Spectroscopic properties of Gd^{3+} -doped fluorozirconate glass

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Abstract

The optical absorption and MCD spectrum of gadolinium-doped ZBLAN fluorozirconate glass were recorded at room temperature. The induced electric dipole contributions to the experimental dipole strengths were parametrized in terms of phenomenological Judd–Ofelt intensity parameters. The parameter set obtained by a standard least-squares fitting procedure is: $\Omega_2 = (3.35 \pm 0.62) \times 10^{-20} \text{ cm}^2$, $\Omega_6 = (2.81 \pm 0.08) \times 10^{-20} \text{ cm}^2$, and Ω_4 is indeterminate. Special attention is given to the characteristic spectroscopic properties of the Gd^{3+} ion. © 1997 Elsevier Science B.V.

1. Introduction

Only a few spectroscopic studies have been devoted to the Gd^{3+} ion. Classical examples are $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ [1], $\text{LaCl}_3:\text{Gd}^{3+}$ [2], $\text{LaF}_3:\text{Gd}^{3+}$ [3] and Gd^{3+} (aquo) [4,5]. This limited attention is due to the fact that all the transitions in the absorption spectrum are in the ultraviolet above 32000 cm^{-1} . Since the majority of the host matrices show a strong broad band absorption in this spectral region, these transitions mask the weak transitions of Gd^{3+} .

As far as glasses are concerned, interesting hosts for Gd^{3+} are mainly restricted to heavy-metal fluoride glasses because of their ultraviolet cut-off at short wavelengths ($< 250 \text{ nm}$). Alonso et al. [6] studied the optical absorption spectrum of Gd^{3+} ions in the fluorozirconate glasses ZBLA and ZBLALi. Brixner et al. [7] reported the X-ray excited emission of Gd^{3+} in the fluorozirconate glass ZBLAN and in

the fluorindate glass BIZYT. McDougall et al. [8,9] published intensity parameters for Gd^{3+} in different fluorozirconate glasses.

In this Letter, we report the absorption and MCD spectrum of the fluorozirconate glass ZBLAN: Gd^{3+} , as a continuation of our combined qualitative–quantitative treatment of the spectroscopic properties of the trivalent lanthanide ions in the ZBLAN matrix [10–12].

2. Experimental details

The sample of the 1% Gd^{3+} -doped ZBLAN glass (53 mol% ZrF_4 , 20 mol% BaF_2 , 20 mol% NaF , 3 mol% AlF_3 , 3 mol% LaF_3 and 1 mol% GdF_3) was prepared using methods described elsewhere [13,14]. The starting reagents for the glass preparation were ZrO_2 , BaF_2 , NaF , Al_2O_3 , La_2O_3 and Gd_2O_3 in appropriate ratios. The oxides were transformed into the fluorides during a fluorination step with NH_4HF_2 . Ammonium hydrogen fluoride was added to the

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reaction mixture in excess ($2 \times$ the stoichiometric ratio). The reaction mixture was heated in a platinum crucible at 300°C for several hours. Complex metallic ammonium fluorides are formed and subsequently decomposed by heating to 420°C . At this temperature the excess NH_4HF_2 is also removed. The resulting powder was melted in a dry argon atmosphere (glove box) at 500°C . The batch was further heated to 750°C to refine the melt. Refining is necessary to remove the OH groups. The glass was cast into a brass mould which was preheated to 270°C and the batch was annealed at this temperature for 1 day. Finally, the samples were cut and polished. The sample is colorless, as expected for Gd^{3+} as the doping ion [15].

The Gd^{3+} concentration in the glass sample is 0.32 mol dm^{-3} and the optical path length is 9.96 mm. Absorption spectra were recorded at room temperature on a spectrophotometer (AVIV 17DS) in the 350–230 nm range. MCD spectra were recorded on a circular dichroism spectrometer (AVIV 62DS) extended with an electromagnet (Oxford Instruments). The magnetic field strength was approximately 9000 G (0.9 T). Data collection was digital and data processing was done by commercial software on a PC.

