Methods of studying magnetic circular dichroism in erbium-doped aluminosilicate glass

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Abstract

The magnetic circular dichroism (MCD) spectrum of 3.0 mol% Er^{+3} doped aluminosilicate glass has been measured over a range of temperatures in several optical absorption bands. The method of moments was used to obtain the Faraday A_1, B_0, and C_0 parameters from the spectra, and the spectroscopic splitting factor, g, for the $^4I_{15/2}$ ground state was calculated for each band studied. The ground state g was also calculated from the saturation properties of the magnetic circular dichroism signal vs. magnetic field strength at 1.6 K. The gs obtained by both methods show very good agreement with each other and are compared with those found in previous works.   © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Magnetic circular dichroism (MCD) has previously been used to study the magneto-optical properties of trivalent rare earth ions such as Nd^{+3} [1], Pr^{+3}, Ho^{+3} [2], and Er^{+3} ([3,4]) in glass hosts, where the method of moments has been employed to extract the Faraday A_1, B_0 and C_0 parameters. The ratio of the C_0 parameter to the dipole strength, D_0, has been considered in most of the previous works, as it provides the ground state g for an ion in its glassy host [5]. Collocott and Taylor [1–3] have studied the Faraday rotation in conjunction with the MCD as an additional method of obtaining gs, and in the case of Nd^{+3}, have assumed a simple Kramers doublet ground state in analyzing their results; their two methods show excellent agreement. In this paper, we determine the ground state g for Er^{+3} in an aluminosilicate glass matrix by first analyzing the MCD spectrum with the method of moments to obtain the Faraday parameters, and then by examining the saturation of the MCD signal with increasing magnetic field, where a 4-fold degenerate ground state is assumed.

2. Experimental procedures

The Er^{+3} doped glass used in the experiment had the composition 3.0 mol% Er_2O_3, 20.0 mol% Na_2O, 20.0 mol% Al_2O_3, 57.0 mol% SiO_2; the glass was melted in a platinum crucible for 7 h at 1650°C, during which the furnace was purged with dry N_2 to keep the glass as dry as possible. The glass was then annealed at 700°C and later

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cut into 2 mm × 2 mm × 5 mm samples and polished [1].

Absorption and MCD spectra for the sample were simultaneously recorded for the temperatures 20, 50, 80, 100, 125, and 140 K. The MCD spectrometer used consisted of a 250 W quartz tungsten halogen lamp focused into a Raman type double monochromator having a bandpass less than 5 cm^{-1} over the range 30 000–11 000 cm^{-1}. The output light was then linearly polarized by a Wollaston prism and directed through a 42 KHz photoelastic modulator, which alternately outputs right- and left-hand circularly polarized light. The polarization modulated light was then focused onto the sample, which was mounted in a helium cryostat outfitted with a superconducting magnet operating at 1.7 T with a homogeneity of 1 part in 10^4 over 1 cm^3. Light transmitted by the sample passed through a 670 Hz optical chopper and was focused on to a photomultiplier tube. A lock-in amplifier referenced to the optical chopper frequency measured the absorption spectrum of the sample and another referenced to the modulator frequency measured the differential absorption of the two polarizations of light. The ratio of lock-in voltages gives a quantity proportional to $\Delta A = A_- - A_+$, the difference in optical densities for left and right circularly polarized light [6]. A computer scanned the spectrometer in 2 cm^{-1} steps and recorded the voltages from both lock-ins to obtain full MCD and absorption spectra.

3. Theory

MCD is an effect common to all matter where the application of a static uniform magnetic field induces an asymmetry in the optical densities A_- and A_+. The differential absorption $\Delta A = A_- - A_+$ through an absorption band may be written as a dispersion relation [7]

$$\frac{\Delta A(\upsilon)}{\upsilon} = 152.5\left\{ A_1\left(-\frac{\partial f}{\partial \upsilon}\right) + \left(\frac{C_0}{kT} + B_0\right)f \right\}Hcz,$$

(1)

where ΔA is in optical density units, H is in Tesla, υ is in cm^{-1}, $f(\upsilon)$ is the normalized bandshape function, c is the concentration of Er^{+3} in mol/l, z is the sample thickness in cm, and $152.5 \approx N\pi^3\alpha^2\log_{10}eu_B/125hc$, where N is Avagadro's number and u_B is the Bohr magneton.

