SPECTROSCOPY STUDIES OF ERBIUM AND DYSPROSIUM ACETATE SINGLE CRYSTALS

A. MONDRY AND K. BUKIĘTYŃSKA

Faculty of Chemistry, University of Wrocław
Joliot-Curie 14, 50-383 Wrocław, Poland

Electronic absorption spectra of erbium and dysprosium acetate single crystals were measured. The intensities of 4f–4f transitions were calculated and the Judd-Ofelt $\Omega_\lambda$ parameters evaluated. Heavy lanthanide acetates differ from other lanthanide carboxylate compounds by relatively high “hypersensitive” transition intensities and the $\Omega_2$ parameters. These results are discussed in terms of a stronger polarization effect which can be explained by the distinctly shorter Ln–OH$_2$ bond in comparison with the Ln–OOC bond in the investigated system.

PACS numbers: 78.20.Wc, 81.40.Tv

1. Introduction

Recently we examined the spectral intensities of 4f–4f transitions in holmium acetate single crystal spectra [1]. The relatively high intensity of the “hypersensitive” transition of that compound in comparison with other carboxylate complexes was explained by the dynamic coupling mechanism [2] resulting from the properties of acetate crystals, in which water molecules are bonded closer to the lanthanide ion than oxygen atoms from carboxyl groups.

X-ray data for heavy lanthanide acetates [3–5] indicate the existence of dimeric species with the both lanthanide atoms bridged by acetate oxygen atoms. The coordination number of each metal ion is nine through the three bidentate acetate groups, two water molecules and a bridging oxygen from one of the adjoining acetates.

In this paper we report single crystal spectral investigations of some other heavy lanthanide crystal acetates.

2. Experimental

Lanthanide oxide Ln$_2$O$_3$ (where Ln = Dy, Er) was dissolved in concentrated acetic acid and alkalized to pH = 4. The well shaped crystals of Ln$_2$(CH$_3$COO)$_6$·4H$_2$O were formed during very slow evaporation. The crystals were checked by X-ray diffraction and found to be isomorphic with those known
from literature [3]. The crystallographic axes referred to hereinafter are those defined in [3].

The concentration of Ln(III) ions in the crystals was determined by EDTA titration using xylennol orange as the indicator. The Dy(III) and Er(III) concentrations were: 4.9867 M and 5.0567 M, respectively. The densities, measured by the flotation method in a mixture of chloroform and bromoform, were found to be 2.052 g cm\(^{-3}\) for Dy(III) and 2.105 g cm\(^{-3}\) for Er(III). The refractivity indices \(n\) for the crystals were 1.50.

Absorption spectra of the investigated crystals were recorded on a Cary 2300 spectrophotometer at room temperature (for Dy and Er) and at 5 K (for Er). The investigated spectral range was 250–1900 nm for Dy(III) and 250–1600 nm for the Er(III) crystals.

The natural dimensions of the Dy\(_2\)(CH\(_3\)COO)\(_6\)·4H\(_2\)O crystals restricted the absorption measurements to only one crystal plate orientation perpendicular to the (010) direction. Absorption spectra of the Er\(_2\)(CH\(_3\)COO)\(_6\)·4H\(_2\)O crystals were measured for crystals polished parallel to the planes (001) and (150) as well as for a polycrystalline sample.

The intensities of the 4f–4f transition \((P)\) and values of the \(\Omega_\lambda\) parameters were calculated from the following Judd–Ofelt [6, 7] relation:

\[
P = \chi \frac{8\pi^2 m c \sigma}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_\lambda \langle f^n \psi J \mid U(\lambda) \mid f^n \psi' J' \rangle^2,
\]

where \(P\) denotes the oscillator strength, \(\chi = (n^2 + 2)^2/9n\), \(n\) is the refractive index, \(J\) is the total quantum number of the ground state, \(\langle f^n \psi J \mid U(\lambda) \mid f^n \psi' J' \rangle\) is the reduced matrix element of the unit tensor operator \(U(\lambda)\) tabulated by Carnall et al. [8] and \(\Omega_\lambda\) are the empirical least squares fitted parameters.

