# Polarized spectroscopy of electric and magnetic dipole transitions of Europium (III) ions in $C_2$ sites

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**Abstract**. Polarization anisotropy of luminescent properties of europium (III) ions in low-symmetry $C_2$ sites is studied using monoclinic (sp. gr. *C*2/*c*) tungstate crystal $KY(WO_4)_2$. The $^5D_0 \rightarrow {}^7F_6$ (where $J$ = 0...6) transitions are characterized for the principal light polarizations. Polarization selection rules for the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition are presented. The crystal-field splitting for $Eu^{3+}$ ions is also determined.

## 1. Introduction

Trivalent europium ions ($Eu^{3+}$) having an electronic configuration of [Xe]4f$^6$ are well-known for their emissions in the visible owing to the $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0...6) transitions. Among them, the electric dipole (ED) transition to the $^7F_2$ state falling in the red (~610 nm) typically dominates in the spectrum. This determines the applications of $Eu^{3+}$-doped materials as red phosphors with high colour purity [1]. This ED transition is a hypersensitive one: its intensity depends significantly on the site symmetry and its distortion. The adjacent transition to the $^7F_1$ state is of purely magnetic dipole (MD) nature and it is weakly dependent on the host matrix. Because of this, $Eu^{3+}$ ions are also used as structural probes.

Recently, low-symmetry tungstate and molybdate crystals doped with $Eu^{3+}$ ions located in $C_2$ sites attracted a lot of attention for solid-state lighting and laser applications [2]. In the present work, we have studied the polarization anisotropy of ED and MD transition of $Eu^{3+}$ ions in $C_2$ sites.

## 2. Results and discussion

As a host matrix, we have used monoclinic (sp. gr. *C*2/*c*) double tungstate crystal, $KY(WO_4)_2$, doped with $Eu^{3+}$ ions (2 at.%). The dopant cations ($Eu^{3+}$) replace for the host-forming ones ($Y^{3+}$) in a single type of sites ($C_2$ symmetry) with an VIII-fold coordination by $O^{2-}$. $KY(WO_4)_2$ is optically biaxial and its principal optical directions (optical indicatrix axes) are denoted as ($N_p$, $N_m$ and $N_g$).

An overview luminescence spectrum of $Eu^{3+}$ ions in this crystal (for unpolarised light) is shown in Fig. 1(a). The emissions are due to the transitions from the metastable state ($^5D_0$) to the lower-lying states $^7F_J$ ($J$ = 0...6), $^7F_0$ is the ground-state. The luminescence lifetime of the $^5D_0$ state is 430 μs. The dominant $^5D_0 \rightarrow {}^7F_2$ transition determines the red emission colour of high purity ($p$ > 98%). At first, we focused on the ED transitions terminating at the $^7F_2$ and $^7F_4$ levels. The luminescence spectra were measured for the principal light polarizations and the stimulated-emission cross-sections $\sigma_{SE}$ were calculated, Fig. 1(b,c). Note the difference of the spectra for light polarized along the $C_2$ symmetry axis (|| $N_p$) and orthogonal to it (|| $N_m$, $N_g$), and strong polarization anisotropy of emission properties.

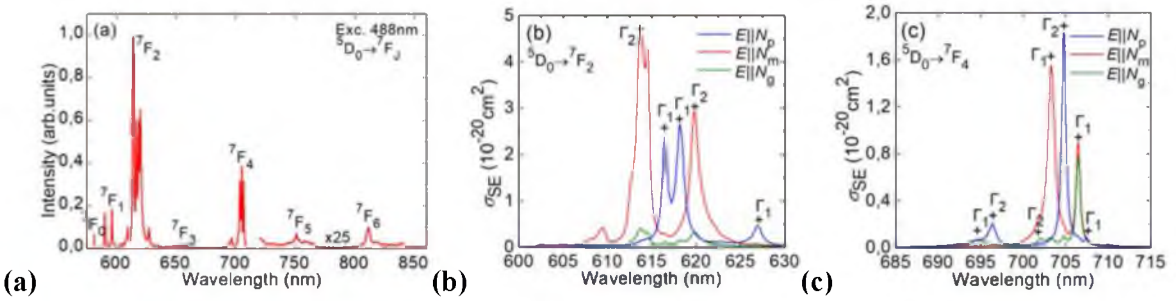


**Figure 1.** Luminescence of $Eu^{3+}$ ion in $C_2$ sites in the monoclinic $KY(WO_4)_2$ crystal: **(a)** unpolarized spectrum showing $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0...6) emission bands, $\lambda_{exc}$ = 488 nm; **(b,c)** polarized stimulated-emission cross-section spectra for electric-dipole (ED) transitions **(b)** $^5D_0 \rightarrow {}^7F_2$ and **(c)** $^5D_0 \rightarrow {}^7F_4$.

For the MD $^5D_0 \rightarrow {}^7F_1$ transition, the number of emission peaks and their relative intensity depend both on the light polarization and the propagation direction, see Fig. 2(a) where the Porto's notations from the Raman spectroscopy are used. The MD transition is caused by an interaction of the active ion with the magnetic field component of the light through the magnetic dipole $\boldsymbol{M}$. Thus, the orientation of the magnetic field vector $\boldsymbol{H}$ with respect to $\boldsymbol{M}$ is relevant. Polarization selection rules for the $^5D_0 \rightarrow {}^7F_1$ transition of $Eu^{3+}$ ions in $C_2$ sites are presented explaining well the observed emission behavior.

The crystal-field splitting for $Eu^{3+}$ ions in $KY(WO_4)_2$ was also determined, cf. Fig. 2(b).

The obtained information is important for the development of complex tungstate and molybdate red phosphors and laser materials.

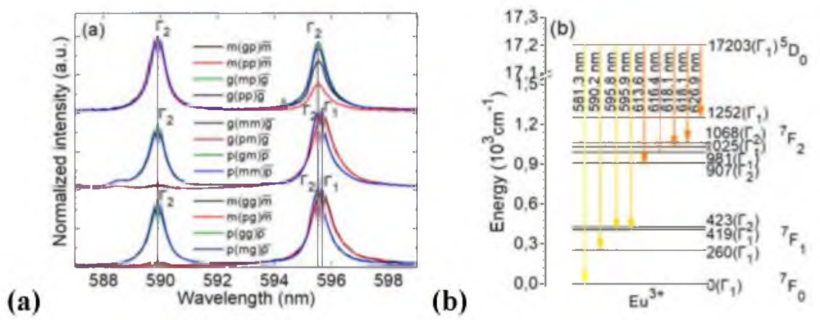


**Figure 2. (a)** Anisotropy of emission corresponding to the magnetic dipole (MD) transition $^5D_0 \rightarrow {}^7F_1$ of $Eu^{3+}$ ions in $C_2$ sites in the monoclinic $KY(WO_4)_2$ crystal, Porto's notations are used; **(b)** Crystal-field splitting of the $^5D_0$ and $^7F_{0\text{-}2}$ $Eu^{3+}$ multiplets, *arrows* indicate the transitions in emission.


## Acknowledgments

The reported study was funded by RFBR, project number 19-32-90199.


## References


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