The Faraday parameters appearing in Eq. (1) for an electronic transition $|a\rangle \rightarrow |j\rangle$ are given as [7]

$$A_1 = \frac{1}{d_A}\sum_{a,j}\left[|\langle a|m_-|j\rangle|^2 - |\langle a|m_+|j\rangle|^2\right]$$
$$\times x[\langle j|L_z + 2S_z|a\rangle - \langle a|L_z + 2S_z|j\rangle],$$
$$B_0 = -\frac{2}{d_A}\sum_{a,j}\text{Re}\left\{\sum_{k\neq j}[\langle a|m_-|j\rangle\langle k|m_+|a\rangle\right.$$
$$-\langle a|m_+|j\rangle\langle k|m_-|a\rangle]x\frac{\langle j|L_z + 2S_z|k\rangle}{E_k - E_j}$$
$$+\sum_{k\neq a}[\langle a|m_-|j\rangle\langle j|m_+|k\rangle$$
$$\left.-\langle a|m_+|j\rangle\langle j|m_-|k\rangle]x\frac{\langle k|L_z + 2S_z|a\rangle}{E_k - Ea}\right\},$$
$$C_0 = -\frac{1}{d_A}\sum_{a,j}\left[|\langle a|m_-|j\rangle|^2 - |\langle a|m_+|j\rangle|^2\right]$$
$$\times x\langle a|L_z + 2S_z|j\rangle,$$

(2)

where $m_\pm = m_x \pm im_y$ (electric dipole operator) and d_A is the degeneracy of la>; A_1 and C_0 are in units of Debye^2 (D^2) and B_0 is in D^2/cm^{-1}. To eliminate the effects of c and z on ΔA, the Faraday parameters are typically quoted in ratios with respect to the dipole strength D_0, given by [7]

$$D_0 = \frac{1}{2d_A}\sum_{a,j}\left[|\langle a|m_+|j\rangle|^2 + |\langle a|m_-|j\rangle|^2\right],$$

(3)

which is in units of D^2.

To extract the Faraday parameters from an MCD spectrum, the method of moments is employed. Defining the center of gravity of an absorption band as

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[1] Polishing done by Center for Optical Manufacturing in Rochester, NY, USA.

$$\bar{v} = \frac{\int_{\text{band}} A(v)\,dv}{\int_{\text{band}} \frac{A(v)}{v}\,dv} \qquad (4)$$

the 0th moments of the absorption and MCD bands may be respectively written as [7]

$$\langle A(v) \rangle_0 = \int_{\text{band}} \frac{A(v)\,dv}{v} = 326.6 D_0 cz,$$

$$\langle \Delta A(v) \rangle_0 = \int_{\text{band}} \frac{\Delta A(v)}{v}\,dv = 152.5 \left[B_0 + \frac{C_0}{kT} \right] HcZ,$$

$$(5)$$

and the 1st MCD moment as

$$\langle \Delta A(v) \rangle_1 = \int_{\text{band}} \frac{\Delta A(v) * (v - \bar{v})}{v}\,dv$$
$$= 152.5 A_1 Hcz. \qquad (6)$$

The three Faraday parameters represent the contributions to the MCD signal from separate manifestations of the Zeeman effect. A_1 is temperature independent and results from Zeeman splitting of a degenerate ground or excited state; either is sufficient for its existence. B_0 is temperature and degeneracy independent and results from the mixing of nearby states by the magnetic field. C_0 describes the population redistribution among the ground state magnetic sublevels brought on by the Zeeman splitting, its contribution to ΔA being temperature dependent; it will exist only if the ground state is degenerate [7,8].

