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# Spectroscopic properties of neodymium monochloroacetate single crystal as an example of complex containing Nd(III) in three different symmetry sites

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## Abstract

The neodymium monochloroacetate complex was obtained in the form of monocrystal. The absorption and emission spectra for this single crystal were recorded at room and low temperatures down to 4.2 K. Intensities of electronic lines and Judd–Ofelt parameters were calculated. Splitting and energies of electronic levels were considered and compared to those for the neodymium trichloroacetate single crystals. The covalent effect in the spectra was discussed. The results obtained from the low temperature spectra for $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ indicated three different symmetry sites of $Nd^{3+}$ ion. Correlation with the X-ray data was made.

*Keywords:* Electronic spectra; Neodymium monochloroacetate crystal

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## 1. Introduction

Properties of chemical bonds between rare earth ions and ligands in crystals have attracted great attention for a long time. Researches were carried out extensively from various angles. Interest in the spectroscopy of rare earth ions in different dimeric and polymeric compounds is continuously increasing, especially in connection with laser research and related applications, e.g., upconversion laser materials. The upconversion processes are most efficient in lanthanide compounds when two-ions energy transfer takes place (the multisite character of the matrix) [1]. A crystal lattice in which lanthanide ions form dimers is therefore ideally suited for the study of such processes [2]. Of special interest are 4*f*–4*f* transitions in which the nondegenerated levels are involved (e.g. for $Pr^{3+}$ $^3H_4 \rightarrow {}^3P_0$; for $Nd^{3+}$ $^4I_{9/2} \rightarrow {}^2P_{1/2}$). Splitting of these lines must be due to $Ln^{3+}$ located in different crystal field sites. Conclusions and suggestions arising from studies of such systems can be extended to other lanthanide ions and compounds. Thus, recently our group has been systematically investigating the effect of dimeric and polymeric structure on spectroscopy of lanthanide ions [3–6].

The spectroscopic properties of lanthanide trichloroacetates were also studied [7–10] as they are examples of one-dimensional molecular systems formed as polymeric chains composed of two different lanthanide dimeric subunits. In the erbium(III) trichloroacetate dihydrate [11], there are two kinds of crystallographically independent metal ions; both of them have a geometry almost identical to the SAP (square antiprism) geometry. Each pair of these dimers is bridged by two *Z*,*Z*-type bidentate carboxylate ions as well as by one water oxygen atom. This type of crystal structure is the same along the rare earth series. The spectral properties of lanthanide ions in such systems have been clearly manifested by the single crystal spectra at low temperature. One can easily find the double structure of bands in the absorption, excitation and emission spectra at 4.2 K [7–10].

In the heavy lanthanide monochloroacetates [12], there are dimers of the SAP-type complexes in which a couple of the side-by-side unit complexes commonly share two apices. There are two crystallographically independent dimers (coordination number; C.N. = 8), and pairs of dimers are connected with a monocapped square antiprism type (C.N. = 9) to the other unit complex, forming a chain structure. In the light lanthanide monochloroacetates [13], pairs of the two crystallographically independent dimers of tricapped trigonal prism-type (C.N. = 9) are connected by another unit complex of bicapped SAP geometry (C.N. = 10) forming a linear chain.

Thus, the created system is unusual, containing three different symmetry sites of $Ln^{3+}$ ions (see Fig. 1). Three different types of coordination of carboxyl groups are

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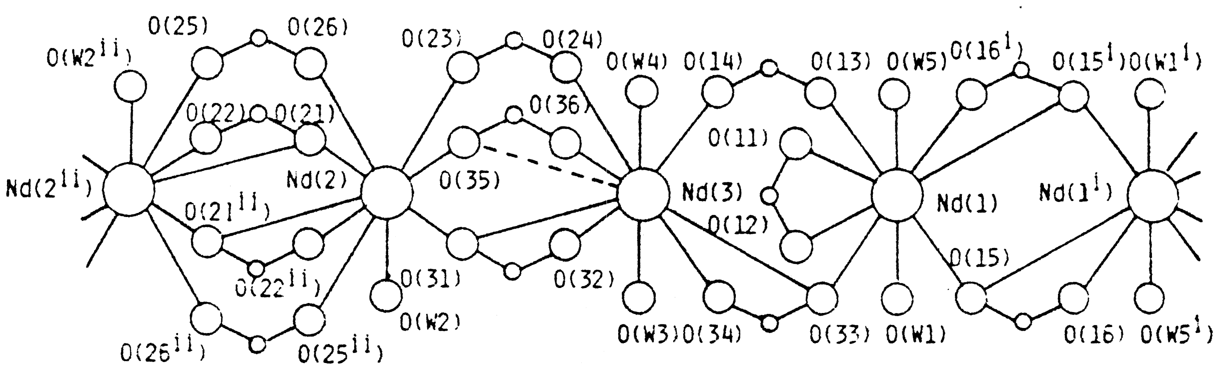

