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Spectroscopic study of lanthanide squarate hydrates

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Abstract

In the present investigation some spectroscopic properties of several lanthanide squarate hydrates are reported. The Raman spectra show the same distinctive Jahn–Teller intensity pattern for non-totally symmetric modes, as previously observed for the free anion. In the case of the terbium salt, the Tb^{3+} emission is very intense even at room temperature, revealing an efficient excitation via the ligand electronic levels. The Tb^{3+} dilution in Gd^{3+} or La^{3+} hosts increases this excitation efficiency without any appreciable variation in the 5D_4 excited-state lifetime. However, the Eu^{3+} emission is very weak, with excited states located above the 5D_2 level (ca. $21\,550\text{ cm}^{-1}$) being completely quenched at room temperature. At lower temperatures higher-lying levels are not so efficiently quenched. The broad band observed in the UV excitation spectra of Eu^{3+} and Tb^{3+} is easily assigned to an intra-ligand transition leading to ligand-to-lanthanide ion energy transfer processes. As observed for Tb^{3+} , Eu^{3+} dilution in Gd^{3+} or La^{3+} hosts also increases the relative emission intensity mediated by the ligand, without variation in the 5D_0 excited-state lifetime. The Eu^{3+} 5D_0 excitation spectra show vibronic structures that can be interpreted on the basis of the data available from the vibrational spectra. An increase in the vibronic intensities is observed as the lanthanide concentration is increased.

Keywords: Lanthanide squarate hydrates; Lanthanide spectroscopy; Vibronic spectra; Synthetic procedures

1. Introduction

Lanthanide squarate hydrates (squatrate is the anion of 1,2-dihydroxycyclobutenedione) have recently been investigated regarding their synthetic procedures, crystal structures and thermal behaviour [1,2]. In fact, Petit et al. [1] have established that, depending on the experimental conditions and the particular lanthanide ion utilized, five different families of crystal structures result. In all the cases polymeric structures are obtained, where the squarate anions participate as bridging ligands between metal ions. As far as the spectroscopic properties of such compounds are concerned, the literature is relatively sparse [2,3]. Huskowska et al. [2] presented Eu^{3+} and Nd^{3+} emission spectra at 4.5 K, discussing the observed crystal field splittings in a qualitative way. Piriou et al. [3] worked at 77 K and could probe three sites for Eu^{3+} in the La^{3+} host, using site-selective excitation and time-resolved spectroscopy. The absorption and excitation spectra have not been reported.

Aiming to better characterize the spectroscopic properties of the lanthanide squarate hydrates, the present study was undertaken using Raman, IR absorption,

electronic absorption, excitation and emission spectroscopies as well as emission kinetics. Particular attention was given to coupling between ligand and metal ions excited states. This last aspect is of utmost importance for clarifying the possibility of sensitization of the characteristic Ln^{3+} ($Ln=Eu$ and Tb) emission via UV ligand absorption.

2. Experimental

2.1. Syntheses

Lanthanide squarate hydrates were obtained from mixtures of aqueous solutions containing stoichiometric amounts of lanthanide chlorides and squaric acid (Aldrich Co.). The synthetic procedure is well described in the literature [1,2]. Formulae have been confirmed by elemental analysis (C, H, Ln) and X-ray diffraction. The following microcrystalline compounds were obtained: $Ln_2(C_4O_4)_3(H_2O)_8$ and $Ln_2'(C_4O_4)_3(H_2O)_{13}$ with $Ln=Eu, Tb, [Gd_{0.9}Eu_{0.1}], [Gd_{0.99}Eu_{0.01}], [Gd_{0.9}Tb_{0.1}]$,

[Gd_{0.99}Tb_{0.01}] and Ln' = La, [La_{0.9}Eu_{0.1}], [La_{0.99}Eu_{0.01}], [La_{0.9}Tb_{0.1}], [La_{0.99}Tb_{0.01}].