The above equations will be valid provided that the Zeeman energy (~ 1 cm^{-1}, typically) is much smaller than the bandwidth, Γ as well as kT. Γ in rare earth doped glasses is usually 100s of cm^{-1}, making the former approximation excellent. However, at low temperatures, ΔA will no longer be linear in H for sufficiently high field strengths due to depopulation of the higher energy crystal field levels, rendering Eq. (1) inaccurate; this nonlinear dependence of ΔA with increasing H is known as saturation. If we assume the Er^{+3} ions to occupy near-octahedral symmetry sites in the glass, the $^4I_{15/2}$ ground state will split into five terms, the lowest in energy approximated as a quartet of degenerate states [9–11]. Modifying Stephen's expression for saturation of a Kramers doublet ground state [7] gives the relation

$$\frac{\Delta A}{v} \propto \frac{\sin \text{h}(gu_B H/2kT) + \sin \text{h}(3gu_B H/2kT)}{\cos \text{h}(gu_B H/2kT) + \cos \text{h}(3gu_B H/2kT)},$$

$$(7)$$

where we assume the other ground state terms are sufficiently high in energy as to be completely unpopulated for the temperatures and field strengths used in this experiment.

4. Results

The absorption and MCD spectra for each of the four bands measured are given in Figs. 1 and 2. The respective dependencies of A and ΔA on temperature are shown, both tending to broaden and flatten with increasing temperature. The ratioed Faraday parameters are given in Table 1, where the contributions of B_0 and C_0 to ΔA have been separated by plotting $(B_0/D_0 + C_0/D_0 kT)$ as a function of $1/kT$, the slope yielding C_0/D_0 and the y-intercept B_0/D_0; the listed Rs are linear correlation coefficients indicating the quality of the least squares fit made to the data. An A_1/D_0 value is not given for the $^4F_{7/2}$ band as the integral $\langle \Delta A \rangle_1$ showed an uncharacteristically large temperature dependence, a behavior that merits further investigation. The Faraday parameters fall roughly into the ratio $A_1 : B_0 : C_0 = 1 : 1/\Delta E : 1$ expected by Stephens [7], the band separation ΔE being on the order of thousands of cm^{-1} in rare earth doped glasses. The calculated ground state gs mostly fall into the range 3.3–3.6, the exception being the $^4S_{3/2}$ band. The A_1/D_0s given were averaged for all temperatures studied, where the assumption that D_0 will not vary with temperature must be made.

