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SPECTROSCOPIC PROPERTIES OF Eu^{3+} ION IN $KEu(MoO_4)_2$ CRYSTAL

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IR, Raman, electron absorption and emission spectra of $KEu(MoO_4)_2$ crystal were measured at the temperature range 8–300 K. The oscillator strengths of f–f transitions were evaluated.

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1. Introduction

The aim of this study is to perform an analysis of the optical properties of the Eu^{3+} ion in $KEu(MoO_4)_2$ in order to derive the energy level scheme and its relation to the structure of the crystal.

2. Experimental

The $KEu(MoO_4)_2$ crystals were grown by the melt method from the stoichiometric amounts of the substrates. The electron absorption spectrum was recorded at 8 and 300 K on a Cary 17 Varian spectrophotometer. The fluorescence spectra were measured at 10, 77 and 300 K using a Spex 500M monochromator equipped with a cooled Hamamatsu R 4929 photomultiplier. The 532 nm line of a Nd:YAG laser and EG and G 2100 dye lasers were used for excitation. Decay studies were performed under 532 nm excitation using a Tektronix 2440 digital storage oscilloscope.

3. Structure and phonon properties

In the spontaneous growth from the melt we obtained β-phase of $KEu(MoO_4)_2$ crystal. The structure of that phase was described briefly by Klevtsov and Klevtsova [1] as monoclinic with $Z = 12$. Our analysis of the powder diffraction pattern of this compound reveals that they omitted in their calculations several low-angle diffraction lines. We have found that this crystal is monoclinic with space group $P2_1/C \equiv C_{2h}^5$ and its primitive unit cell contains 16 molecules. This structure is a modification of the scheelite $CaWO_4$. The unit cell of the crystal

studied consists of isolated WO_4^{2-} tetrahedra of the C_1 symmetry. Europium(III) ions lie inside several different oxygen polyhedrons with the Eu–O average bonding equal to 2.43 Å and Eu–Eu smallest distance equal to 3.88 Å.

The phonon properties of $KEu(MoO_4)_2$ have been previously reported by us [2]. The IR and Raman spectra were published and discussed in detail. These data were employed in the analysis of the vibronic sidebands of emission spectra and the role of electron–phonon coupling in the energy transfer.

4. Electron absorption and emission studies

Absorption spectra measured at 300 and 8 K are shown in Fig. 1. The assignment of absorption bands and their oscillator strengths are given in Table I.

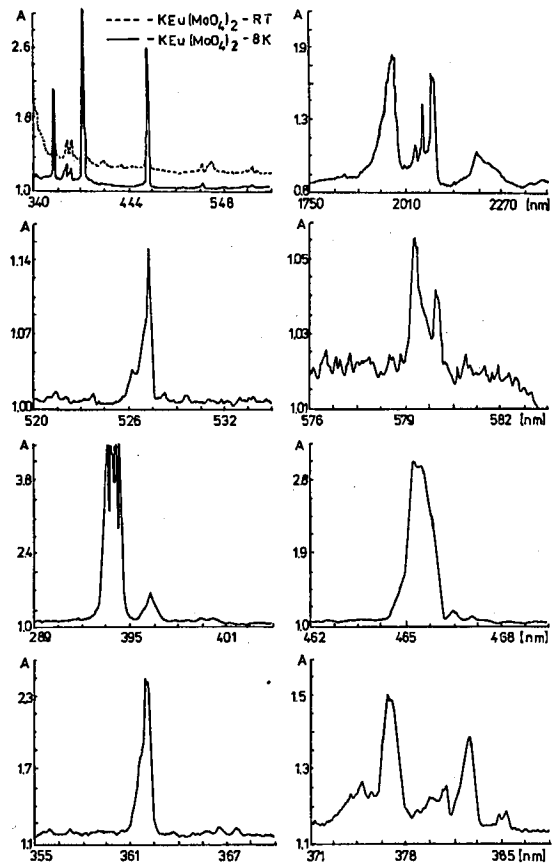

Fig. 1. Absorption spectra of $KEu(MoO_4)_2$ crystals measured at 300 and 8 K.