Fig. 1. Schematic presentation of the bridgings between the metal atoms for $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ crystal, redrawn from Ref. [13].

involved in linking of the metal ions. All the above described structural aspects should be reflected in spectroscopic properties of such systems. The aim of this work was to determine spectral properties of the neodymium monochloroacetate single crystals. These results should be helpful in better understanding of the spectral parameters correlations with structure and bonding of lanthanide dimeric and polymeric compounds, especially carboxylic complexes.

## 2. Experimental

The good optical quality crystals of $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ were formed during slow evaporation of aqueous solutions. Neodymium monochloroacetate were synthesized by slow reaction between Nd(III) oxide and monochloroacetate acid, at controlled pH. Concentration of Nd(III) ion was determined complexometrically and by the ICP-AES method, and was equal to: $C_{Nd} = 5.08$ moldm$^{-3}$.

Crystal density was measured by the flotation method using tribromomethane and ethylene dibromide and was $\rho = 2.28$ gcm$^{-3}$.

The X-ray diffraction showed the isomorphism of now investigated crystal to be the same as reported in the literature [13].

Well resolved absorption spectra of the single crystals of $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ were obtained at 293 K and 4.2 K temperatures with a Cary-Varian 5 spectrophotometer equipped with an Oxford helium flow cryostat. The investigated spectral range was 300–950 nm. The areas of the absorption bands were determined numerically (using the TAUS program) by integration and expressed in terms of the oscillator strengths:

$$P = 4.33 \cdot 10^{-9} \int_{\sigma_1}^{\sigma_2} \epsilon(\sigma)\, d\sigma \qquad (1)$$

where: $\epsilon$ is the molar extinction coefficient of the band at wave number $\sigma$ in cm$^{-1}$. The experimental oscillator strengths values were used for calculation of Judd–Ofelt parameters $\tau_\lambda$ (cm) [14,15] according to the equation in the form given by Carnall et al. [16]:

$$P = \sum_{\lambda=2,4,6} \tau_\lambda\, \sigma\, (f^N \Psi_J \,\|U^{(\lambda)}\|\, f^N \Psi'_{J'})^2/(2J+1) \qquad (2)$$

where: $(f^N \Psi_J \|U^{(\lambda)}\| f^N \Psi'_{J'})$ are the reduced matrix elements of the unit tensor operator $U^{(\lambda)}$ calculated by Carnall et al. [17–21] in the intermediate coupling scheme, $f^N \Psi_J$, $f^N \Psi'_{J'}$ are the initial and final states of electronic transition, and $J$ is the total angular quantum number.

Emission spectra of the neodymium monochloroacetate single crystal were measured at 293 and 77 K using a GDM 1000 grating monochromator (Carl Zeiss, Jena). Fluorescence of $Nd^{3+}$ ions was excited with the 488 and 514 nm lines; an argon laser was used as the excitation source.

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

## 3. Results and discussion

Spectral intensities of $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ crystals at 293 K and 4.2 K together with the $\tau_\lambda$ parameter values at the room temperature are presented in Table 1. The Judd–Ofelt parameters were calculated with considerably low errors of estimation. The oscillator strength values of almost all transitions at 293 K in the system under investigation are very similar to the respective values for the neodymium trichloroacetate single crystal [7] and for the neodymium acetate complex in solution [22]. However, the intensity of the ''hypersensitive'' $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition is a bit lower for monochloroacetate compared to $Nd(Cl_3CCOO)_3 \cdot 2H_2O$ ($1345.50 \cdot 10^{-8}$ [7]) but distinctly lower than for $Nd(CH_3COO)_3 \cdot H_2O$ ($1802.00 \cdot 10^{-8}$ [22]) single crystals. When we consider charge distribution on the COO group in the above mentioned systems (the covalency contribution is in a sequence: $Cl_3CCOO^- < ClH_2CCOO^- < H_3CCOO^-$), the highest oscillator strength value ($P \cdot 10^{-8}$) should be expected for the neodymium acetate complex,