2.2. Spectroscopic measurements

Raman spectra of the pure solids were obtained with the 514.5 nm excitation line of a Coherent Innova 400 Ar⁺ laser and a Jarrel–Ash double monochromator with photon-counting detection. The spectral resolution was 7 cm⁻¹, the rotating disk technique being used to avoid thermal decomposition. IR absorption spectra were obtained using KBr pellets in a FTIR Nicolet 730 FX spectrometer. Absorption spectra were obtained at room temperature using KBr pellets with a Beckman DU-70 spectrophotometer.

Excitation and emission spectra, as well as decay time measurements, were obtained at room and liquid N₂ temperatures (LNT) in a SPEX Fluorolog F121I fluorimeter equipped with both continuous (450 W) and pulsed (5 J/pulse, 3 μs bandwidth) Xe lamps. All spectra were corrected for lamp intensity, optics and detection spectral variations.

3. Results and discussion

The Raman spectra are displayed in Fig. 1, and the Raman shift values are listed in Table 1, which also includes data from the vibronic structure of the Eu³⁺ excitation spectra. Following the notation suggested by Petit et al. [1], the Eu³⁺, Gd³⁺ and Tb³⁺ compounds are referred to as having the '2-Ln' double-layered structure (monoclinic, P2/c). For the lighter lanthanide ions (La³⁺–Nd³⁺) the structure is referred to as the '1-Ln' double-chained structure (monoclinic, Pc). In Fig. 1 the Raman spectra for the La³⁺ and Tb³⁺ squarate hydrates, representatives of the two structures mentioned above, are shown. The Raman spectrum of sodium squarate is also included for the sake of comparison. Table 1 also includes the Raman values for sodium squarate (solid and aqueous solution) and a feature assignment based on data available in the literature [4,5].

The Raman spectrum of sodium squarate in aqueous solution displays six bands according to the vibrational representation 2A_{1g} + 2B_{1g} + 2B_{2g}, in a D_{4h} symmetry. The E_g mode, being weak, is observed only in the solid [4]. The Raman spectrum of sodium squarate in the solid state (Fig. 1(a)) shows bands at 647, 1320 and 1600 cm⁻¹ split into doublets, which can be explained by correlation splitting.

For both the 2-Ln and 1-Ln structures there are squarate anions bridging two lanthanide ions in a cis-bimonodentate mode. In the case of the La³⁺ compound there is also a squarate anion relating three metal ions in a trismonodentate mode. Petit et al. [1]

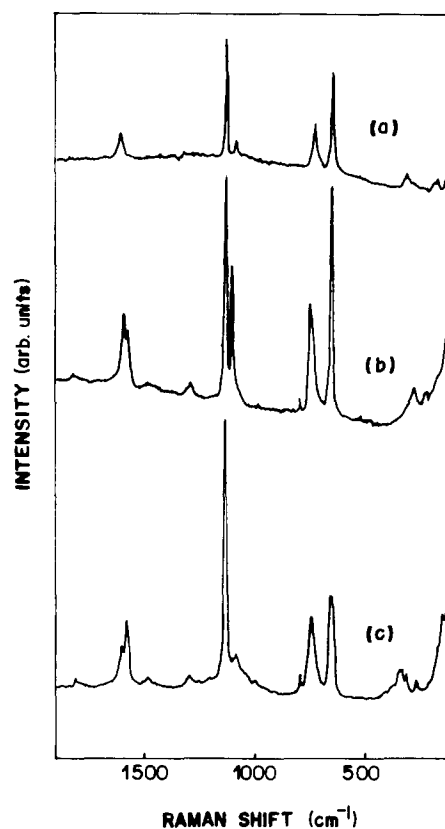


Fig. 1. Room-temperature Raman spectra for the squarates of (a) sodium, (b) lanthanum and (c) terbium.

suggest, in addition, significant deviations from planarity for some of the squarate anions in the structure.

