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Electronic absorption spectroscopy of neodymium acetate single crystals

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Abstract

Electronic absorption spectra of neodymium acetate single crystals were measured at 293 and 4 K. The intensities of 4f–4f transitions were calculated and the Judd–Ofelt Ω_λ parameters evaluated. These results differ in comparison with other lanthanide carboxylate compounds by relatively high 'hypersensitive' transition intensity and the Ω_2 parameter value. The vibronic mechanism of the 4f–4f transitions is discussed and the role of low-energy phonons is shown. © 1998 Published by Elsevier Science S.A.

Keywords: Absorption; Intensity analysis; Lanthanides; Acetate

1. Introduction

It is well known that crystal structures of the light (Ce–Sm) [1,2] and heavy lanthanide (Eu–Lu) acetates [2–4] are different. In the structures of both types, acetate ligands act as bridges between two Ln(III) ions. The light lanthanides form polynuclear chains, whereas dinuclear structures are typical for heavy lanthanide acetates.

The influence of the crystal structure of heavy Ln(III) acetate single crystals on their spectral properties has been previously discussed [5–7]. It was found that spectral intensities of the $Ln_2(CH_3COO)_6 \cdot 4H_2O$ single crystals were different as compared to other Ln(III) carboxylate compounds with acetic acid derivatives [8–12]. The possible explanation of this fact was assumption of more significant contribution of the polarization mechanism [13] to the spectral intensities of the f–f transitions. It can be related to the fact that contrary to other heavy lanthanide carboxylate compounds, the $Ln–OH_2$ bonds are distinctly shorter than the $Ln–OOC^-$ bonds in the Ln(III) acetate crystal.

So far, absorption and luminescence spectra of chain lanthanide acetates have been analyzed for the $Pr(CH_3COO)_3 \cdot H_2O$ crystal [14]. The aim of this paper is to report the spectroscopic properties of another light lanthanide acetate, $Nd(CH_3COO)_3 \cdot H_2O$.

2. Experimental

Nd_2O_3 (99.9% Koch and Light Laboratory Ltd) was dissolved in glacial acetic acid and alkalized with NaOH to pH=4. The well shaped crystals of $Nd(CH_3COO)_3 \cdot H_2O$ were formed during slow evaporation. The X-ray check showed them to be isomorphic with those reported in literature [1]. The concentration of Nd(III) ion was determined complexometrically (6.132 M). The crystal density was measured by the flotation method in a chloroform/bromoform mixture (d^{20}=2.184 g cm^{-3}). The refractive index (n_D) of the investigated crystals was assumed to be 1.50.

The IR spectra of the compound were recorded in the range of 50–4000 cm^{-1} with a Brucker IFS 113V spectrophotometer.

Electronic absorption spectra of good optical quality crystals were recorded on a Cary 2300 and Cary 5 spectrophotometers at room and liquid helium temperatures. No changes of the crystal quality were noticed on repeated cooling and heating measurements. The investigated spectral range was 250–2500 nm.

The intensities of the 4f–4f transition (P) and values of the Ω_λ parameters were calculated from the following Judd–Ofelt [15,16] relation:

$$P = \chi \frac{8\pi^2 mc\sigma}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_\lambda (f^n \psi J \| U^{(\lambda)} \| f^n \psi' J')^2 \tag{1}$$

where: P denotes oscillator strength, $\chi=(n^2+2)^2/9n$, n is the refractive index, J is the total quantum number of the

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ground state, $(f^n\Psi J\|U^{(\lambda)}\|f^n\Psi' J')$ is the reduced matrix element of the respective unit tensor operator $U^{(\lambda)}$, tabulated by Carnall et al. [17] and Ω_λ are empirical least-squares-fitted parameters.

3. Results

The spectral intensities of the $Nd(CH_3COO)_3 \cdot H_2O$ crystal at 293 and 4 K together with the Ω_λ parameter values for the room temperature are presented in Table 1. For comparison purposes the spectral data for Nd(III) acetate solution (1:20) are also included. It may be noticed that oscillator strength values of all 4f–4f transitions for the crystal are slightly lower in comparison to those found for the solution. As it can be seen from Table 1, an intensity decrease in almost all transitions in the crystal with the change of temperature from 293 to 4 K is observed. Similarly, as for Ho(III) [5], Dy(III), Er(III) [6] and Eu(III) acetates [7] also for Nd(III) acetate, a relatively high intensity of the 'hypersensitive' $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition and Ω_2 parameter value is observed. They are distinctly higher than for other known compounds of Nd(III) ion with acetic acid derivatives i.e. glycinates [8,9], trichloroacetates [12] and cyanoacetates [18].

