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ELECTRON ABSORPTION AND EMISSION SPECTRA OF Eu^{3+} IN $KEu(WO_4)_2$

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Electron absorption and emission spectra of Eu^{3+} ion in stoichiometric $KEu(WO_4)_2$ were measured at the temperature range 15–300 K. The oscillator strengths of f–f transitions and the Judd–Ofelt parameters were evaluated. The assignment of vibronic transitions is given and mechanism of emission decay is discussed.

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1. Introduction

Numerous studies [1–11] have been made on the nature of the f–f transitions in rare earth tungstate crystals. The studies were concerned with analysis of the spectral shapes and discussion of the energy transfer mechanism between the active ions. In these host crystals strong interaction between the tungstate group and the rare earth ions exists which is evident in the vibronic pattern of the electron absorption and emission transitions. Vibronic transitions observed in optical spectra reflect one of the important effects resulting from electron–phonon interaction, which also causes various types of nonradiative transitions. In this paper we have investigated the vibronic transitions associated with Eu^{3+} ion in $KEu(WO_4)_2$ single crystal. We have been interested in the problem what types of phonons are coupled in the vibronic transitions and what kind of mechanism governs them.

2. Experimental

The single crystals were grown by the melt method. The electron absorption spectrum was recorded on a Cary 17 spectrophotometer. The luminescence spectra were measured with a Spex 500M monochromator equipped with a cooled Hamamatsu R 4929 photomultiplier. The 532 nm line of Nd:YAG laser and EG and G 2100 dye lasers were used for excitation.

3. Electron absorption and emission studies

The electron absorption and emission studies of $KEu(WO_4)_2$ at 10 and 300 K were performed. These spectra are presented in Fig. 1 and their analysis is given in Table. The assignment of bands was made on the basis of our previous on phonon properties and structure of this crystal [12].

In the emission measurements we excited resonantly $^5D_2$ bands. The emission originated only from $^5D_0$ level both in low and room temperature. The most intense bands were associated with the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$, satisfying the selection rule $|\Delta J| \leq 2$. These transitions are accompanied with well resolved

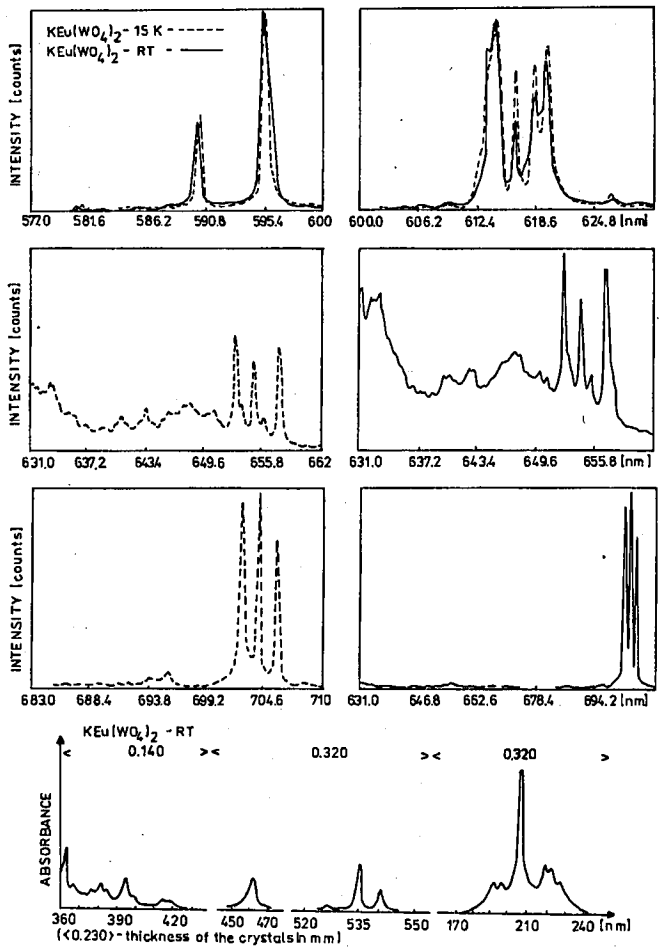

Fig. 1. Electron absorption and emission spectra of $KEu(WO_4)_2$ crystals at 300 and 15 K.

and strong vibronic transitions. This vibronic pattern roughly coincides with the

TABLE

Analysis of the emission and absorption lines of Eu^{3+} in $KEu(WO_4)_2$ crystals at 300 and 15 K.

Emission lines [cm^{-1}]			Absorption lines [cm^{-1}]	
300 K	15 K	Transition	300 K	Transition
17223	17218	$^7F_0 \leftarrow {}^5D_0$	4890	$^7F_6 \leftarrow {}^7F_0$
17077	17077	$^7F_1 \leftarrow {}^5D_0$	18501	$^5D_1 \leftarrow {}^7F_1$
17050	17047			
16995			18685	$^5D_1 \leftarrow {}^7F_0$
16949	16943		18929	
16798	16795		18965	
16614	16606	vibronic	21155	$^5D_2 \leftarrow {}^7F_1$
16551	16540	transi-		
16485	16485	tions		
16428	16420		21413	$^5D_2 \leftarrow {}^7F_0$
	16329		21468	
16311	16308			$5D_3 \leftarrow {}^7F_0$
			23838	
16289	16297	$^7F_2 \leftarrow {}^5D_0$	24027	
	16287			
16231	16234			
16181	16181		24832	$^5L_6, {}^5G_2, {}^5L_7,$
16150	16145		25025	$^5G_3 \leftarrow {}^7F_0$
			25284	
	15995	vibronic		
15992	15969	transi-	25873	$^5G_4, {}^5G_5, {}^5G_6,$
15838	15838	tions	26042	$\leftarrow {}^7F_0$
15793	15793		26164	
15738	15738		26462	
15708	15704		26702	
15654	15659			
15620	15610		27226	$^5L_8 \leftarrow {}^7F_0$
15555	15547		27525	
	15489			
15444	15437			
15387	15382			
15323	15323	$^3F_3 \leftarrow {}^5D_0$		
15305	15305			
15281	15277			
15258	15253			
15216	15216			
14411	14413	$^7F_4 \leftarrow {}^5D_0$		
14380	14376			
14255	14261			
14237	14237			
14209	14205			
14174	14172			

energies of the $k = 0$ phonons [11, 12]. Two types of optical phonons are observed, one related with internal modes localized in WO_4^{2-} ion and the other related with external vibrational modes due to the Eu^{3+} translation. The integrated intensities of the vibronic transitions depend very much on the nature of the electronic states involved in the transitions. The vibronic transitions associated with $^5D_0 \rightarrow {}^7F_2$ ones have nearly the same strengths and are one order of magnitude stronger than those of $^5D_0 \rightarrow {}^7F_{1,3}$. According to the Judd–Ofelt theory, the vibronic transitions between the same parity levels are first-order electric dipole-allowed, while that of $^5D_0 \rightarrow {}^7F_1$ is electric dipole-forbidden. The experimental results indicate that the second-order electric dipole and first-order magnetic dipole contribute to the vibronic transitions of $^5D_0 \rightarrow {}^7F_1$.

The emission lifetime of $KEu(WO_4)_2$ does not significantly change with temperature: 414 μs at 10 K $\div$ 372 μs at 300 K.

The mechanisms responsible for the appearance of intense vibronic transitions in noncentrosymmetric lanthanide(III) systems have been recently discussed by Blasse [9]. Following his argumentation, the fact that the vibronic lines accompany the hypersensitive transition in tungstate crystal may be elucidated by assuming an admixture of the lower lying charge transfer states.

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