Despite all such features, indicative of a lowering of the symmetry of the free anion, the Raman spectra do not show any evidence for lowering in the squarate local symmetry. In fact, the Raman spectra display the same Jahn–Teller pattern of intensities characteristic of the high symmetry of the free anion. Even far from resonance with the first allowed electronic transition of the squarate anion, the most intense modes are non-totally symmetric, and more particularly, those effective in promoting the Jahn–Teller distortions in a D_{4h} symmetry [6]. In the case of the Tb³⁺ compound, the additional lines in the Raman spectrum could in principle be indicative of a lower symmetry of the anion, although correlation effects due to the presence of two squarate moieties in the unit cell could account for the extra Raman bands in the low-frequency region. The CO stretching mode (B_{2g}) and CC stretching mode (B_{1g}) are both sensitive to coordination to the lanthanides.

Electronic absorption spectra for sodium, lanthanum and terbium squarates in the solid state are shown in Fig. 2. In solution, squarate and oxocarbon ions in general, display the lowest energy allowed transition ($\pi \rightarrow \pi^*$) in the form of a doublet. This fact has been interpreted as a manifestation of the Jahn–Teller effect

Table 1
Energy position (cm^{-1}) for the lines observed in Raman spectra and also in Eu^{3+} vibronic spectra

Na^{+a}		La^{3+}	Tb^{3+}	Vibronics ^b (Eu^{3+})	
Aq. sol.	Solid			Stokes	anti-Stokes
			110		
			140	125	170
			159		
			180		
		237	223		
		288	274		
294(ν_6)	307		318	320	320
			350		
			390		450
647(ν_{10})	647	656	650	640	660
	660(ν_{11})		661		
723(ν_2)	721	748	743	715	
		797	794		
		1084	1000		
	1087	1109	1087		
1123(ν_5)	1129	1138	1133	1125	
	1320	1293	1291		
		1475	1482	1470	
1593(ν_9)	1603	1577	1580	1570	
		1594	1606		
1794(ν_1)	1794	1806	1800	1800	

^aAssignments: ν_1 (A_{1g}), CO stretching; ν_2 (A_{1g}), ring breathing, ν_5 (B_{1g}), CC stretching; ν_6 (B_{1g}), in-plane CO bending; ν_9 (B_{2g}), CO stretching; ν_{10} (B_{2g}), ring bending; ν_{11} (E_g), out-of-plane CO bending.

^bRelative to the 0-phonon line ${}^7F_0 \rightarrow {}^5D_2$.

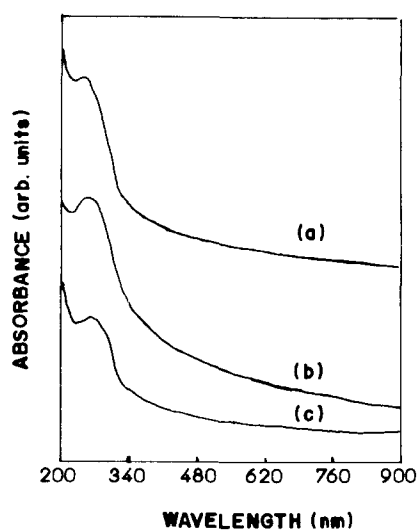


Fig. 2. Room-temperature absorption spectra for the squarates of (a) sodium, (b) lanthanum and (c) terbium.

in such highly symmetrical and electronic delocalized structures [6]. In the solid state such doublet structure is lost due to band broadening, but the band maxima are all very similar for the investigated compounds, i.e. at ca. 270 nm (the same is true for the Eu^{3+} compound, not shown in the figure). For the Tb^{3+} compound an incipient shoulder is present around 300 nm.

Fig. 3 shows $\text{Eu}^{3+} {}^5D_0$ excitation spectra at room and liquid nitrogen temperatures (Figs. 3(a) and 3(b)). As is well known, ligand field effects do not shift the lanthanide energy levels significantly, making it possible to assign the transitions by comparison with data available in the literature [7]. In Fig. 3(a) no band is observed above ca. 21550 cm^{-1} (464 nm), and in fact even the electric dipolar transition ${}^7F_0 \rightarrow {}^5D_2$ at ca. 464 nm shows up weakly relative to the magnetic dipolar transition ${}^7F_0 \rightarrow {}^5D_1$ at ca. 535 nm. Since Eu^{3+} ions are not located on inversion centres in such structures, the observed relative intensities do not follow directly from selection rules.

