was recorded with Horiba Jobin-Ivon T64000 triple monochromator spectrometer equipped with Advanced Research Systems CS204 helium cryostat. The spectral resolution was $2 \, cm^{-1}$. No polarizers were used in the optical signal channel of T64000, but the CCD array used has the sensitivity for the polarization coinciding with that of exciting radiation five times higher than for the perpendicular polarization.

3. Results and discussion

The exciting radiation at 355 nm must fall into the wing of the transitions from the ground state $^5I_8$ to whether $^5G_5$, $^3H_6$, or $^3D_2$ levels of holmium ion [10]. Despite the high concentration of holmium and expected concentration quenching of the luminescence, we have easily observed green–yellowish luminescence from our sample at room temperature. The overall view of Rb_2KHoF_6 luminescence under 355 nm excitation is presented in Fig. 1. $^5S_2$–$^5I_8$ luminescence is dominating in this spectrum, but $^5G_4$–$^5I_7$, $^5G_4$–$^5I_8$, and $^5F_5$–$^5I_8$ luminescence contributions are detectable, too.

The $^5S_2$–$^5I_8$ luminescence spectra of Rb_2KHoF_6 at 7 K and at 100 K are presented in Fig. 2. The positions of the bands are presented in the first column of Table 1. Comparison of low temperature spectrum with the relevant spectrum of cubic Cs_2NaHoF_6 [4] (second column of Table 1) shows that origin of the most of the lines in our spectrum can be traced in the spectrum of Ho^{3+} ion in O_h crystal field. The lines in the region below $18,050 \, cm^{-1}$ as well as in the region from 18,200 to $18,400 \, cm^{-1}$ are due to electric dipole-allowed transitions with odd phonon excitation, and they are only modestly modified due to the monoclinic distortion of HoF_6^{3-} octahedra. This modification is due to splitting of both electronic sublevels and vibrational frequencies of the lattice and results in broadening of corresponding luminescent lines. The two most intense peaks in our spectrum (shown with solid arrows in Fig. 2) can also be found in the spectra of undistorted HoF_6^{3-} [4] as pure magnetic dipole transitions with the intensity slightly above the detection threshold. In weakly distorted O_h crystal field these lines experience growth and become dominant due to crystal field induced electric dipole transition. Experimental energy of $^5S_2$ Γ_5–$^5I_8$ $b\Gamma_4$ transition in undistorted octahedra is $18130 \, cm^{-1}$ [4] while in our crystal we observe it at $18,121 \, cm^{-1}$. Corresponding values for $^5S_2$ Γ_5–$^5I_8$ $a\Gamma_4$ are $18,482 \, cm^{-1}$ in undistorted octahedra and $18,461 \, cm^{-1}$ in our crystal. Small peak at $18,150 \, cm^{-1}$ in our

crystal can be associated with $^5S_2$ Γ_3–$^5I_8$ $b\Gamma_4$ transition observed in undistorted octahedra. Position of the group of sublevels (in distorted octahedra) originating from $^5S_2$ Γ_5 level (in undistorted octahedra) is estimated to be $18,498 \, cm^{-1}$. Energies of sublevels belonging to $^5I_8$ manifold are found to be 0, 37, 77, 377, 422, 488, and $487 \, cm^{-1}$.

However, the prominent enough peak at $18,076 \, cm^{-1}$ (dashed arrow in Fig. 2) in our crystal cannot be associated with any identified peak in undistorted octahedra [4]. This peak is positioned in the vicinity of $^5S_2$ Γ_5–$^5I_8$ $b\Gamma_4$ peak (below by $45 \, cm^{-1}$) and thus can be tentatively considered as a result of the splitting of this transition forced by a low-symmetry component of the crystal field in distorted octahedra. Partially this can be supported by the existence of similar satellite at $18,421 \, cm^{-1}$, $40 \, cm^{-1}$ below the main peak of $^5S_2$ Γ_5–$^5I_8$ $a\Gamma_4$ transition. Another proof is the similarity in the temperature behavior of the peaks at 18,076 and $18,121 \, cm^{-1}$. Thin line in Fig. 2 presents the part of the luminescence spectra of our crystal at 100 K being multiplied by 7 with respect to 7 K spectrum. It is noticeable that phonon-assisted transitions keep their relative intensity and remain resolvable in the 100 K spectrum while both peaks at 18,076 and $18,121 \, cm^{-1}$ experience the same decrease as compared to the intensity of those phonon-assisted transitions. This means that both 18,076 and $18,121 \, cm^{-1}$ peaks are not phonon-assisted but crystal field induced ones. However, another possibility of assignment exists for $18,076 \, cm^{-1}$ peak. It can be associated with transition to $^5I_8$ $a\Gamma_5$. In this case the presence of this peak in our crystal is also due to crystal field induced electric dipole transition.