Table 1
The oscillator strength values of $f$–$f$ transitions $P \cdot 10^{-8}$ and the $\tau_\lambda \cdot 10^{-9}$ parameters values for the $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ single crystals at different temperatures

| | $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ | |
|---|---|---|
| $^4I_{9/2} \rightarrow$ | 293 K | 4.2 K |
| $^4F_{3/2}$ | 135.59 | 128.46 |
| $^4F_{5/2}$, $^2H_{9/2}$ | 804.01 | 429.79 |
| $^4S_{3/2}$, $^4F_{7/2}$ | 835.37 | 509.76 |
| $^4F_{9/2}$ | 68.95 | 40.53 |
| $^2H_{11/2}$ | 18.44 | 15.28 |
| $^4G_{5/2}$, $^2G_{7/2}$ | 1315.87 | 1021.50 |
| $^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$ | 661.22 | 633.06 |
| $^2K_{15/2}$, $^2G_{9/2}$, $(^2D,^2F)_{3/2}$, $^4G_{11/2}$ | 188.16 | 147.34 |
| $^2P_{1/2}$, $^2D_{5/2}$ | 27.52 | 26.58 |
| $^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{1/2}$, $^2L_{15/2}$ | 742.64 | |
| $^2I_{13/2}$, $^4D_{7/2}$, $^2L_{17/2}$ | 186.17 | |
| $\tau_2 \cdot 10^9$ (cm) | $4.95 \pm 0.64$ | |
| $\tau_4 \cdot 10^9$ (cm) | $3.95 \pm 0.58$ | |
| $\tau_6 \cdot 10^9$ (cm) | $9.97 \pm 0.84$ | |

then lower for the monochloro derivative and the lowest for trichloro analogues. This relation is not fulfilled because of several reasons. The $f$–$f$ transitions of $Nd^{3+}$ ion are shifted towards low energies coming from trichloro to monochloro and acetate crystalline complex, confirming well the increase of the covalency contribution (e.g. we can find the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ line at 23 414 $cm^{-1}$ [7], 23 318 $cm^{-1}$, 23 312 $cm^{-1}$ [22] for $Nd(Cl_3CCOO)_3 \cdot 2H_2O$, $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ and $Nd(CH_3COO)_3 \cdot H_2O$, respectively). In spite of this fact, the $P \cdot 10^{-8}$ of $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition for monochloro analogue is lower comparing to that for the trichloroacetate complex. That is connected both with high average bond lengths Nd–O (2.51 Å [13] and 2.40 Å [11], respectively) and the change of C.N. from 9; 10 to 8 [13,11].

Fig. 2 presents absorption spectra for $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ single crystal at 293 K and 4.2 K. In the region of $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition at 293 K one can find five broad components with $\Delta E = 23\,320$ $cm^{-1}$–22 889 $cm^{-1}$ = 431 $cm^{-1}$. This splitting is higher than the earlier reported values for $Nd^{3+}$ ion with C.N. = 9 (370–420 $cm^{-1}$) [23]. The appearance of one component (23 318 $cm^{-1}$) of the band for $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition at 4.2 K (half-width 9 $cm^{-1}$) with two well visible inflections (23 313 $cm^{-1}$ and 23 324 $cm^{-1}$) is indicative of the three symmetry site of $Nd^{3+}$ ions what is in agreement with the X-ray data; these ions differ in Nd–O distances: $Nd_1$–O 2.501 Å (C.N. = 9), $Nd_2$–O 2.486 Å (C.N. = 9) and $Nd_3$–O 2.553 Å (C.N. = 10) [13]. This type of splitting for the excited state $^2P_{1/2}$ as Kramer's doublet is rarely observed at 4.2 K. Further analysis of the absorption spectra of $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ at low temperature indicates the complicated structure of the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ band. Except for two distinct optical lines one can also find four weak but visible components. This suggests the presence of three different $Nd^{3+}$ ions in the system under investigation, too. In the region of the ''hypersensitive'' transition ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) at 4.2 K one can find more components than for the one symmetry site of the $Nd^{3+}$ ion but less than for the three sites. This may be a reason for broadening of electronic lines observed for the mentioned transition. For the ''hypersensitive'' transition, which obeys the selection rule $\Delta J = 2$, additional very weak side bands can be noticed (marked as **v** in Fig. 2). They are vibronic in origin. On the basis of the IR spectra (see Fig. 3) analysis of the vibronic components was performed and the results are collected in Table 2. The low temperature spectra confirm vibronic contribution in intensities of $4f$–$4f$ transitions. Decrease of temperature leads to a decrease of intensities (see Table 1).

