Absorption and magnetic circular dichroism spectra of praseodymium doped fluorozirconate (ZBLAN) glass

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Abstract

Optical absorption and magnetic circular dichroism (MCD) spectra of 1% Pr3+ doped ZBLAN fluorozirconate glass have been recorded at several temperatures between 4.2 K and room-temperature. The dipole strengths of the 4f–4f transitions are parametrized in terms of three phenomenological Judd–Ofelt intensity parameters Ωi (i=2, 4 and 6). The method of moments was used to extract the Faraday parameters from the MCD spectra. While the room-temperature MCD spectra are dominated by A-terms (which have the shape of the first derivative of an absorption curve), C-terms become more important at lower temperature. The temperature dependence of the $P_r\rightarrow H_4$ transition is a typical example. The temperature dependent change of the MCD spectrum can be explained by the differential thermal population of the Zeeman levels from which absorption of left and right circularly polarized light takes place.

Keywords: Pr3+; Rare earths; Lanthanides; MCD; Judd–Ofelt theory

1. Introduction

The spectroscopic properties of fluoride glasses have been studied extensively during the past two decades [1]. Most studies are however restricted to optical absorption and luminescence data. In this paper, we report the magnetic circular dichroism (MCD) spectra of a Pr3+ doped fluorozirconate (ZBLAN) glass.

Only a few MCD studies of lanthanide ions in vitreous matrices have been reported until now: Boccara [2] investigated the $^3D_2\rightarrow^1F_3$ transitions of Eu2+ in barium-crown glass. Colloct and Taylor studied the magneto-optical properties of Er3+ [3], Pr3+ [4] and Ho3+ [4] in soda glass. Valiev et al. [5] and Klochkov et al. [6] have published the MCD spectra of Er3+ doped phosphate glass. Binnemans et al. have studied the magnetic circular dichroism spectra of Eu2+ in fluorophosphate glass [7], Ho3+ in ZBLAN [8] and Nd3+ in ZBLAN [9]. The advantage of a glass matrix over a solution is that the magneto-optical properties of randomly oriented lanthanide systems can be studied also at low temperatures. In addition to the MCD spectra, the optical absorption spectra have been recorded too. The intensities of the 4f–4f induced electric dipole transitions have been parametrized in terms of three Judd–Ofelt intensity parameters. Since the infrared transparency of the glass matrix allows the observation of the hypersensitive transition $^3F_4\rightarrow^1H_4$, the intensity parameter Ω2 could be determined with a fairly high accuracy. The determination of the latter parameter is often a problem for Pr3+ complexes in an aqueous solution. Spectroscopic studies of comparable glasses have been reported by Adam and Sibley [10], Ranga Reddy et al. [11], Arauza et al. [12], Nachimuthu and Jagannathan [13], Seeber et al. [14], Quimby and Miniscalco [15] and by Adam et al. [16].

2. Experimental

The samples of the 1% Pr3+ doped ZBLAN glass were prepared using methods described elsewhere [17]. The starting composition of the batch was 53 mol% ZrF4, 20 mol% BaF2, 20 mol% NaF, 3 mol% AlF3, 3 mol% LaF3 and 1 mol% PrF3. The samples have the typical green colour of the trivalent praseodymium ion [18]. Absorption spectra were recorded on an AVIV 17DS spectrophotometer in the 400–2500 nm range. The MCD spectra were recorded on an AVIV 62DS circular dichroism spectrometer, extended with an electromagnet (Oxford Instruments). The magnetic field strength was 0.9 Tesla (9000 Gauss).

The wavelength range for the MCD measurements was
400–650 nm. The spectral band width for both the absorption and MCD spectra was 0.10 nm. Spectra of ZBLAN:Pr3+ (1%) have been recorded at different temperatures between 4.2 K and room-temperature.

3. Results and discussion

The room-temperature (293 K) absorption and MCD spectrum between 15 000 and 25 000 cm⁻¹ is shown in Fig. 1. The transitions were assigned by comparing the band positions in the absorption spectrum with the energy level scheme of LaF₃:Pr₃⁺, published by Carnall et al. [19]. All transitions in the absorption spectrum of Pr₃⁺ start from the ¹H₄ ground state. The spectral transitions can be divided into four groups: transitions to the ¹H₆, ¹F₂, ¹F₄ and ¹F₈ manifolds in the infrared, the weak transition to the ¹G₈ state at 9895 cm⁻¹, the ¹D₄→¹H₄ transition at 17 024 cm⁻¹ and the complex group of the transitions to the ³P₀, ³P₁, ¹I₆ and ³P₂ manifold in the violet-blue region. The latter group is responsible for the green color of the Pr³⁺ ion [18]. The ³P₂ and the ¹I₆ overlap and cannot be even resolved at low temperatures. At cryogenic conditions the ³P₂ levels show distinct crystal-field splitting.