So, we observed enhancement of luminescence mainly at $^5S_2$ Γ_5–$^5I_8$ $b\Gamma_4$, $a\Gamma_4$ transitions, and probably at $^5S_2$ Γ_5–$^5I_8$ $a\Gamma_5$ transition. Presumably this means that the sample under study, despite being highly randomized due to its domain structure, has nevertheless a preferable intrinsic orientation of domains. More definite conclusions can be done if local symmetry of holmium ions will be established via XRD studies.

4. Conclusions

Monoclinic elpasolites with stoichiometric rare earth ions content represent good objects for investigation of the role of

Table 1
Energies of transitions from $^5S_2$ Γ_5 to the sublevels of $^5I_8$ in 7 K spectrum (Fig. 2).

Peak position of bands in distorted octahedra (cm^{-1})	Energies of transitions in undistorted octahedra [4] (cm^{-1})	Origin of terminal sublevels in undistorted octahedra	Average value of vibrational frequency of the band in distorted octahedra (cm^{-1})
17,647	17,578–17,645	$^5I_8$ $b\Gamma_3+S_6$ and $^5I_8$ $b\Gamma_5+S_6$	
17,702	17,624–17,691	$^5I_8$ $a\Gamma_5+S_6$	374 (S6)
17,775	17,694–17,761	$^5I_8$ $b\Gamma_4+S_6$	346 (S6)
17,840	17,811–17,849	$^5I_8$ $b\Gamma_3+S_7$ and $^5I_8$ $b\Gamma_5+S_7$	170 (S7)
17,902	17,857–17,895	$^5I_8$ $a\Gamma_5+S_7$	174 (S7)
17,943	17,915–17,929	$^5I_8$ $a\Gamma_5+S_{10}$	133 (S10)
17,959	17,927–17,965	$^5I_8$ $b\Gamma_4+S_7$	162 (S7)
18,015–18,031	17,985–17,999	$^5I_8$ $b\Gamma_4+S_{10}$	106, 90 (S10)
18,076	18,060	$^5I_8$ $a\Gamma_5$ or crystal field split $^5I_8$ $b\Gamma_4$	
18,121	18,130	$^5I_8$ $b\Gamma_4$	
18,130	Absent	Crystal field split $^5I_8$ $b\Gamma_4$	
18,150	Absent	Crystal field split $^5I_8$ $b\Gamma_4$	
18,248–18,264	18,229–18,267	$^5I_8$ Γ_1+S_7	173, 157 (S7)
18,324	18,297–18,335	$^5I_8$ $a\Gamma_3+S_7$	174 (S7)
18,360–18,377	18,355–18,369	$^5I_8$ $a\Gamma_3+S_{10}$	138 (S10)
18,421	18,432	$^5I_8$ Γ_1	
18,461	18,482	$^5I_8$ $a\Gamma_4$	
18,468	Absent	Crystal field split $^5I_8$ $a\Gamma_4$	
18,498	18,500	$^5I_8$ $a\Gamma_3$	

lattice and local symmetry distortion on the luminescent properties of these ions. The manifestation of local symmetry distortion in their luminescence is found to be clear and distinctive. The luminescence spectrum of monoclinic Rb_2KHoF_6 is well analyzable by the comparison with the spectra of cubic $Cs_2Na\text{-}HoF_6$ [4]. In the absence of detailed structural data, luminescence spectra evidence that the distortion of HoF_6^{3-} octahedra in Rb_2KHoF_6 leads to formation of non-centrosymmetric environment of Ho^{3+} ions. The concentration quenching of holmium luminescence in Rb_2KHoF_6 is found to be rather modest.

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