The number of Stark components of electronic bands in the 4 K spectra of Nd(III) acetate is in a good agreement with the $J + \frac{1}{2}$ manifold predicted by the group theory for a single Nd(III) ion site with the C_1 symmetry. In spite of the fact that the Nd–Nd distances are very short (for the isomorphous Pr(III) acetate they are 4.216 Å [2]), in no f–f transition an additional splitting due to an ion-pair effect [19] was observed. Some examples of the Stark splitting of f–f transitions at 4 K are presented in Fig. 1. The appearance of a single, sharp peak of the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition at 23312 cm^{-1} with a half-width of 6 cm^{-1}, as well as a splitting of the $^4F_{3/2}$ term into two optical lines: 11 510 and 11 544 cm^{-1} is indicative of a single Nd(III) site, consistent with the X-ray analysis. Since the excited state $^2P_{1/2}$ is a Kramer's doublet, we could deduce the splitting of the $^4I_{9/2}$ ground term, which has been found as: 0, 71, 178, 348, 412 cm^{-1}. Some of these energies are perfectly accordant with the frequencies obtained from the far IR spectrum for Nd(III) acetate crystal (73, 77, 111, 126, 140, 158, 180, 203, 226, 236, 243, 253, 335, 469 cm^{-1}). They are also consistent with frequencies from a laser Raman spectrum of the $Pr(CH_3COO)_3 \cdot H_2O$ [14].

Table 1
Oscillator strength values (P_{exp}) and Ω_λ parameters for the neodymium acetate complex in solution ($c_{Nd} = 0.01997$ M, $c_{Ac} = 0.4001$ M) and for the single crystal of $Nd(CH_3COO)_3 \cdot H_2O$ ($c_{Nd} = 6.132$ M).

Transition(s) $^4I_{9/2} \rightarrow$	Solution	Single crystal	
	$P_{exp} \times 10^8$	293 K $P_{exp} \times 10^8$	4 K $P_{exp} \times 10^8$
$^4F_{3/2}$	220.56	183.80	59.60
$^4F_{5/2}$, $^2H_{9/2}$	827.17	668.94	362.90
$^4F_{7/2}$, $^4S_{3/2}$	890.03	677.92	464.06
$^4F_{9/2}$	65.15	44.35	14.33
$^2H_{11/2}$		19.17	8.12
$^4G_{5/2}$, $^2G_{7/2}$	1971.35	1802.00	893.97
$^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$	769.27	552.06	385.38
$^2K_{15/2}$, $^2G_{9/2}$, $(^2D,^2F)_{3/2}$, $^4G_{11/2}$	174.06	129.77	110.43
$^2P_{1/2}$	29.18	17.86	4.76
$^2D_{5/2}$	29.18	7.30	2.88
$(^2P, ^2D)_{3/2}$		1.92	
$^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{1/2}$, $^2L_{15/2}$	886.98	757.47	761.75
$\Omega_2 \times 10^{20}$ [cm^2]	6.27 ± 0.51	5.37 ± 0.19	
$\Omega_4 \times 10^{20}$ [cm^2]	3.73 ± 0.47	2.82 ± 0.17	
$\Omega_6 \times 10^{20}$ [cm^2]	7.95 ± 0.67	5.39 ± 0.26	
rms $\times 10^7$	9.39	4.01	

It can be noticed from Fig. 1 that for transitions which obey the selection rule $\Delta J = 0, \pm 2$ additional very weak side bands are observed (asterisks in Fig. 1b and c). They are vibronic in origin and are 30–1542 cm^{-1} apart from the main electronic lines. For the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition even the vibronics of 3342 cm^{-1} ($\bar{\nu}_{OH}$) in the spectral region of 485–495 nm are observed. These vibronics can also belong to the $^4I_{9/2} \rightarrow {}^4G_{9/2}$ transition ($\approx$330 cm^{-1} from the Stark components of the $^4G_{9/2}$ term).

The majority of vibronics of about 200 cm^{-1} from Stark components of the $^2H_{9/2}$ term lie inside the $^4I_{9/2} \rightarrow {}^4F_{5/2}$ transition. This may be a reason of electronic lines broadening which is observed only for this transition. Apart from that, some additional peaks are observed for the $^4I_{9/2} \rightarrow {}^2H_{9/2}$ transition at 4 K (the insert in Fig. 1c). These side bands are shifted 21–80 cm^{-1} towards lower energies from the lowest sublevel (12 527 cm^{-1}) of the $^2H_{9/2}$ term. Also very similar strong peaks located on the red wavelength side of the $^4I_{9/2} \rightarrow {}^2H_{9/2}$ transition were found by us in the Nd(III)-diethylenetriaminepentaacetate (dtpa) crystal [20]. In both these cases there is only one water molecule in the inner sphere of Nd(III) ion with a rather short $Nd\text{–}OH_2$ bonding. The reason for appearing these bands is not completely clear for us, however one may notice that positions of the additional vibronics correspond to the sum of the energies of the $^4I_{15/2}$ Stark components and the first $\bar{\nu}_{OH}$ overtone. One of sublevels which is undoubtedly a Stark component of the $^4I_{15/2}$ term has the energy 5835 cm^{-1}. The highest energy of vibronics lying before the $^4I_{9/2} \rightarrow {}^2H_{9/2}$ transition is 12 506 cm^{-1} ($5835\ cm^{-1} + 2 \times 3342\ cm^{-1} = 12\ 519\ cm^{-1}$).

