

VIBRONIC TRANSITIONS IN CENTROSYMMETRIC [Eu_xLa_{1-x}(AP)₆](ClO₄)₃ CRYSTALS

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The optical excitation and emission spectra of Eu(III) in [Eu_xLa_{1-x}(AP)₆](ClO₄)₃ centrosymmetric complex were measured. The vibronic transitions were observed in excitation and emission spectra. Following the vibrational analysis of the infrared and Raman spectra of [Pr_xLa_{1-x}(AP)₆](ClO₄)₃, the assignment of [Eu_xLa_{1-x}(AP)₆](ClO₄)₃ vibronics was given. The concentration effect on excitation and emission spectra was investigated. It was found that the vibronic intensities were changed upon the concentration effect. The intensive charge transfer bands were observed in blue region. Their intensities decreased with increasing concentration.

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1. Introduction

The well pronounced vibronic transitions were reported for Eu(III) in [Eu(AP)₆](ClO₄)₃ by Berry et al. [1]. The authors assigned the zero-phonon origins of ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₂ and ⁷F₀ → ⁵D₂ bands. The vibronic transitions were associated with the skeletal and internal ligand modes. The most characteristic feature of these transitions was that the vibronic intensities combined with internal ligand modes were comparable to the skeletal modes. Recently van Vliet and Blasse [2] have reported the concentration effect on vibronic transition intensities. They have found the pronounced concentration effect manifesting in variations of vibronic intensities.

The purpose of our studies were detailed investigations of the concentration effect on vibronic transitions appearing in emission and absorption spectra of [Eu_xLa_{1-x}(AP)₆](ClO₄)₃ crystals. Following the vibrational analysis of IR and Raman spectra, we assigned the vibronic transitions. The Eu³⁺ concentration dependence of vibronic transition intensities was found in both emission and excitation spectra, however not all of those were affected in the same degree.

2. Experimental results

The crystals of $[\text{Eu}_x\text{La}_{1-x}(\text{AP})_6](\text{ClO}_4)_3$ and $[\text{Pr}(\text{AP})_6](\text{ClO}_4)_3$ were obtained by reaction of $\text{Eu}(\text{ClO}_4)_3$ solution with antipyrine at $\text{pH} \approx 4$. The structure of synthesized sample was checked by X-ray measurements.

TABLE I
FTIR and Raman spectra of the free antipyrine (AP) and $[\text{Pr}(\text{AP})_6](\text{ClO}_4)_3$ in the 30–2000 cm^{-1} range.

IR spectra		Raman spectra		Assignment
ligand (AP)	$\text{Pr}(\text{AP})_6$	ligand (AP)	$\text{Pr}(\text{AP})_6$	
1662vs		1658s	1663m	$\nu(\text{C}=\text{O})^a$
1592m	1607vs	1592vs	1599s	
1578m	1582vs	1580sh	1581m	
	1548m		1547s	
1499w	1518w		1502m	benzene ring vibration $\nu(\text{C}=\text{C})$ and $\delta_{\text{as}}(\text{CH}_3)^a$
1495s	1497s	1487m	1488m	
		1462w	1466w	
1453s	1461vs	1450m		
1416s	1413s	1441w	1435w	$\delta_s(\text{CH}_3)$ and $\delta_s(\text{NCH}_3)$ $\nu(\text{CN})^a$
		1417m	1415w	
		1404m	1390s	
1378s	1377s	1379m	1366s	
1325s	1322m	1326vs	1326m	
1307s	1301m	1307s	1304m	
		1293w		
	1245w		1246s	in-plane (CH) bending of benzene ring ^a
1227m		1220w	1215w	
1177m	1180w		1191w	
		1168m	1165m	
1153m	1148w	1155m	1146m	
1138s		1138m	1123w	
	1092vs,b			$\nu_3(\text{ClO}_4)^d$
1099s		1101m	1093m	in-plane aromatic $\delta(\text{CH})$ $\nu(\text{C}-\text{N})$ and $\rho(\text{CH}_3)^a$
1080s		1082m	1075w	
1053s	1148	1054s		
		1037w	1039ms	
1024m		1025m		
		1006vs	1005vs	
988m	980	989sh	989m	
		987vs		

TABLE I (cont.)