The saturation behavior of the Er^{+3} doped glass at 1.6 K as a function of H is shown in Fig. 3. The curve was obtained by setting the spectrometer to the peak of the $^4F_{7/2}$ band (20 500 cm^{-1}) and scanning the magnet from 0 to 1700 mT, the MCD being measured every 5 mT. A deviation from linearity becomes obvious beyond a few hundred mT. Fitting the saturation function (7) to the data gives a $g = 3.58 \pm 0.02$, the correlation coefficient, R, of the fit being 0.99865. Included in Fig. 3 is the
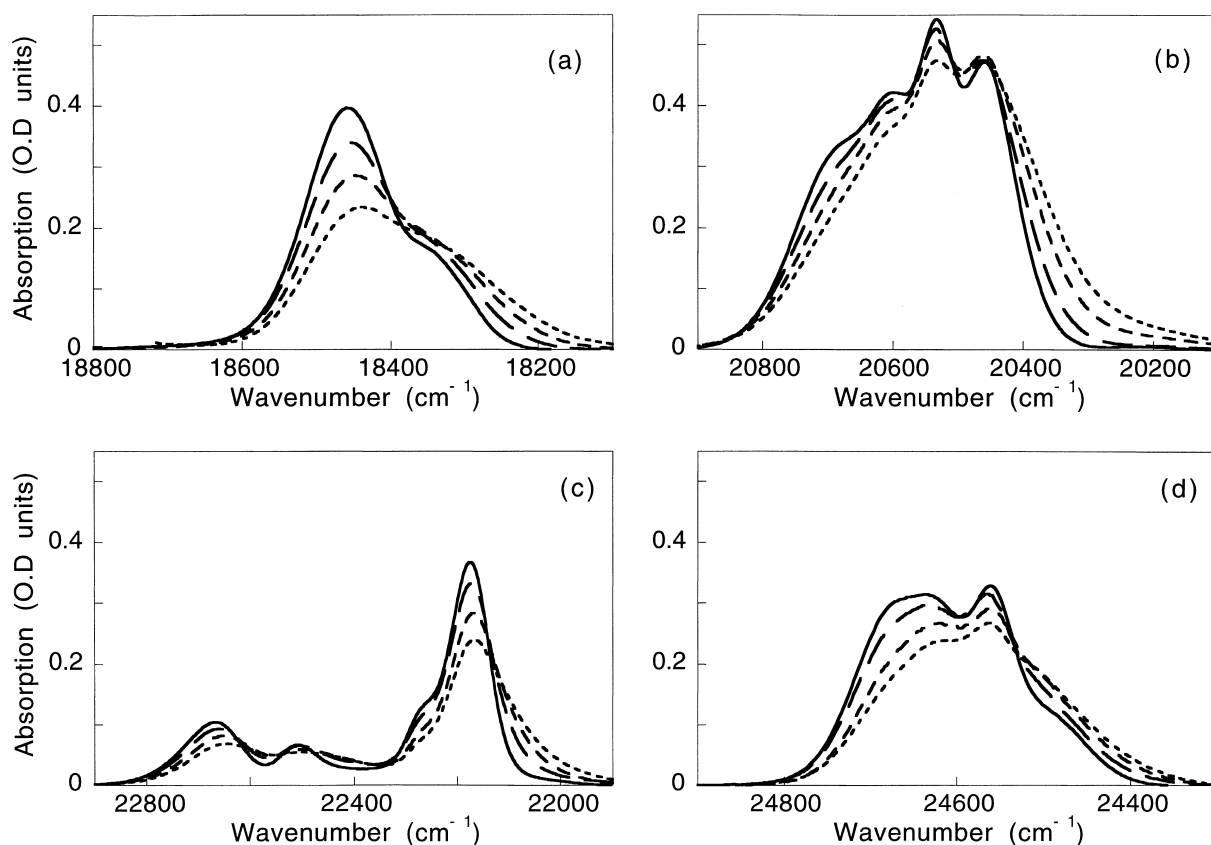
Fig. 1. Absorption spectra (optical density units) of 3.0 mol% Er^{+3} doped aluminosilicate glass measured at four temperatures (20 K (solid line), 50 K (long dashed line), 80 K (medium length dashed line), and 125 K (shortest dashed line)) for four bands: (a) $^4S_{3/2}$, (b) $^4F_{7/2}$, (c) $^4F_{3/2}$ and $^4F_{5/2}$, (d) $^2H_{9/2}$. The ordinate is the same for all four graphs for comparison.

1.6 K saturation curve for a 0.12 mol% Er^{+3} doped aluminosilicate glass sample for the $^4G_{11/2}$ band (26 500 cm^{-1}). Fitting (7) to its saturation curve yields a $g = 5.06 \pm 0.03$, the increase in g with decrease in concentration being similar to Collocott's findings in Nd^{+3} doped soda glass [1]. No moments analysis is shown for this sample as its MCD spectra suffered from signal-to-noise problems due to its concentration, particularly at higher temperatures.

The saturation procedure was then repeated at 20 K for the 3.0 mol% sample to ensure that Eq. (1) was indeed linear in H, allowing the moment equations to be used for analysis of the MCD spectra. The plot of ΔA vs. H shown in Fig. 4 shows a linear relationship, indicating no saturation effects are present at this temperature.