Fig. 3 presents IR spectra for $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ in comparison with the trichloro analogue [10]. In the case of neodymium monochloroacetate complex, $\nu(CH_2)$ and $\delta(CH_2)$ bands appear but the $\nu(CCl_3)$ one observed at 845 $cm^{-1}$ for trichloro analogue disappears. The main peaks both of the $\nu_{as}(COO)$ band at 1582 $cm^{-1}$ and the $\nu_s(COO)$ at 1433 $cm^{-1}$ split, suggesting different types of $COO^-$ ions. Thus, the above confirms the X-ray data for $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ [13]; three coordinating forms of the carboxylate ions are present: chelating-type bidentate, *Z,Z*-type bridging bidentate and bridging tridentate [24].

In the emission spectra for $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ (see Fig. 4) the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions present complicated structure similar to the $Nd(Cl_3CCOO)_3 \cdot 2H_2O$ crystal [7] and their resolution needs selective luminescence measurements.

## 4. Summary

1. The $f$–$f$ transitions in the neodymium monochloroacetate single crystal spectra are shifted towards low energies (e.g. $^2P_{1/2}$ 23 318 $cm^{-1}$) in comparison to those for trichloroacetate analogue, confirming well a change in charge distribution on the COO group. An increase of the oscillator strength values should be expected for the $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ crystal.
2. Intensity of the ''hypersensitive'' transition ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) is a bit lower for monochloroacetate ($1315.87 \cdot 10^{-8}$) comparing to the trichloroacetate complex ($1345.50 \cdot 10^{-8}$), that is connected both with high average bond lengths Nd–O (2.51 Å [13] and 2.40 Å [11] respectively) and the change of coordination number from 9; 10 to 8.
3. Analysis of the absorption spectra for $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ at 4.2 K indicates more than one symmetry site of $Nd^{3+}$ ion in the investigated system:
   (a) complicated structure of $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition at 4.2 K.