The dipole strengths of the 4f–4f transitions were determined by integrating the absorption bands and using the expression

\[ D = \frac{1}{108.9 \times C \times d} \int \frac{A(P)}{p} dp \]  

where \( D \) is the dipole strength (in Debye²), \( C \) is the concentration of the lanthanide ion (in mol/L) and \( d \) is the sample thickness (in cm). The concentration of Pr³⁺ ions is 0.3166 mol/L. It is assumed that all ions are in the ¹H₄ ground state at ambient temperature, so that the Boltzmann population factor is unity. Notice that for oriented systems (e.g., single crystals), the definition of the dipole strength contains an additional factor 1/3 in the right hand side of Eq. (1) [20]. The dipole strength \( D \) is related to the often used oscillator strength \( f \) (dimensionless):

\[ D = \frac{2.127 \times 10^6 \cdot f}{\bar{v}_0} \]  

\( \bar{v}_0 \) (in cm⁻¹) is the barycenter of the absorption band.

According to the Judd–Ofelt theory [21,22], the dipole strength \( D \) of an induced electric dipole transition is

\[ D = \frac{10^{36}}{8 \cdot \lambda \cdot \frac{(n^2 + 2)^2}{9n} \cdot e^2} \sum_{\lambda=4, 6} \Omega_\lambda \langle \Psi | U | \Psi' \rangle^2 \]  

where \( \Omega_\lambda \) (λ=2, 4, 6) are the phenomenological Judd–Ofelt intensity parameters which have to be determined by a least-squares fit. The \( \langle \Psi | U | \Psi' \rangle^2 \) are squared reduced matrix elements between the ground state \( \Psi \) and the excited state \( \Psi' \), \( U \) is a unit tensor operator. The reduced matrix elements are relatively insensitive to the environment and can be considered as constants for a given lanthanide ion. We used the reduced matrix elements reported by Carnall et al. [23]. For the overlapping transitions ³P₁→¹H₄ and ¹I₆→¹H₄, a combination of the respective matrix elements has been taken. \( g_\lambda \) is the degeneracy of the ground state and is equal to 2J+1. J is the total angular momentum. \( n \) is the refractive index. \( e \) is the charge of the electron (\( e = 4.803 \times 10^{-10} \) esu). The factor 10³⁶ is necessary to convert to calculated intensity from esu²⋅cm² into Debye².

A measure for the goodness of the fit is the root-mean-square error \( \sigma \), which is defined as:

\[ \sigma = \sqrt{\frac{\sum (D_{\text{exp}} - D_{\text{calc}})^2}{N-3}} \]

where \( D_{\text{exp}} \) and \( D_{\text{calc}} \) are the experimental and calculated dipole strength, respectively. \( N \) is the number of transitions used in the fitting procedure. The number of parameters is 3.

The intensity parametrization is performed using the room-temperature absorption spectrum.

The Judd–Ofelt theory requires that all crystal-field levels of the ground state are equally populated. This approximation is valid at room-temperature, but a decrease of the temperature will depopulate the excited crystal-field levels of the ground level. The Judd–Ofelt parametrization
Table 1
Peak positions, experimental dipole strengths (\(D_{\text{exp}}\)) and calculated dipole strengths (\(D_{\text{cal}}\)) for the 4f-4f transitions in ZBLAN:Pr\(^{3+}\) at ambient temperature