We may then suppose that all levels situated above the threshold at ca. 21550 cm^{-1} are almost completely quenched at room temperature, whereas at LNT the quenching is not so pronounced. At low temperature the most intense transition is the ${}^7F_0 \rightarrow {}^5D_2$ at ca. 464 nm followed by the ${}^7F_0 \rightarrow {}^5L_6$ transition at ca. 394 nm and by a broad structureless band in the UV (Fig. 3(b)). By diluting Eu^{3+} in La^{3+} or Gd^{3+} hosts, an increase in the relative intensity of the UV band (maximum ca. 360 nm, Fig. 3(c)) is observed, with no difference for Gd^{3+} or La^{3+} hosts.

Fig. 4 displays a selected region of the Eu^{3+} excitation spectrum (the scale has been changed to cm^{-1}). Several weak vibronic lines may be observed related to the

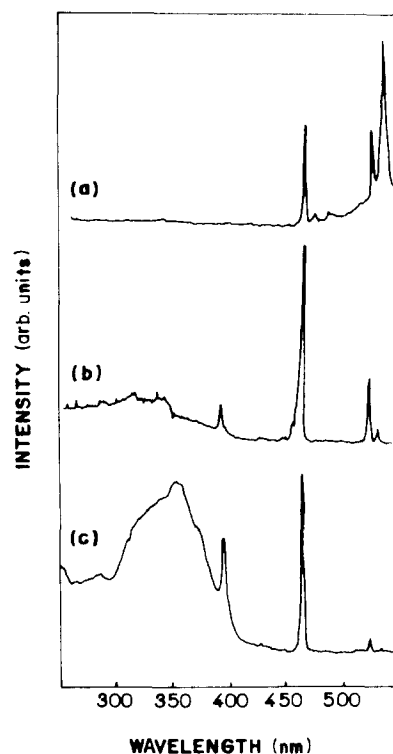


Fig. 3. Excitation spectra ($\lambda_{em} = 615 \text{ nm}$) for the europium squarate hydrate at (a) room temperature and (b) liquid nitrogen temperature (LNT), and also (c) the europium-doped (10%) lanthanum squarate hydrate at LNT.

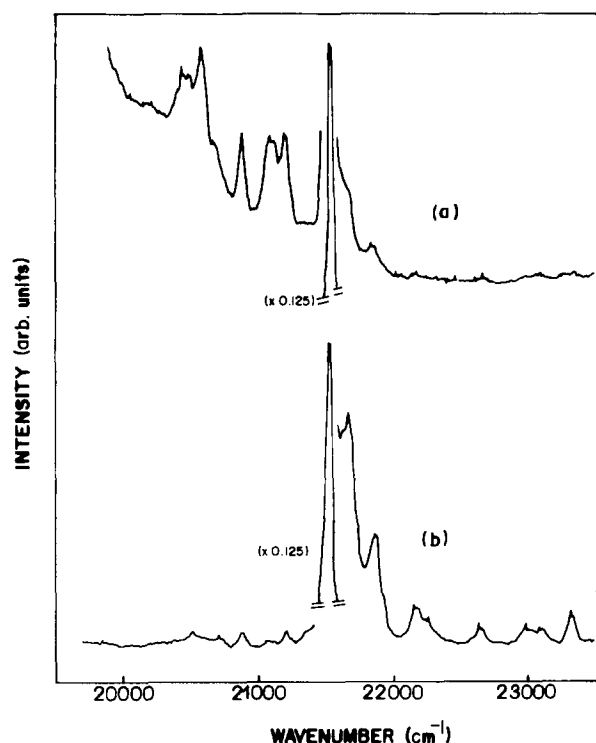


Fig. 4. Selected region of the Eu^{3+} excitation spectra showing vibronic structure related to the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ electronic transition: (a) room temperature; (b) LNT.

${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ electronic transition [8]. They correspond at the high-energy side to transitions from the vibrationless level of ${}^7\text{F}_0$ to a one-phonon excited vibrational level of ${}^5\text{D}_2$. Some lines also can be observed at the low-energy side of the electronic line, corresponding to transitions from thermally populated excited vibrational levels of ${}^7\text{F}_0$.