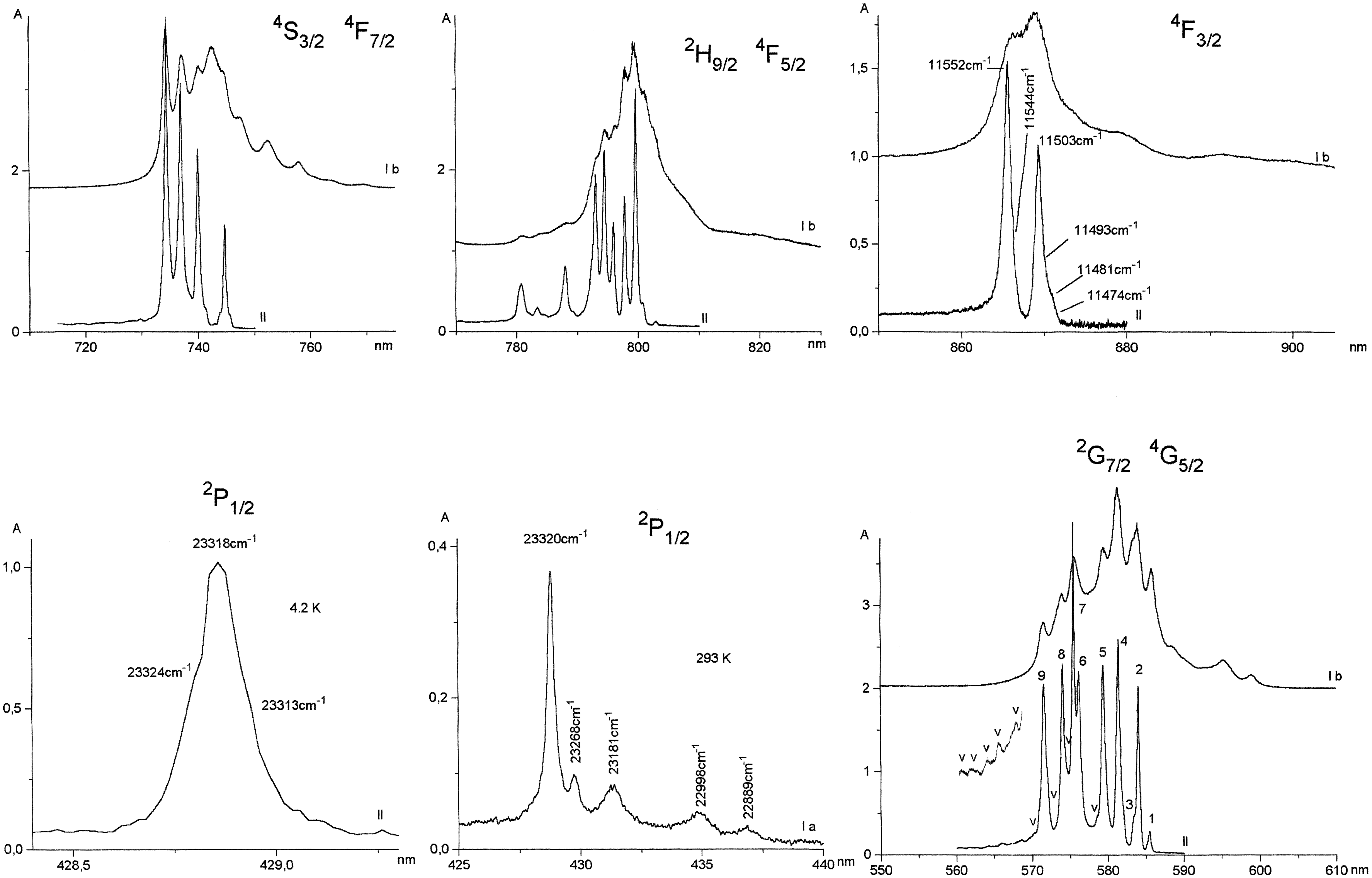

Fig. 2. Absorption spectra of the $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ crystal at 293 K (I a, b) and 4.2 K (II); $d_{293}=0.066$ cm (a); 0.049 cm (b); $d_{4.2}=0.0335$ cm.