			932vs	$\nu_1(\text{ClO}_4)^d$
915w	920w	921m		$\nu(\text{C-C-N})^a$
			908w	
853m	870s	857s	895w	
			873s	
817s	802m	813w	820w	
			794w	benzene ring puckering
772vs	771s	774m	776m	$\delta(\text{CH})$ out-of-plane ^a
739s		739s	727s	
720s	725s	723s		
700m	696m	702m	698m	
668w			670s	
	658s			$\nu_4(\text{ClO}_4)^d$
			664s	$\delta(\text{CCH}_3)^a$
639m		639s	637w	
616s	617s	617s	619s	
		603s		
588s	596m	587vs	595w	
540w				
501s	496m	504w	500w	
460s		470w	464w	
	444m		442w	$\nu_2(\text{ClO}_4)$
		419m		$\delta(\text{NCO}), \delta(\text{CCO}), \delta(\text{NNC}),$
	414w	410m		$\delta(\text{NCC}),$ and $\delta(\text{CNC})^a$
385w	390m	387m	394m	in-plane and out-of-plane
322s	310s	327m	310sh	ligand librations
305s	293s	300s	288m	mixed with
277m		278m		C-O-Pr and O-Pr-O
262s	264w	261s		bending modes
211w	218w	206w	214w	
	174s,b		171w	$\nu(\text{Pr-O})^b$
166vw		150m		$\delta(\text{NCO})$ coupled
147w				with $\delta(\text{O-Pr-O})^{a,b}$
138w	137w		130m	
130m				
126m	125w			
121w				
100w	105w		107m	
89w	71w		80sh	
	51w			lattice modes ^c
	44w			
	34w			

^aligand modes, ^blocal modes, ^clattice modes, ^danion modes

t_{1u} local modes: $\nu(\text{Pr-O}) - 174 \text{ cm}^{-1}$, $\delta(\text{O-Pr-O}) - 170-110 \text{ cm}^{-1}$.

$2E_u + A_{2u}$ lattice modes: $30-70 \text{ cm}^{-1}$.

The "localised" ligand t_{1u} modes: $\nu(\text{C-O}) 1500-1600 \text{ cm}^{-1}$, $\delta(\text{NCO})(\text{M}) 290-300 \text{ cm}^{-1}$, $\delta(\text{CCO})(\text{M}) 210-216 \text{ cm}^{-1}$.

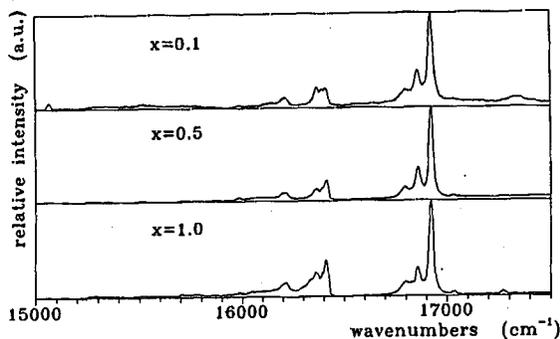


Fig. 1. Luminescence spectra of $\text{Eu}_x\text{La}_{1-x}(\text{AP})_6$ ($T = 77 \text{ K}$).

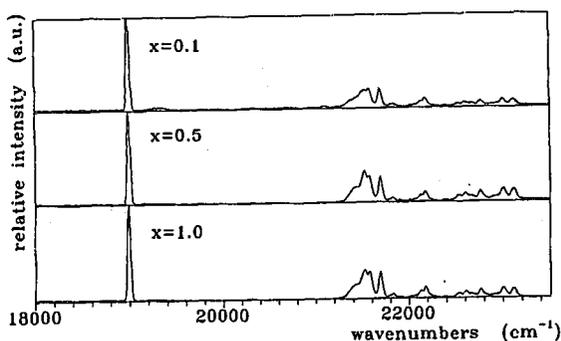


Fig. 2. Excitation spectra of $\text{Eu}_x\text{La}_{1-x}(\text{AP})_6$ ($T = 77 \text{ K}$, monitored at 16477 cm^{-1}).

The infrared and Raman spectra were measured on a FTIR Bruker IFS 88 spectrometer in KBr and Nujol suspensions at 290 K and on a Jobin-Yvon Raman spectrometer equipped with an argon ion laser. The Fourier transform infrared (FTIR) and Raman transition energies of the free antipyrine and $[\text{Pr}(\text{AP})_6](\text{ClO}_4)_3$ complex in the region $30\text{--}1700 \text{ cm}^{-1}$ and their assignments are given in Table I.