Considering the electronic 0-phonon line as the origin, the most intense vibronic lines occur at 125 and 320 cm^{-1} . The former can be related to either lattice modes or to a Eu–O mode. The latter may be tentatively assigned to squarate CO bending [4]. The other vibronics appearing in the excitation spectra may also be assigned to the squarate internal vibrational modes appearing in either the Raman or IR spectra. Tentative assignments can also be found in Table 1. In particular, the line corresponding to a 1800 cm^{-1} mode appears with high intensity in the vibronic spectrum. In the Raman spectrum it is assigned to the CO stretching mode A_{1g} , and appears as a very weak line at ca. 1800 cm^{-1} . In the IR absorption spectrum a strong and broad band assigned to the CO stretching mode, E_u , appears at lower wavenumber (at ca. 1550 cm^{-1}).

Curiously, the 'Stokes' lines are hardly observed in the room-temperature spectrum. The energy position (relative to the 0-phonon line) for the 'anti-Stokes' lines observed at room temperature (Fig. 4(a)) is in close agreement with the IR absorption spectra as shown in Table 2.

Table 2

Energy position (cm^{-1}) for the lines observed in IR absorption and room temperature anti-Stokes vibronic spectra for the europium squarate

Vibronics ^a (anti-Stokes, 300 K)	IR absorption (300 K)
315	305
335	346
405	401
645	650
830	740
955	1000
1045	1100
	1500
	3140

^aRelative to the 0-phonon line.

The intensity ratio between vibronics and the related electronic (0-phonon) line may be taken as a measure of the electron-phonon coupling strength [9]. For the Eu^{3+} compounds this ratio shows a concentration dependence, amounting to 0.04 (1% Eu^{3+}), 0.09 (10% Eu^{3+}) and 0.14 for the neat compound (those values are the same for both the Gd^{3+} and La^{3+} hosts).

This concentration dependence of the vibronics was first observed by Hoshina et al. [10]. Also, Auzel et al. showed such effects in emission spectra explaining with it part of the self-quenching process for lanthanide ions [11]. More recently a quantitative model was proposed for Pr^{3+} compounds by Donega et al. [12], taking into account superexchange interactions over distances up to 11 Å. Since, in the neat Eu^{3+} squarate, Eu–Eu distances are within 6.2–6.6 Å [2], superexchange interactions would also be a plausible explanation, although it must be pointed out that the same vibronic structure can be observed for the diluted compounds where the Eu–Eu distances are supposed to be longer.

Fig. 5 shows the $\text{Tb}^{3+} {}^5\text{D}_4$ excitation spectra, where, contrary to those observed for Eu^{3+} compounds, emission seems to be efficiently excited under UV excitation. At room temperature (Fig. 5(a)) one observes the weak Tb^{3+} f–f lines and a very strong and broad band in the UV region, the latter showing up at least two components at ca. 350 and 300 nm. At low temperature (Fig. 5(b)) the overall bandwidth decreases, but both components are still present.

Considering the relative intensities between the broad UV band and the f–f lines, one may qualitatively suggest that the efficiency for the Tb^{3+} excitation via UV absorption increases with dilution in the Gd^{3+} or La^{3+} hosts. The band at ca. 350 nm is also present in the Eu^{3+} compound, being assigned to an intra-ligand transition, and is very likely involved in the energy transfer mechanism from the ligand to the lanthanide ion. In fact, the molecular orbital scheme for squarate shows a 1E_u level at this energy position [13], revealed