3. Results and discussion

The oscillator strength values \((P)\) for 4f–4f transitions observed for erbium acetate at 293 K and 5 K are presented in Table I. It can be seen that the oscillator strength values measured for two orientations of the crystals – along the crystallographic \(c^*\) axis and in the direction (150) — differ slightly within the limit of experimental error. The direction (150) of the polished crystal is nearly parallel to the \(b^*\) axis (deviation is about 14°).

Our primary results on intensity measurements for erbium acetate crystal (a polycrystalline sample) are also included in Table I. The polycrystallinity can be a reason that oscillator strength values are much lower, especially for the \(^4I_{15/2} \rightarrow ^4G_{11/2}\) and \(^4I_{15/2} \rightarrow ^2H_{11/2}\) “hypersensitive” transitions in comparison with intensities measured along the \(c^*\) and \(b^*\) axes.

As can be seen from Table I, an intensity decrease in almost all transitions in the single crystal with the change of temperature from 293 K to 5 K is observed. This decrease ranges for the individual transitions from 74% to 14%. Such effect was also observed for holmium acetate crystals [1] as well as for other light and heavy lanthanide acetates [9]. None of the known carboxylate compounds [10–12] loses the intensities so efficiently as the acetates.
### TABLE I

<table>
<thead>
<tr>
<th>Transition(s)</th>
<th>Polycrystalline sample 0.048</th>
<th>(001) 0.0295</th>
<th>(I50) 0.023</th>
<th>(I50) 0.023</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T = 293$ K</td>
<td>$T = 293$ K</td>
<td>$T = 293$ K</td>
<td>$T = 5$ K</td>
</tr>
<tr>
<td>$^4I_{15/2} \Rightarrow$</td>
<td>$P_{exp}$ x10^8</td>
<td>$P_{calc}$ x10^8</td>
<td>$P_{exp}$ x10^8</td>
<td>$P_{calc}$ x10^8</td>
</tr>
<tr>
<td>$^4I_{13/2}$</td>
<td>201.15</td>
<td>130.54</td>
<td>274.47</td>
<td>170.58</td>
</tr>
<tr>
<td>$^4I_{11/2}$</td>
<td>56.82</td>
<td>60.21</td>
<td>89.23</td>
<td>84.76</td>
</tr>
<tr>
<td>$^4I_{9/2}$</td>
<td>33.43</td>
<td>26.06</td>
<td>26.26</td>
<td>25.46</td>
</tr>
<tr>
<td>$^4I_{7/2}$</td>
<td>157.15</td>
<td>181.49</td>
<td>184.94</td>
<td>204.80</td>
</tr>
<tr>
<td>$^4S_{3/2}$</td>
<td>41.98</td>
<td>50.93</td>
<td>64.52</td>
<td>66.75</td>
</tr>
<tr>
<td>$^2H_{11/2}$</td>
<td>640.85</td>
<td>560.34</td>
<td>920.98</td>
<td>978.30</td>
</tr>
<tr>
<td>$^4F_{7/2}$</td>
<td>157.90</td>
<td>194.70</td>
<td>179.12</td>
<td>243.02</td>
</tr>
<tr>
<td>$^4F_{5/2}$</td>
<td>85.71</td>
<td>97.99</td>
<td>119.41</td>
<td>128.44</td>
</tr>
<tr>
<td>$^2G_{7/2}$</td>
<td>57.50</td>
<td>74.24</td>
<td>68.58</td>
<td>95.44</td>
</tr>
<tr>
<td>$^2H_{9/2}$</td>
<td>946.84</td>
<td>992.95</td>
<td>1766.63</td>
<td>1735.18</td>
</tr>
<tr>
<td>$^2F_{5/2}$</td>
<td>154.12</td>
<td>117.66</td>
<td>172.28</td>
<td>127.48</td>
</tr>
<tr>
<td>$^2G_{7/2}$</td>
<td>111.95</td>
<td>94.34</td>
<td>142.17</td>
<td>133.65</td>
</tr>
<tr>
<td>$^2D_{5/2}$</td>
<td>688.93</td>
<td>1119.11</td>
<td>937.22</td>
<td>528.42</td>
</tr>
</tbody>
</table>

| $\Omega_2 \times 10^{20}$ [cm$^2$] | 3.58 ± 0.33 | 6.91 ± 0.37 | 5.72 ± 0.29 |
| $\Omega_6 \times 10^{20}$ [cm$^2$] | 1.24 ± 0.51 | 1.19 ± 0.57 | 1.06 ± 0.45 |
| $\Omega_8 \times 10^{20}$ [cm$^2$] | 1.36 ± 0.27 | 1.78 ± 0.30 | 1.48 ± 0.23 |

* $l$ = crystal thickness.