3. Results and discussion

The optical absorption spectrum at ambient temperature is shown in Fig. 1. The transitions were assigned by comparing the band positions in the absorption spectrum with the energy level scheme of $\text{LaF}_3:\text{Gd}^{3+}$ published by Carnall et al. [3] (see Table 1). The transition energies correspond well with those observed in the $\text{ZBLA}:\text{Gd}^{3+}$ glass by Alonso et al. [6]. All transitions start from the $^8\text{S}_{7/2}$ ground state of the $4f^7$ configuration of Gd^{3+} . The excited terms which could be observed are ^6P , ^6I and ^6D . The ^6G term ($49000\text{--}50000 \text{ cm}^{-1}$) could not be seen because of strong absorption by the glass matrix. In comparison with the other lanthanide ions, the absorption bands for Gd^{3+} are very sharp. The strongest transitions are those to the $^6\text{I}_J$ levels.

The intensities of the transitions can be characterised by the dipole strength D :

$$D = \frac{1}{108.9 \times C \times d} \int \frac{A(\bar{\nu})}{\bar{\nu}} d\bar{\nu}, \quad (1)$$

where C is the concentration of the gadolinium ion (mol dm^{-3}), d is the optical path length (cm), A is the absorbance and $\bar{\nu}$ is the wavenumber (cm^{-1}). The dipole strength is expressed in debye^2 (or D^2).

Fig. 1. Optical absorption spectrum of $\text{ZBLAN}:\text{Gd}^{3+}$ at room temperature.

The transitions observed in the absorption spectra of trivalent lanthanide ions are intraconfigurational f–f transitions. The majority of these transitions are induced electric dipole (ED) transitions. Magnetic dipole (MD) transitions are scarce. However, several transitions in the absorption spectrum of Gd^{3+} are mixed ED–MD transitions. The greatest MD contributions are found for the transitions ${}^6\text{P}_{7/2} \leftarrow {}^8\text{S}_{7/2}$ (32170 cm^{-1}) and ${}^6\text{P}_{5/2} \leftarrow {}^8\text{S}_{7/2}$ (32770 cm^{-1}). Although there is both an electric dipole and a magnetic dipole transition moment, no circular dichroism can be observed, because the cross-term averages to zero in an achiral glass.

The induced electric dipole transitions are described by the Judd–Ofelt theory [16,17]. The intensity of induced electric dipole transitions can be described in terms of three phenomenological intensity parameters Ω_λ ($\lambda = 2, 4$ and 6). The total calculated dipole strength, including both magnetic dipole and induced electric dipole contributions, is given by

$$D = \frac{10^{36}}{2J+1} \left[nD_{\text{MD}} + \frac{(n^2+2)^2}{9n} \times e^2 \sum_{\lambda=2,4,6} \Omega_\lambda |\langle J \| U^\lambda \| J' \rangle|^2 \right] \quad (2)$$

The factor 10^{36} convert D^2 units into esu cm. The

elementary charge e is 4.803×10^{-10} esu. The $\langle J \| U^{(\lambda)} \| J' \rangle$ are reduced matrix elements. The degeneracy of the ground state is equal to $2J+1$ (i.e. 8 for Gd^{3+}). The factors n and $(n^2+2)^2/9n$ take into account the fact that the gadolinium ion is not in a vacuum but in a dielectric medium (n is the refractive index of the glass). D_{MD} is the magnetic dipole contribution to the total dipole strength. In order to determine the intensity parameters for the induced electric dipole intensities, the experimental dipole strengths have to be corrected for the magnetic dipole contribution D_{MD} . The magnetic dipole intensities are insensitive to the host matrix and we used therefore the values reported by Carnall et al. [4]. Those values are given in terms of the oscillator strength and these values have been transformed to values in terms of the dipole strength by using formula (7) of Ref. [12].

Matrix elements for Gd^{3+} have been published by Carnall et al. [5]. In the case of overlapping transitions, we made a summation of the appropriate matrix elements. The matrix elements used in the fitting procedure are listed in Table 2. All the $|\langle J \| U^{(4)} \| J' \rangle|^2$ matrix elements are zero or have a negligible value. Therefore, it is impossible to determine the Ω_4 parameter with a reasonable accuracy and this parameter will thus be indeterminate. For Gd^{3+} , the Ω_4 parameter can be determined only if the ${}^6\text{G}_7$ level can be observed. Since the Judd–Ofelt

Table 1

Transition energies, experimental dipole strengths (D_{exp}), calculated dipole strengths (D_{calc}) and $D_{\text{calc}}/D_{\text{exp}}$ ratios for the 4f–4f transitions in ZBLAN: Gd^{3+} glass at ambient temperature