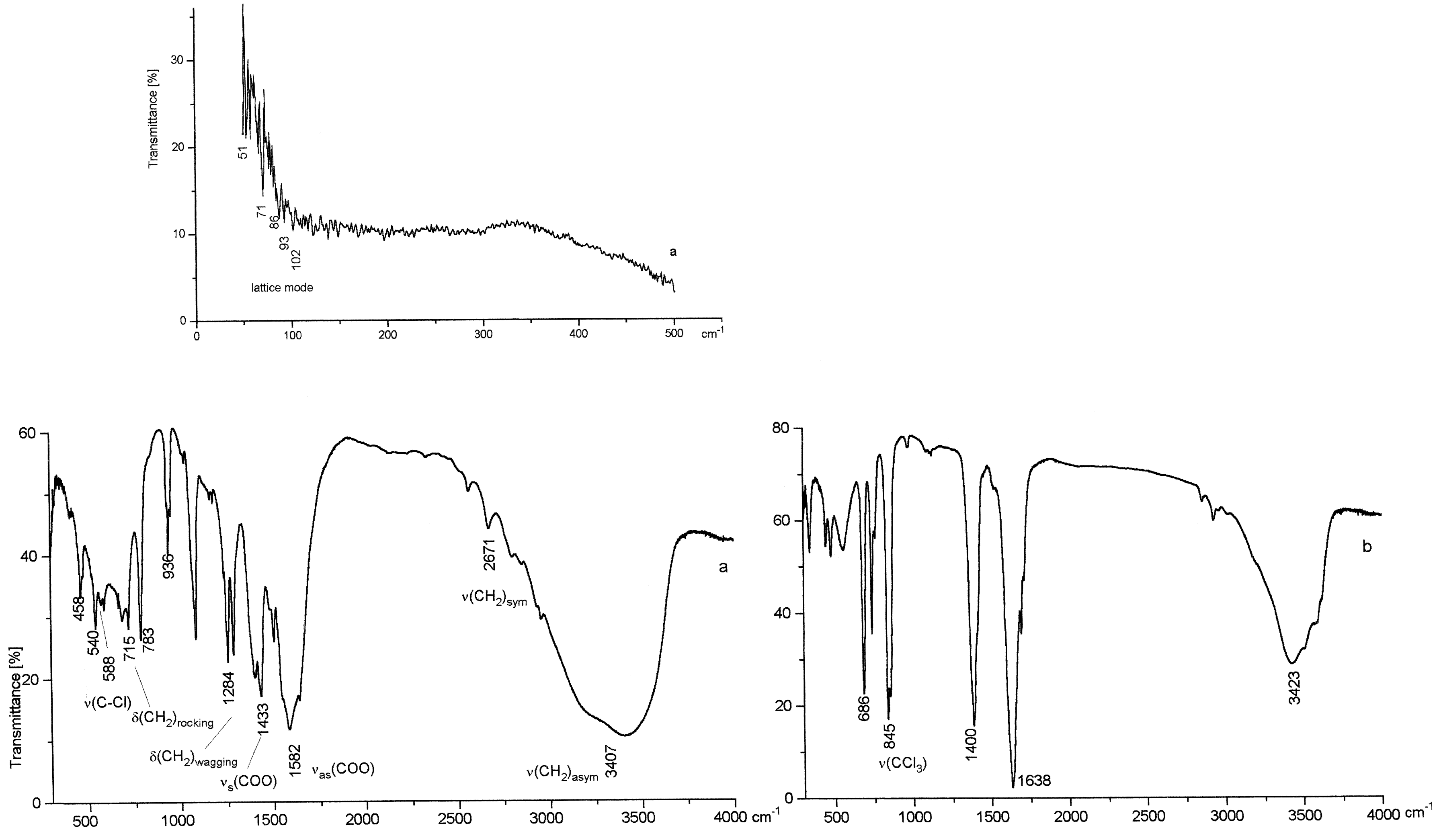

Fig. 3. IR spectra of the $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ crystal (a) in comparison with $Nd(Cl_3CCOO)_3\cdot 2H_2O$ crystal (b) [10].