<table>
<thead>
<tr>
<th>Level</th>
<th>Energy (cm(^{-1}))</th>
<th>(D_{\text{exp}}) ((10^{-6}) Debye(^2))</th>
<th>(D_{\text{cal}}) ((10^{-6}) Debye(^2)) set a</th>
<th>(D_{\text{cal}}/D_{\text{exp}})</th>
<th>(D_{\text{cal}}) ((10^{-6}) Debye(^2)) set b</th>
<th>(D_{\text{cal}}/D_{\text{exp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{3})H(<em>{4}) (\leftrightarrow) (^{3})H(</em>{4})</td>
<td>4259</td>
<td>n.d.</td>
<td>258</td>
<td>-</td>
<td>681</td>
<td>-</td>
</tr>
<tr>
<td>(^{4})F(<em>{1}) (\leftrightarrow) (^{4})H(</em>{4})</td>
<td>5120</td>
<td>1231</td>
<td>1223</td>
<td>0.99</td>
<td>1224</td>
<td>0.99</td>
</tr>
<tr>
<td>(^{4})F(<em>{3}) (\leftrightarrow) (^{4})H(</em>{4})</td>
<td>6468</td>
<td>1782</td>
<td>1719</td>
<td>0.96</td>
<td>1722</td>
<td>2.09</td>
</tr>
<tr>
<td>(^{4})F(<em>{3}) (\leftrightarrow) (^{4})H(</em>{4})</td>
<td>6947</td>
<td>557</td>
<td>575</td>
<td>1.36</td>
<td>2258</td>
<td>4.05</td>
</tr>
<tr>
<td>(^{5})G(<em>{5}) (\leftrightarrow) (^{5})H(</em>{4})</td>
<td>9895</td>
<td>41</td>
<td>52</td>
<td>1.27</td>
<td>133</td>
<td>3.14</td>
</tr>
<tr>
<td>(^{5})D(<em>{3}) (\leftrightarrow) (^{5})H(</em>{4})</td>
<td>17024</td>
<td>225</td>
<td>107</td>
<td>0.48</td>
<td>262</td>
<td>1.16</td>
</tr>
<tr>
<td>(^{3})P(<em>{1}) (\leftrightarrow) (^{3})H(</em>{4})</td>
<td>20881</td>
<td>177</td>
<td>90</td>
<td>2.19</td>
<td>296</td>
<td>1.67</td>
</tr>
<tr>
<td>(^{1})P(<em>{1}) (\leftrightarrow) (^{1})H(</em>{4})</td>
<td>21454</td>
<td>591</td>
<td>533</td>
<td>0.90</td>
<td>488</td>
<td>0.82</td>
</tr>
<tr>
<td>(^{3})P(<em>{1}) (\leftrightarrow) (^{3})H(</em>{4})</td>
<td>22676</td>
<td>672</td>
<td>260</td>
<td>0.39</td>
<td>669</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The dipole strengths have been calculated with different two sets of parameters, one with inclusion of all transitions (set a), the other with exclusion of the transitions to \(^{3}\)F\(_{1}\) and \(^{3}\)F\(_{3}\).

Set a: \(\Omega_{2} = 0.94 \times 10^{-20}\) cm\(^2\), \(\Omega_{3} = 6.54 \times 10^{-20}\) cm\(^2\), \(\Omega_{5} = 3.84 \times 10^{-20}\) cm\(^2\) (all transitions).

Set b: \(\Omega_{2} = 0.04 \times 10^{-20}\) cm\(^2\), \(\Omega_{3} = 4.99 \times 10^{-20}\) cm\(^2\), \(\Omega_{5} = 15.06 \times 10^{-20}\) cm\(^2\) (\(^{3}\)F\(_{1}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) excluded).

n.d.: not determined.

The 4f-4f transition intensities works less well for Pr\(^{3+}\) than for other lanthanide ions. It has been noticed by Carnall et al. [24] that difficulties are experienced when trying to fit both the \(^{3}\)F\(_{3}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) and \(^{3}\)P\(_{0,1,2}\) \(\leftrightarrow\) \(^{1}\)H\(_{4}\) transitions with the same parameter set. Peacock [25] has discussed these problems also. A reason why the Judd–Ofelt theory fails partially in the case of Pr\(^{3+}\) is because the energy gap between the ground configuration 4f\(^2\) and the first excited configuration 4f\(^5\)5d\(^1\) is only small. Assumptions which are made in the Judd–Ofelt theory are not valid. The hypersensitive \(^{3}\)F\(_{1}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) transition has to be included in the fit, because otherwise values with no physical significance (e.g., negative values) are found for the \(\Omega_{2}\) parameter. Extraction of a reliable \(\Omega_{2}\) parameter is often a problem for Pr\(^{3+}\), since the \(^{3}\)F\(_{3}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) transition is situated in the infrared spectral region and cannot be observed in an aqueous solution. Fortunately, the \(^{3}\)F\(_{3}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) transition is found in the absorption spectrum of ZBLAN:Pr\(^{3+}\).