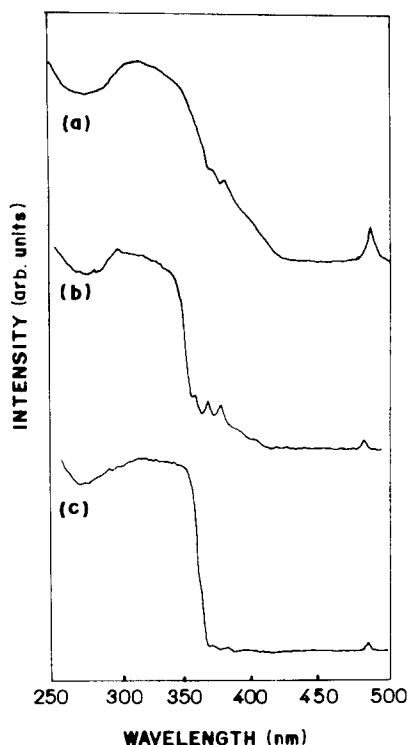


Fig. 5. Excitation spectra ($\lambda_{em}=545$ nm) for the terbium squarate hydrate at (a) room temperature and (b) LNT, and also (c) the terbium-doped (10%) lanthanum squarate hydrate at LNT.

as a weak band in the absorption spectrum. Curiously enough, the strongest band of squarate at ca. 270 nm (Fig. 2) is not observed in the Tb^{3+} or Eu^{3+} squarates excitation spectra. In addition, lower triplet levels that might be active in the ligand to lanthanide ion energy transfer are hardly observed for those squarates. Theoretical studies indicate a triplet level at ca. 660 nm [14], quite a low value for resonance with Eu^{3+} or Tb^{3+} excited states to be effective. In fact, the proposed mechanisms for explaining these energy transfer processes do account for triplet or singlet donor levels [15].

The component at ca. 300 nm in the Tb^{3+} excitation spectra seems to correspond to the one observed as a shoulder in the absorption spectra. It is not observed in the Eu^{3+} spectra and may be tentatively assigned to the allowed $4f \rightarrow 5d$ transition of Tb^{3+} .

When Eu^{3+} or Tb^{3+} are embedded in Gd^{3+} or La^{3+} squarate hosts, the different structures proposed for the latter ones show up clearly in the emission spectra (Figs. 6 and 7). Both crystal field splittings and relative lines intensities show marked differences as a consequence of different environments.

The Eu^{3+} 5D_0 lifetime is ca. 130 μs for lanthanum squarate and ca. 140 μs for gadolinium squarate, with no variation with the Eu^{3+} concentration. Although the lifetime values agree with the ones reported by Piriou et al. [3], the Eu^{3+} emission spectra in the lanthanum squarate host are at variance with the ones

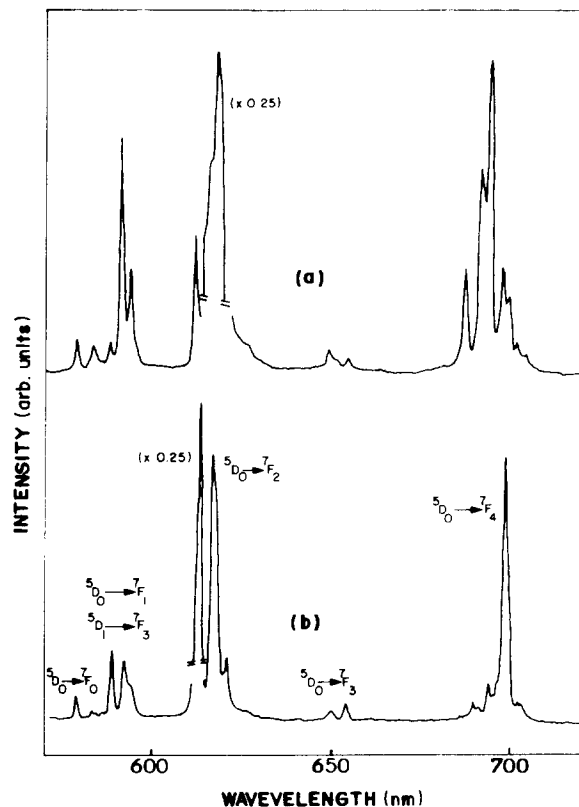


Fig. 6. Emission spectra (LNT, $\lambda_{exc}=464$ nm) for the europium-doped (a) lanthanum squarate hydrate and (b) gadolinium squarate hydrate.