**Fig. 1.** The $^4I_{15/2} \rightarrow ^2H_{11/2}$ "hypersensitive" transition of the Er$_2$(CH$_3$COO)$_6$·4H$_2$O crystal at 5 K (crystal thickness $l = 0.023$ cm).
In Table I the $\Omega_{\lambda}$ parameter values for erbium acetate are also included. Similarly as for holmium acetate, a relatively high $\Omega_2$ parameter value is observed. It is distinctly higher than for the two other known simple Er(III) carboxylate compounds i.e. formamide solvates [13] and trichloroacetate hydrates [11].

The Stark splitting of electronic bands in the 5 K spectra of Er(III) acetate is in agreement with the $J + 1/2$ manifold resulting from the group theory for a single Er(III) ion site. It means that each Er(III) ion in the dimeric species has the same environment. It can be well exemplified in Fig. 1 where the Stark splitting of the $^4I_{15/2} \rightarrow ^2H_{11/2}$ transition is presented. In this figure, besides the electronic lines, also a side band of vibronic origin can be observed. It is 25 cm$^{-1}$ apart from the electronic sublevel of lowest energy. For the whole erbium acetate spectrum, a rich side band structure is observed. Among them the lowest energy side bands which appear in some of the electronic Er(III) transitions are the bands situated at 25 cm$^{-1}$ from adjacent electronic levels. These side bands (about 25 cm$^{-1}$) are also observed in the spectra of other lanthanide acetates as those of neodymium and europium [9].

The next investigated heavy lanthanide acetate single crystal was dysprosium acetate. The spectral intensity results of this compound are presented in Table II.

It is interesting to compare the received results for the acetate crystals with those reported for other lanthanide monocarboxylates i.e. with ligands similar to acetates such as glycinites and trichloroacetates. Single crystals of Dy(III) glycinites and trichloroacetates were studied recently [14,15].

Dysprosium glycinate as well as acetate have the same coordination number (C.N. = 9). The most important difference between the crystal structures of both compounds is the distinctly shorter Dy-OH$_2$ bond in comparison with the Dy-OOC bond in the acetate crystal. For dysprosium glycinate the values of the oscillator strength for the $^6H_{15/2} \rightarrow ^6H_{9/2}$, $^6F_{11/2}$ "hypersensitive" transition as well as the $\Omega_2$ parameter are distinctly lower than for dysprosium acetate. These results are very similar to those obtained by us for holmium acetate [1] and thus confirm also the role of the dynamic-coupling mechanism in lanthanide compounds [2].

Since the lanthanide trichloroacetates have dimeric structures in which the two Ln(III) ions have different coordination numbers 7 and 8, no such comparison with the lanthanide acetate crystals could be done. Furthermore, the number of water molecules in the inner sphere of heavy lanthanide ions is different for trichloroacetates (3 molecules) and for acetates (4 molecules). However, even in the case of a lowering of the coordination number in trichloroacetates one does not state a shortening of the Ln-OH$_2$ bonds, similar to that in the acetates. On the other hand, because of the lower coordination numbers, the average Ln-O distances for trichloroacetates are shorter than for acetates mainly, due to the contraction of Ln-OOC bonds. Nevertheless, both the oscillator strength of "hypersensitive" transitions and the $\Omega_2$ parameters for Dy(III) and Er(III) trichloroacetates are lower than those for dysprosium and erbium acetates.
It means that the polarization effect [2] caused by the more tightly bonded water molecules in the acetate structure plays an important role in the enhancement of intensity.

Acknowledgement

The authors would like to thank Dr. P. Starynowicz for X-ray identification of the crystals.

References