The emission spectra were measured at 77 and 15 K with ATC 330 (Lake Shore Cryotechnics Inc.) using a Jobin-Yvon THR 1000 spectrophotometer and an argon laser ILA120 (C. Zeiss Jena) as an excitation source. The emission spectra of $[\text{Eu}_x\text{La}_{1-x}(\text{AP})_6](\text{ClO}_4)_3$ for $x = 0.1, 0.5$ and 1.0 are shown in Fig. 1. The assignment of vibronic transitions is given in Table II. An inspection of Fig. 1 allows us to see that the intensities of vibronic transitions in the range $16500\text{--}16100 \text{ cm}^{-1}$ increased significantly with decreasing concentration.

The excitation spectra were detected by SPF-500 SOPRA spectrofluorometer at 77 K. They are reproduced in Fig. 2. One can note that the most intensive vibronic lines accompany the ${}^7F_0 \rightarrow {}^5D_2$ bands. The most characteristic feature we observed was an enhancement of vibronic intensities of the 5D_2 band with increasing concentration of Eu(III) ions. This effect is opposite to that observed in

emission spectra. Moreover, we found that the vibronic sidebands accompanying the 5D_1 line were clearly observed at low concentrations $x = 0.1$, which were practically not observed at higher concentrations. At the region 26000–34000 cm^{-1} we observed the pronounced charge transfer (CT) band centred at 28500 cm^{-1} . The intensity of that band decreased evidently with increasing Eu(III) concentration.

TABLE II
Luminescence vibronic peak positions and assignments of ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu(III) in $[\text{Eu}(\text{AP})_6](\text{ClO}_4)_3$ crystal at 15 K.

Wave number [cm^{-1}]				Assignment
ν_1	$(0-0_1)-\nu_1$	ν_2	$(0-0_2)-\nu_2$	
16477				$(0-0_1)$
		16363		$(0-0_2)$
16210	267			δ (ligand) librations and Ln-ligand bending modes
16191	286	16076	287	
16141	336	16055	308	
15981	496	15867	496	$\delta(\text{C}-\text{CH}_3)$
		15772	591	
15857	620	15744	619	
		15723	640	
15794	683	15678	687	δ (CH) out-of-plane benzene ring puckering
15703	774			
		15515	848	$\nu(\text{C}-\text{C}-\text{N})$
15495	982			$\nu(\text{C}-\text{N})$ and $\rho(\text{CH}_3)$ in plane aromatic δ (CH)
		15348	1015	
		15275	1088	
15293	1184			
		15130	1233	benzene ring bending
		15120	1243	
		14966	1397	$\nu(\text{C}-\text{N})$
14971	1506			benzene ring vibrations
		14785	1578	$\nu(\text{C}=\text{O})$
		14775	1588	
		14770	1593	
		14705	1658	
		14700	1663	

3. Conclusions

In this paper we have reported the vibronic spectra of centrosymmetric $[\text{Eu}_x\text{La}_{1-x}(\text{AP})_6](\text{ClO}_4)_3$ crystals. We have found that the intensities of vibronic transitions were affected by concentration. The vibronic intensities linked with emission spectra decreased with concentration whereas the vibronic intensities for some transitions measured in excitation spectra increased with increasing concentration of Eu(III) ions. A similar behaviour of vibronic transitions of Eu^{3+} with concentration for $\text{Na}_5\text{Eu}_x\text{Gd}_{1-x}(\text{WO}_4)_4$ was reported earlier by van Vliet and Blasse [2].

It should be noted that the vibronic transitions linked with high energy ligand vibrations appear extremely intensive in excitation spectra whereas in emission spectra they are much weaker. The ligand localized vibronic transitions change intensity in the same degree as metal ligand mode involving vibronic transitions. An increase in vibronic intensity may be explained by increasing covalency of the Eu(III)-ligand bond [3]. It is in agreement with decreasing CT band energy and the vibronic intensity decrease with concentration may result from the borrowing intensity mechanism [4]. However, such mechanism cannot explain a quite opposite behaviour found in emission spectra. Moreover, within the framework of that mechanism it is difficult to understand the puzzle of intensive ligand-localized vibronics appearing only in excitation spectra. The nature of concentration dependence of vibronic transitions needs further investigations.

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