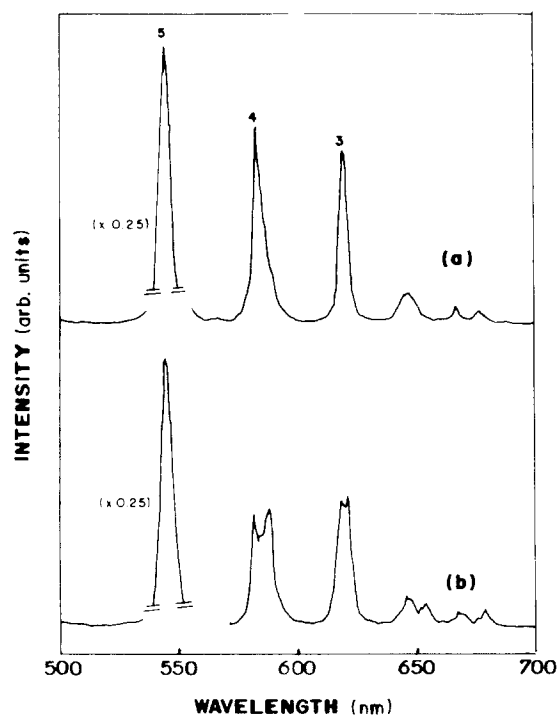


Fig. 7. Emission spectra (LNT, $\lambda_{exc}=310$ nm) for the terbium-doped (a) lanthanum squarate hydrate and (b) gadolinium squarate hydrate. Numbers denote J values for $^5D_4 \rightarrow ^7F_j$ transitions.

shown by those authors. In the Gd^{3+} host the emission spectrum is independent of the Eu^{3+} concentration, thus confirming the suggested identical crystal structures of the Gd^{3+} and Eu^{3+} compounds. On the other hand, the emission spectrum does agree with that reported by Huskowska et al. [2], who suggest that Eu^{3+} emission could be sensitized by squarate. It was our observation that in fact the Eu^{3+} luminescence is rather weak in such compounds, whereas Tb^{3+} emission seems to be very efficient under UV excitation. As observed for the Eu^{3+} ${}^5\text{D}_0$ lifetime, the Tb^{3+} ${}^5\text{D}_4$ lifetime does not change with Tb^{3+} concentration, amounting to 500 μs in the Gd^{3+} host, and 530 μs in the La^{3+} host.

4. Conclusions

Lanthanide squarate hydrates show the same Raman spectra observed for the free squarate, despite the lowering in the symmetry observed from crystallographic studies. The same Jahn–Teller pattern is observed with non-totally symmetric modes presenting the most intense bands.

Tb^{3+} emission is efficiently excited in the UV region even at room temperature. With Tb^{3+} dilution in La^{3+} or Gd^{3+} hosts this efficiency seems to increase. The broad band in the UV part of the excitation spectra may be decomposed into two components, one due to an intra-ligand forbidden transition and the other probably to a $4f \rightarrow 5d$ transition of the Tb^{3+} ion. The ${}^5\text{D}_4$ lifetime is 500 μs in the Gd^{3+} compound and 530 μs in that of La^{3+} , with no variation with Tb^{3+} concentration.

Eu^{3+} emission is almost completely quenched at room temperature. At 77 K it is excited with a weak and broad band in the UV region, in the same energy position observed for the Tb^{3+} compound. This broad band can be tentatively assigned to intra-ligand transitions involved in the ligand–lanthanide ion energy transfer process. As observed for the Tb^{3+} compound, the efficiency for excitation via this ligand level increases with Eu^{3+} dilution in the Gd^{3+} or La^{3+} compounds. The ${}^5\text{D}_0$ lifetime does not change with dilution, being 130 μs for the La^{3+} compound and 140 μs for the Gd^{3+} compound.

Excitation spectra show intense vibronic structure for the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition of Eu^{3+} , with a close agreement

between the vibronic structure and vibrational data. Relative intensities between vibronic components and the 0-phonon line increase with Eu^{3+} concentration, and this phenomenon has recently been explained with a superexchange interaction between lanthanide ions [12].

Further investigations are in progress taking into account emission quantum yields, vibronic intensities and the influence of the lanthanide active ion concentration on these features.

Acknowledgments

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