Transition ($\leftarrow {}^8\text{S}_{7/2}$) ⁶	Wavelength (nm)	Energy (cm^{-1})	D_{exp} (10^{-6} D^2)	D_{MD}^{a} (10^{-6} D^2)	$D_{\text{calc}}^{\text{b}}$ (10^{-6} D^2)	$D_{\text{calc}}/D_{\text{exp}}$
$\text{P}_{7/2}$	310.8	32170	5.75	0.51	1.79	0.31
${}^6\text{P}_{5/2}$	305.2	32770	2.95	0.28	0.80	0.27
${}^6\text{I}_{7/2}$	278.5	35910	5.50	0.00	4.42	0.80
${}^6\text{I}_{9/2}, {}^6\text{I}_{17/2}$	275.4	36310	33.88	0.00	34.29	1.01
${}^6\text{I}_{11/2}$	273.7	36540	20.89	0.00	19.08	0.91
${}^6\text{I}_{15/2}, {}^6\text{I}_{13/2}$	272.6	36680	54.63	0.00	55.11	1.01
${}^6\text{D}_{9/2}$	251.7	39730	7.08	0.01	7.33	1.04
${}^6\text{D}_{7/2}$	245.3	40770	5.26	0.04	5.70	1.08
${}^6\text{D}_{5/2}, {}^6\text{D}_{3/2}$	243.5	41070	3.83	0.02	4.26	1.11

All the transitions are from the ${}^8\text{S}_{7/2}$ ground state to the level indicated.

^aThe calculated magnetic dipole contribution to the total calculated dipole strength. The values were taken from Carnall et al. [4] and converted to dipole strengths. The correction factors $1/(2J+1)$ and χ_{MD} have been included.

^bTotal calculated dipole strength (incorporating ED and MD contributions). The Judd–Ofelt intensity parameters used for the calculation of the dipole strengths are $\Omega_2 = (3.35 \pm 0.62) \times 10^{-20} \text{ cm}^{-1}$, $\Omega_6 = (2.81 \pm 0.08) \times 10^{-20} \text{ cm}^{-1}$ (Ω_4 is indeterminate).

Table 2
Matrix elements for Gd^{3+} ^a

Transition ($\leftarrow {}^8\text{S}_{7/2}$) ⁶	$ \langle J \ U^{(2)} \ J' \rangle ^2$	$ \langle J \ U^{(4)} \ J' \rangle ^2$	$ \langle J \ U^{(6)} \ J' \rangle ^2$
$\text{P}_{7/2}$	0.0010	0	0
${}^6\text{P}_{5/2}$	0.0004	0	0
${}^6\text{I}_{7/2}$	0	0	0.0041
${}^6\text{I}_{9/2}, {}^6\text{I}_{17/2}$	0	0	0.0318
${}^6\text{I}_{11/2}$	0	0	0.0177
${}^6\text{I}_{15/2}, {}^6\text{I}_{13/2}$	0	0	0.0511
${}^6\text{D}_{9/2}$	0.0057	0.0001	0
${}^6\text{D}_{7/2}$	0.0044	0	0
${}^6\text{D}_{5/2}, {}^6\text{D}_{3/2}$	0.0033	0	0

^aThe matrix elements were adapted after Carnall et al. [5] in the sense that a combination of the matrix elements was made for overlapping transitions. A zero value for the matrix element can either indicate a very small value or a vanishing matrix element due to the selection rules.

theory predicts a smooth decrease of the parameter values over the lanthanide series, it is in principle possible to obtain an interpolated value for Ω_4 . However, just as for the crystal-field parameters [18], the actual values of the intensity parameters do not always follow the trend predicted by the theory. Since the values for the $|\langle J \| U^{(2)} \| J' \rangle|^2$ matrix element are also small, a relatively large error can be expected for the Ω_2 parameter. The Ω_2 parameter mainly describes the intensity of the weak transitions to the ${}^6\text{D}_J$ multiplets. Only the Ω_6 parameter can be determined with high accuracy. The Ω_6 parameter describes the intensity of the transitions to the ${}^6\text{I}_J$ multiplet. As mentioned above, the transition to the

${}^6\text{I}_J$ multiplets are the most intense transitions in the spectrum of Gd^{3+} and these transitions are the only pure induced electric dipole transitions.