4. Conclusions

It is well known that polarizability of the ligand has a considerable contribution to the 'hypersensitive' transitions

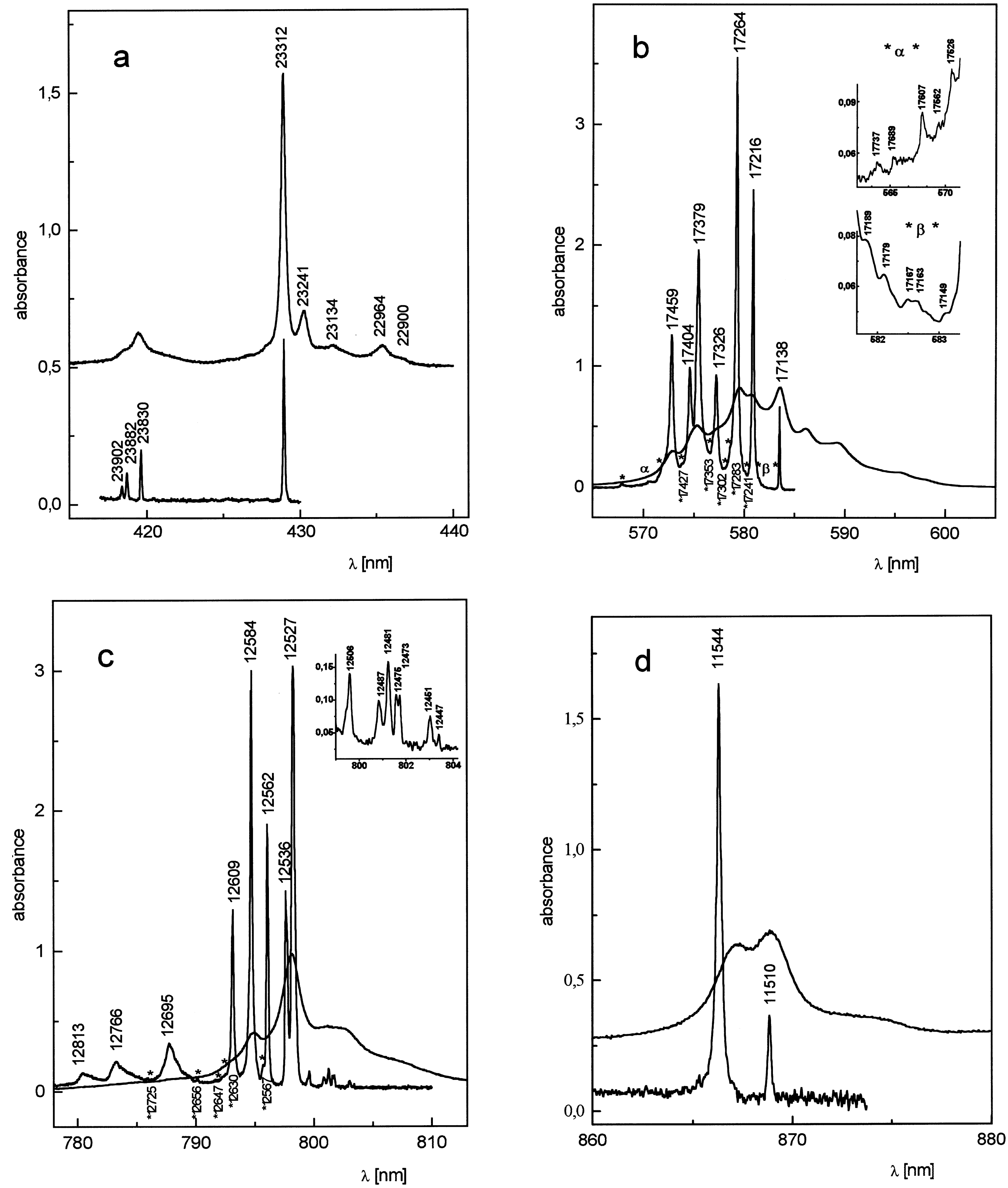

Fig. 1. Absorption spectra of the $Nd(CH_3COO)_3 \cdot H_2O$ crystal at 293 and 4 K for transitions: (a) $^4I_{9/2} \rightarrow {}^2D_{5/2}, {}^2P_{1/2}$, (b) $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$, (c) $^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$, (d) $^4I_{9/2} \rightarrow {}^4F_{3/2}$; vibronics are indicated by asterisks. ($c_{Nd} = 6.132$ M, crystal thickness $l = 0.071$ cm for a and 0.0145 cm for b, c, d)

[13]. In the crystals of lanthanide acetates tightly bonded water molecules exert more polarization effect on the metal centre than the carboxylic groups. This might explain qualitatively the high intensity of the 'hypersensitive' transitions at room temperature. This does not explain, however a strong decrease of some transitions intensity with lowering the temperature to 4 K, what was especially well observed for Eu(III) acetate crystal [7]. A possible explanation of this phenomenon can be given if we assume that low energy phonons play an important role in the enhancement of intensities of Ln(III) acetates at 293 K. These low energy phonons are particularly strongly coupled with Stark components of the Ln(III) ground state.

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