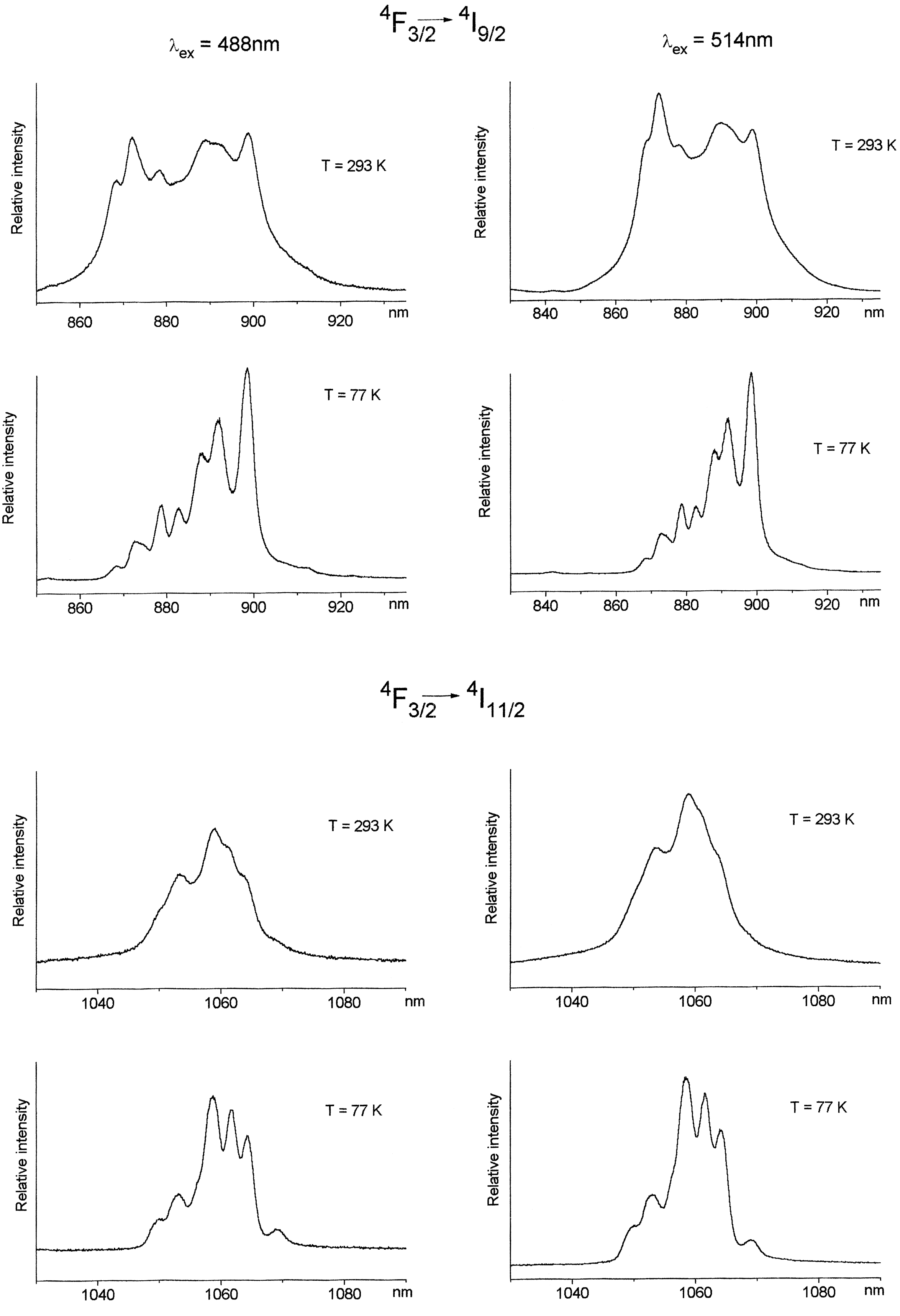

Fig. 4. Luminescence spectra of the $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ crystal at different temperatures.

Table 2
The electronic and vibronic components in absorption spectra of $[\{Nd(ClH_2CCOO)_3\}_3(H_2O)_5]_n$ for the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition

| | Energy ($cm^{-1}$) | ΔEnergy (from 0-phonon line) | |
|---|---|---|---|
| $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ | 17 081 (1) | | |
| | 17 123 (2) | | |
| | 17 141 (3) | | |
| | 17 199 (4) | | |
| | 17 259 (5) | | |
| | 17 281 | 82 (4) | Lattice mode |
| | 17 356 (6) | | |
| | 17 377 (7) | | |
| | 17 407 | 51 (6) | Lattice mode |
| | 17 420 (8) | | |
| | 17 472 | 95 (7) | Lattice mode |
| | 17 495 (9) | | |
| | 17 533 | 452 (1) | $\delta$(COO) |
| | 17 587 | 464 (2) | $\delta$(COO) |
| | 17 664 | 541 (2) | $\nu$(C–Cl) |
| | 17 722 | 581 (3) | $\nu$(C–Cl) |
| | 17 799 | 718 (1) | $\delta(CH_2)_{rocking}$ |
| | 17 843 | 720 (2) | $\delta(CH_2)_{rocking}$ |

(b) triplet structure of the band for $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition: one component (23 318 $cm^{-1}$) (half-width 9 $cm^{-1}$) with two well visible inflections (23 313 and 23 324 $cm^{-1}$). These conclusions are in agreement with the X-ray data: three different symmetry sites of $Nd^{3+}$ ion: $Nd_1$–O 2.501 Å (C.N. = 9), $Nd_2$–O 2.486 Å (C.N. = 9) and $Nd_3$–O 2.553 Å (C.N. = 10) [13].

4. Decrease of the oscillator strength values with temperature indicates the contribution of vibronic mechanism in intensities of the *f–f* transitions.
5. On the basis of IR spectra, the rich and complicated structure found for the neodymium monochloroacetate system in comparison with $Nd(Cl_3CCOO)_3 \cdot 2H_2O$ spectra testifies existence of different types of coordinated carboxyl groups in the system under investigation.

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