5. Discussion

The gs obtained by both experimental methods indicate a ground state g in the range 3.3–3.6. The $^4S_{3/2}$ band yields a somewhat lower C_0/D_0 ratio of 2.15, which is primarily due to its overlap with the $^2H_{11/2}$ band, especially for higher temperatures. The $^2H_{11/2}$ band was not analyzed due to the fact that the MCD spectrometer used had insufficient range to properly evaluate $\langle A \rangle_0$. Collocott quotes C_0/D_0's in the range 2.71–4.83 for the same bands (using 10% Er_2O_3 by wt glass samples), but obtains A_1/D_0's approximately a factor of 100 smaller than those listed here [3]. The discrepancy likely stems from difficulties in evaluating $\langle \Delta A \rangle_1$, as it can be very sensitive to the position of $\bar{v}$. $\bar{v}$ can be difficult to reproduce and also shows a temperature de-
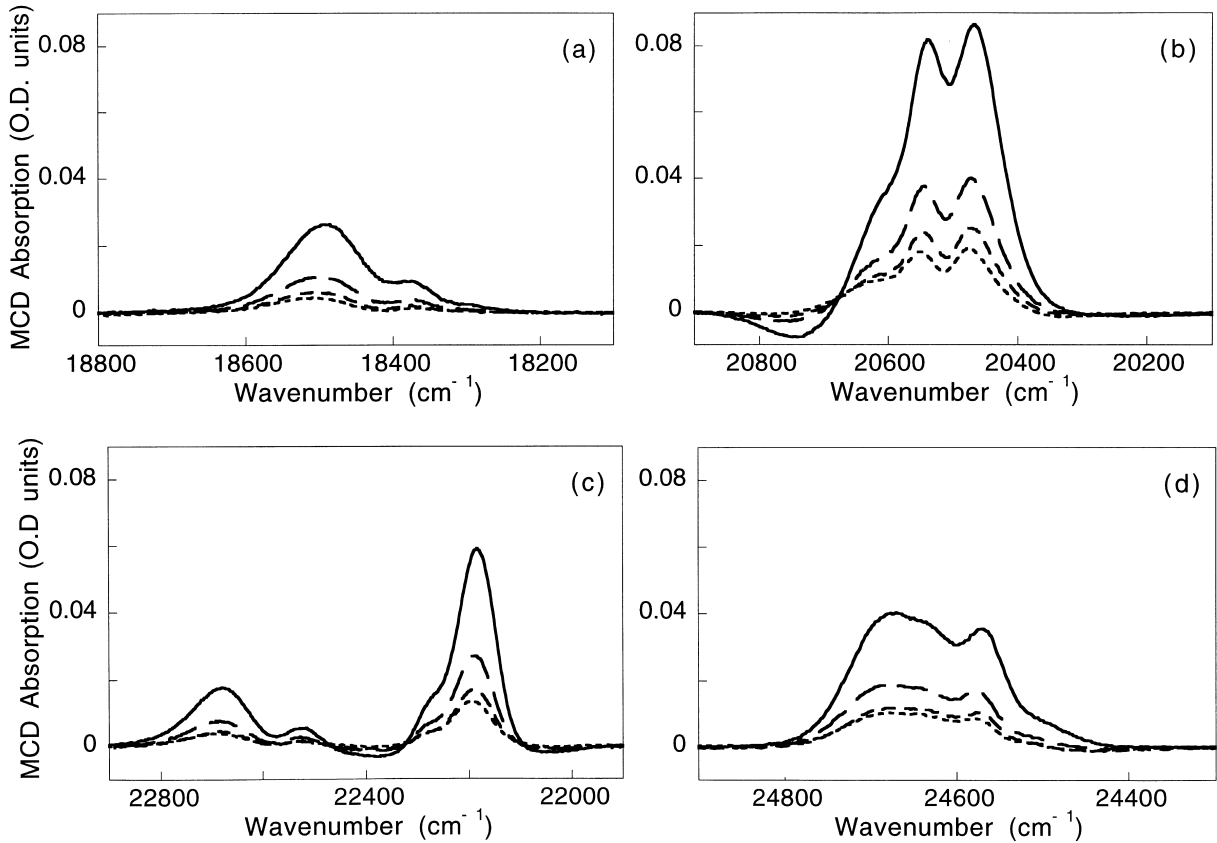
Fig. 2. MCD absorption spectra (optical density units) of 3.0 mol% Er^{+3} doped aluminosilicate glass measured at four temperatures (20 K (solid line), 50 K (long dashed line), 80 K (medium length dashed line), and 125 K (shortest dashed line)) for four bands: (a) $^4S_{3/2}$, (b) $^4F_{7/2}$, (c) $^4F_{3/2}$ and $^4F_{5/2}$, (d) $^2H_{9/2}$. The ordinate is the same for all four graphs for comparison.