The Ω_λ intensity parameters have been determined by a standard least-squares fitting procedure and are $\Omega_2 = (3.35 \pm 0.62) \times 10^{-20} \text{ cm}^2$, $\Omega_6 = (2.81 \pm 0.08) \times 10^{-20} \text{ cm}^2$ (Ω_4 is indeterminate). The experimental and calculated dipole strengths can be found in Table 1. In Table 3, the parameters are compared with parameters for Gd^{3+} in other host matrices. Our values are comparable with those found for other fluorozirconate glasses. Although the Ω_2 parameter is larger than the corresponding parameter of Gd^{3+} (aquo), the Ω_6 parameter of ZBLAN is considerably smaller than that of Gd^{3+} in water. Notice also that the intensity parameters are larger in solutions and glasses than in crystalline compounds.

The MCD spectrum could only be observed for the transitions to the ${}^6\text{I}_J$ multiplets, since the other transitions are too weak. The MCD signals are complex and hard to interpret quantitatively. The spectrum consists of a series of A-terms (signals with the shape of the first derivative of an absorption band). The majority of the A-terms have a positive sign [19], which means that the positive lobe is at the high energy side. The spectrum shows the use of the MCD spectrum for the detection of overlapping transitions. Whereas in the absorption spectrum, the transition to the ${}^6\text{I}_{9/2}$ level is only observed as a shoulder of the transitions to the ${}^6\text{I}_{17/2}$ level, the two transitions can easily be observed in the MCD spectrum. On the other hand the transition to the ${}^6\text{I}_{13/2}$

Table 3
Phenomenological intensity parameters Ω_λ for Gd^{3+} in various matrices

Matrix	$\Omega_2 (/10^{-20} \text{ cm}^2)$	$\Omega_4 (/10^{-20} \text{ cm}^2)$	$\Omega_6 (/10^{-20} \text{ cm}^2)$	Ref.
$\text{LiYF}_4:\text{Gd}^{3+}$ (crystal)	0.32	—	1.8	[20]
$\text{LaF}_3:\text{Gd}^{3+}$ (crystal)	1.1	1.2	0.5	[21]
Gd^{3+} (aquo)	1.94 ± 0.43	5.27 ± 1.7	4.46 ± 0.11	[22]
ZBLA: Gd^{3+} glass	2.44	—	2.12	[8]
ZBLAN: Gd^{3+} glass	2.49	—	2.30	[9]
ZBLALi: Gd^{3+} glass	2.58	—	2.34	[9]
ZBLA: Gd^{3+} glass	2.7	—	2.5	[6]
ZBLALi: Gd^{3+} glass	2.7	—	2.5	[6]
ZBLAN: Gd^{3+} glass	3.35 ± 0.62	—	2.81 ± 0.08	this work
ZBLAK: Gd^{3+} glass	4.66	—	1.88	[9]
Gd^{3+} in lanthanum borate glass	7.27	—	4.11	[23]

The matrices are classified according to increasing values of Ω_2 .

Fig. 2. MCD and absorption spectrum of the transitions to the 6I_J levels in ZBLAN:Gd $^{3+}$ at room temperature.

level cannot be distinguished from the transition to the ${}^6I_{15/2}$ level, because the separation between the two levels is too small. Carnall et al. [5] calculated a difference of only 15 cm $^{-1}$ (Fig. 2).

4. Conclusions

The Gd $^{3+}$ ion shows several typical spectroscopic features. The most characteristic features in solutions and glasses are (1) a large gap between the ground state and the first excited state (> 30000 cm $^{-1}$), (2) very narrow line widths due to weak vibronic interaction, and (3) transitions with a mixed induced electric dipole–magnetic dipole character. We discussed in this Letter the absorption and MCD spectra of the fluorozirconate glass ZBLAN:Gd $^{3+}$. The Judd–Ofelt intensity parameters determined from the room temperature absorption spectrum are: $\Omega_2 = (3.35 \pm 0.62) \times 10^{-20}$ cm 2 , $\Omega_6 = (2.81 \pm 0.08) \times 10^{-20}$ cm 2 and Ω_4 is indeterminate. The parameter values are comparable with those in other fluoride

glasses, but larger than in crystalline fluorides, so that the transitions of Gd $^{3+}$ in glasses are more intense than in crystals. The MCD spectrum is used to detect the individual contributing transitions to a complex band.

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