The low-temperature emission spectra recorded at 15 K are shown in Fig. 2. The emission transitions have originated from $^5D_0$ and terminated on ^7F_J lev-

TABLE I

The assignment of absorption bands and their oscillator strength values for $KEu(MoO_4)_2$ crystal.

Term	Spectral range [cm^{-1}]	$P_{exp} \times 10^8$
$^7F_6$	4292–5882	296.89
$^5D_0$	16600–17500	3.49
$^5D_1$	18868–19066	30.89
$^5D_2$	20833–21978	55.01
$^5D_3$	23419–24096	16.93
$^5L_6$, $^5G_2$, $^5L_7$, $^5G_3$	24814–25543	162.17
$^5G_4$, $^5G_5$, $^5G_6$	25510–26882	129.36
$^5L_8$	26846–27972	54.81

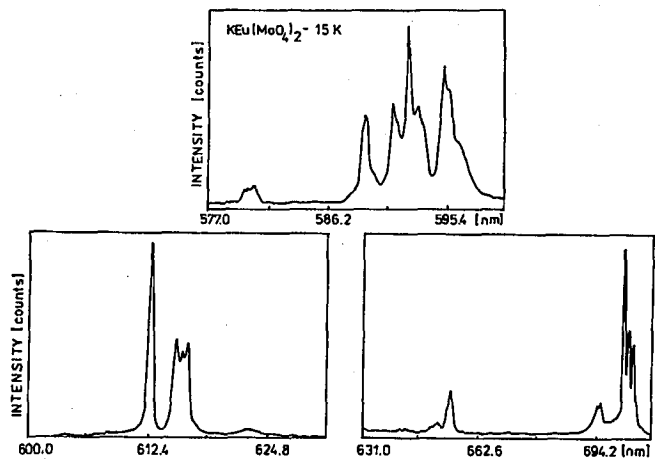

Fig. 2. The low-temperature (15 K) emission spectra of $KEu(MoO_4)_2$ crystals.

els, where $J = 0 \div 4$. The assignment of emission lines is given in Table II. The most intensive observed band is associated with the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$, $|\Delta J| \leq 2$. The intensities of successive bands change as $^7F_0 : {}^7F_1 : {}^7F_2 : {}^7F_3 : {}^7F_4 = 1 : 10 : 144 : 4 : 15$. We have found that the band associated with the $^5D_0 \rightarrow {}^7F_0$ transition, which is expected to be a single line, was splitted into three peaks. A similar behaviour was noted for $^7F_0 \rightarrow {}^5D_0$ bands in absorption spectra which also was splitted into three peaks. Their energy positions are almost identical (see Table II). Such a behaviour means that at least three crystallographic sites of Eu(III) coexist in $KEu(MoO_4)_2$ crystal and give contribution to the observed spectra.

TABLE II

The emission lines of Eu^{3+} at 300 and 15 K in the $KEu(MoO_4)_2$ crystals.

Transition	300 K	15 K	Transition	300 K	15 K
$^7F_0 \leftarrow {}^5D_0$	17265	17253	$^7F_2 \leftarrow {}^5D_0$	16455	16477
	17247	17241		16420	16442
		17230		16337	16324
				16265	16260
$^7F_1 \leftarrow {}^5D_0$		17013		16258	16244
	16989	16978		16239	16234
	16978	16955		16085	16067
	16949	16932			
	16926	16915	$^7F_3 \leftarrow {}^5D_0$	15344	15347
	16915	16903		15305	15295
	16886	16880		15281	15277
	16875	16863			
	16863	16846	$^7F_4 \leftarrow {}^5D_0$	14438	14422
	16812	16801		14397	14401
	16801	16790		14364	
	16779	16762		14269	14269
	16762			14247	14245
	16750			14217	14217
				14201	
				14170	14168

References

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[2] A. Pietraszko, J. Hanuza, L. Macalik, M. Mączka, in preparation.