Table 1
Faraday parameters obtained from Er^{+3} doped aluminosilicate glass

Band	Wavenumber (cm^{-1})	A_1/D_0 (D^2)	B_0/D_0 (D^2)	C_0/D_0 (D^2)	R
$^2H_{9/2}$	24 950–24 250	5.6 ± 0.8	$1.8 \pm 0.2 \times 10^{-2}$	3.61 ± 0.07	0.99948
$^4F_{5/2}$	23 000–22 000	5.9 ± 0.9	$3.5 \pm 0.3 \times 10^{-2}$	3.52 ± 0.10	0.99828
$^4F_{3/2}$					
$^4F_{7/2}$	21 000–20 000	****	$1.1 \pm 0.5 \times 10^{-2}$	3.35 ± 0.14	0.99674
$^4S_{3/2}$	18 800–18 100	4.1 ± 0.7	$6.9 \pm 1.5 \times 10^{-3}$	2.15 ± 0.04	0.99944

pendence, its value tending to decrease with increasing temperature.

Robinson's studies of Er^{+3} in alkali silicate glass identify the primary rare earth site as near-octahedral with a trigonal distortion, suggesting D_3 symmetry [9]. Collocott uses Zverev and Smirnov's work on trigonal Er^{+3} centers in CaF_2 to estimate

the range of gs for the Er^{+3} in glass as 4.7–6.6, where the gs in glass are averaged over three dimensions [3,12]. The gs found by both methods here for the 3.0 mol% sample fall in a lower range, a consequence of the fact that gs has been shown to decrease with increasing Er^{+3} concentration in glass.
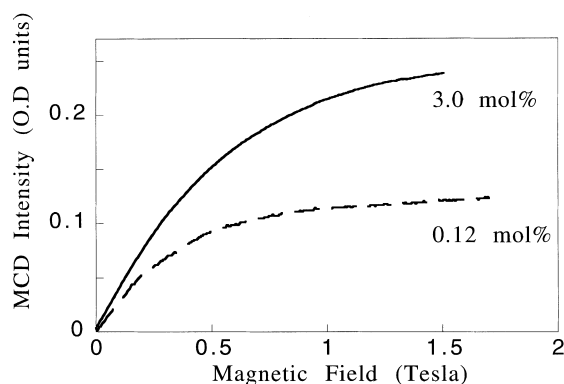
Fig. 3. Saturation curves at 1.6 K for 2 different Er^{+3} concentrations- 3.0 mol% (solid line) and 0.12 mol% (dashed line). The 3.0 mol% sample was measured at the $^4F_{7/2}$ transition peak (20 500 cm^{-1}) while the 0.12 mol% sample was measured at the $^4G_{11/2}$ transition peak (26 500 cm^{-1}). Note that the lesser doped sample saturates at lower field strength exhibiting a greater ground state g-value.
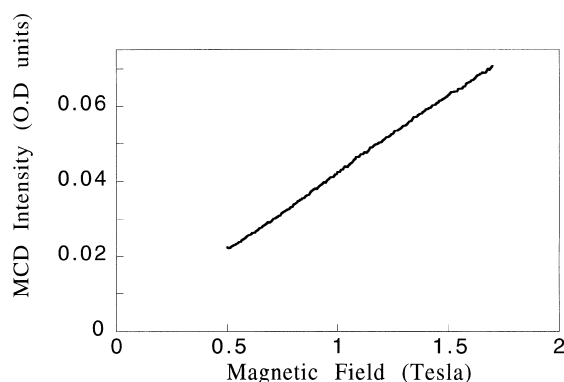

Fig. 4. MCD absorption as a function of magnetic field at 20 K for the 3.0 mol% sample. A linear relationship is seen up to a magnetic field strength of 1.7 T.

6. Conclusion

The Faraday parameters for Er^{+3} doped aluminosilicate glass have been extracted from MCD spectra, obtaining values in the ratio $A_1 : B_0 : C_0 =$ $1 : 1/\Delta E : 1$ as predicted by Stephens [7]. The ground state gs found from the ratio $|C_0/D_0|$ in the various bands studied prove to be self-consistent, yielding a range 3.3–3.6. The ground state $g = 3.58 \pm 0.02$ found from examining the MCD saturation curve at 1.6 K agrees well with those found from the method of moments, indicating that if could serve well as a method for obtaining gs without resorting to moments analysis. Studying the saturation curve at various temperatures also provided a method of ensuring that MCD spectra are linear in H so that the moments equations may be used for analysis.

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