We have determined two parameter sets: one with inclusion of all transitions (set a), the other with exclusion of the \(^{3}\)F\(_{3}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) and the \(^{3}\)F\(_{1}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) transition (set b). The parameter sets are given in Table 1. With parameter set a, the \(^{3}\)F\(_{3}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\), the \(^{3}\)F\(_{3}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) and the \(^{3}\)P\(_{1}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) transitions are simulated rather well, whereas the simulation of the other transitions is bad. \(\Omega_{2}\) is positive, but we find that \(\Omega_{2}\) is larger than \(\Omega_{5}\), \(\Omega_{2} > \Omega_{5}\) is also often found for PbO–PbF\(_{2}\) glass [13]. The root-mean-square error \(\sigma\) is 1.84 \(\times\) 10\(^{-6}\) Debye\(^2\). With parameter set b, the intensity of the \(^{3}\)F\(_{3}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) and the \(^{3}\)F\(_{3}\) \(\leftrightarrow\) \(^{3}\)H\(_{4}\) transition is largely overestimated. The root-mean-square error \(\sigma\) with exclusion of the transitions to \(^{3}\)F\(_{3}\) and \(^{3}\)F\(_{4}\) is 1.14 \(\times\) 10\(^{-6}\) Debye\(^2\).

The agreement for the other transitions is better than in the case of set a.

The experimental and calculated dipole strengths are given in Table 1. In Table 2, the parameters for Pr\(^{3+}\) in different fluoride glasses are compared. It is clear that the parameter values show considerable spread for the same glass composition determined by different authors. The parameter values largely depend on the transitions which are used in the fitting procedure. The exclusion of a transition may considerably change the intensity parameters. In this work, the overlapping transitions \(^{3}\)H\(_{4}\) and \(^{3}\)F\(_{2}\) were separated by fitting gaussian curves under the absorption bands. The transitions to \(^{3}\)F\(_{3}\) and \(^{3}\)F\(_{4}\) could be also separated in this way. The authors in [15,16] have integrated these bands as a whole.

General information about the theory of magnetic circular dichroism can be found in the papers of Stephens [26,27] and in the book of Piepho and Schatz [20].

Table 2
Judd–Ofelt intensity parameters \(\Omega_{i}\) (\(10^{-20}\) cm\(^2\)) for Pr\(^{3+}\) in fluoride glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>(\Omega_{2}) ((10^{-20}) cm(^2))</th>
<th>(\Omega_{3}) ((10^{-20}) cm(^2))</th>
<th>(\Omega_{5}) ((10^{-20}) cm(^2))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBLAN</td>
<td>0.04</td>
<td>6.54</td>
<td>3.84</td>
<td>This work (set a)</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>4.99</td>
<td>13.06</td>
<td>This work (set b)</td>
</tr>
<tr>
<td>ZBLA</td>
<td>0.0668</td>
<td>5.05</td>
<td>6.92</td>
<td>[10]</td>
</tr>
<tr>
<td>BiGdZLuTzPb</td>
<td>0.73</td>
<td>4.91</td>
<td>4.97</td>
<td>[12]</td>
</tr>
<tr>
<td>Fluoride glass</td>
<td>0.19</td>
<td>7.88</td>
<td>4.81</td>
<td>[13]</td>
</tr>
<tr>
<td>Fluorophosphate glass</td>
<td>117</td>
<td>1.91</td>
<td>4.19</td>
<td>[11]</td>
</tr>
<tr>
<td>Fluorophosphate glass</td>
<td>1.4</td>
<td>4.2</td>
<td>5.6</td>
<td>[14]</td>
</tr>
</tbody>
</table>
Application of MCD to lanthanide systems can be found in the work of Görler-Walrand et al. [28–33]. The MCD spectrum is a superposition of three terms: an A-term with the shape of the first derivative of an absorption band, and a B- and a C-term with the shape of an absorption band. MCD signals have a sign. According to the conventions of Piepho and Schatz [20] an A-term is positive if left circularly polarized light is absorbed to the Zeeman component at high energy. This corresponds to a positive lobe at the high wavenumber side of the spectrum. Both a B-term and a C-term are positive if the corresponding MCD signal shows a positive $\Delta e$.

The 293 K MCD spectrum of ZBLAN:Pr$^{3+}$ shows a positive A-term for the $^1D_2 \leftrightarrow ^1H_4$ and the $^3P_0 \leftrightarrow ^3H_4$ transition. A negative A-term is found for the $^3P_0 \leftrightarrow ^1H_4$ transition. The $^3P_1, ^1H_6 \leftrightarrow ^3H_4$ transition is of the C-type (negative C-term). At low temperature, the appearance of the MCD spectrum changes drastically: no A-term like curve is observed at 4.2 K, only C-terms. These C-terms have the same sign as the A-terms at room-temperature. The temperature dependence of the $^3P_0 \leftrightarrow ^3H_4$ transition is given in Fig. 2. This temperature dependence is the same as found by Görler-Walrand et al. [34] for Pr$^{3+}$ in a polyvinyl alcohol matrix. Because the $^3P_0$ level is non-degenerate, an A-term indicates a ground-state degeneracy. From the negative sign of the A-term, it follows that the Zeeman level which is the starting level for a preferential absorption of left circularly polarized light, is energetically above the Zeeman level from which a preferential absorption of right circularly polarized light takes place. In other words, right circularly polarized light is absorbed from the ground state and left circularly polarized light from a thermally populated Zeeman level. A decrease of the temperature depopulates the latter Zeeman level in favour of the ground state. The positive lobe of the A-term disappears and the negative lobe grows. The overall appearance of the MCD signal at low temperature is that of a negative C-term.

The method of moments for the determination of the Faraday parameters [35] gave reproducible results only for the $B_0$ and $C_0$ parameters, not for $A_1$. A linear relation between the zeroth moment of the MCD and $1/T$ was found for the temperature interval 77–293 K. At lower temperatures an appreciable deviation from linearity was noticed. This is due to the fact that at very low temperatures not all crystal-field levels of the $^1H_4$ ground state are populated. The results of the moment analysis are given in Table 3. A MCD spectrum of Pr$^{3+}$ doped soda glass has been published by Colloccott and Taylor [4]. The appearance of their 77 K spectrum is substantially different from our 77 K spectrum. The authors derive only mean values for Faraday parameters of the complex $^3P_{0,1,2,16}$ group as a whole. The $C_0/D$ ratio of their $^1D_2 \leftrightarrow ^1H_4$ transition (+0.7 Bohr magneton) is comparable to our results (+0.8 Bohr magneton). The $B_0/D$ ratio is small for all transitions.

4. Conclusions

The intensity analysis of the absorption spectra of ZBLAN:Pr$^{3+}$ shows that the Judd–Ofelt theory has in the case of trivalent praseodymium only limited validity for the description the dipole strengths of the intraconfigurational 4f–4f transitions. This is mainly due to the small energy gap between the $4f^2$ configuration and the $4f^15d^1$ configuration. The $\Omega_6$ parameters may show considerable spread depending on the transitions included in the fit. Therefore, intensity parameters for Pr$^{3+}$ are difficult to compare.

To our knowledge, a MCD spectrum of Pr$^{3+}$ in a non-oxide glass has not been reported before. A distinct feature is the strong temperature dependence of the transitions, due to population differences between the Zeeman levels of the ground state from which left and right.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$B_0/D$ (in Bohr magneton cm)</th>
<th>$C_0/D$ (in Bohr magneton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1D_2 \leftrightarrow ^1H_4$</td>
<td>+0.0050</td>
<td>+0.81</td>
</tr>
<tr>
<td>$^3P_0 \leftrightarrow ^3H_4$</td>
<td>+0.0008</td>
<td>-0.91</td>
</tr>
<tr>
<td>$(^3P_0, ^1H_6) \leftrightarrow ^3H_4$</td>
<td>+0.0003</td>
<td>-0.25</td>
</tr>
<tr>
<td>$^3P_2 \leftrightarrow ^3H_4$</td>
<td>+0.0080</td>
<td>+0.29</td>
</tr>
</tbody>
</table>

The Faraday-parameters have been determined by the method of moments.
circularly polarised light is absorbed. Whereas A-terms dominate the room-temperature MCD spectrum, the spectrum is overwhelmed by C-terms at low temperatures. Faraday parameters can be determined by the method of moments. These Faraday or MCD parameters describe the magneto-optical behaviour of the lanthanide ion.

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