LETTER TO THE EDITOR

Are the Judd–Ofelt intensity parameters sensitive enough to reflect small compositional changes in lanthanide-doped glasses?

K Binnemans† and C Görller-Walrand

KU Leuven, Department of Chemistry, Coordination Chemistry Division, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

Abstract. Although the Ω_λ intensity parameters and especially the Ω_2 parameter can show a considerable spread for a particular lanthanide ion in different host matrices, the values of these parameters for lanthanide ions in glasses are relatively close to each other. Combined with the fact that large errors are inherent to these parameters, we emphasize that one has to be careful when interpreting or comparing intensity parameters for lanthanide ions in glasses. The analysis of a large data-set of intensity parameters reported for glasses indicates that $\Omega_4 \cong \Omega_6$. No correlation was found between the Ω_2 parameter and the two other parameters.

The absorption spectra of lanthanide-doped single crystals and lanthanide salts show groups of narrow lines. In solutions and in glasses, the lines within a group are broadened to one absorption band. These lines and bands have to be ascribed to electronic transitions inside the 4f shell. Each small line within a group corresponds to a transition between two crystal-field levels. Each group (or band) corresponds to transitions between two $^{2S+1}L_J$ free-ion levels (or J-manifolds). They are not accompanied by a change in configuration (i.e. intraconfigurational transitions). Although some magnetic dipole transitions are found in lanthanide spectra, the majority of the transitions are induced electric dipole transitions. The induced electric dipole transitions are parametrized by the Judd–Ofelt theory [1–3]. 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 is given by

$$D = \frac{1}{2J+1} \frac{(n^2+2)^2}{9n} e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle J || U^{(\lambda)} || J' \rangle \right|^2.$$

The $\langle J || U^{(\lambda)} || J' \rangle$ are reduced-matrix elements. The elementary charge e is 4.803×10^{-10} esu. The degeneracy of the ground state is equal to $2J+1$. The factor $(n^2+2)^2/(9n)$ takes into account that the lanthanide ions are not in a vacuum, but in a dielectric medium (n is the refractive index of the matrix). Since the intensities of f–f transitions in rare-earth complexes are ligand dependent, several authors have tried to correlate the intensity parameters with the chemical nature of the metal–ligand bond, with the properties of the ligand itself or with the structure of the complex. Of course, most attention has been paid

† Author to whom any correspondence should be addressed; e-mail: koen.binnemans@chem.kuleuven.ac.be; telephone: 00 32 16327437; fax: 00 32 16327992.

Table 1. An overview of the Judd–Ofelt parameters of Pr^{3+} in the fluorozirconate glass ZBLAN.

| $\Omega_2/10^{-20}$ cm^2	$\Omega_4/10^{-20}$ cm^2	$\Omega_6/10^{-20}$ cm^2	Reference
−0.37	5.36	0.54	[12]
0.84	4.79	9.13	[13]
0.94	6.54	3.84	[14]
1.60	5.06	4.79	[15]
2.5 ± 3.2	5.4 ± 1.8	6.0 ± 1.2	[16]
2.9 ± 1.4	6.4 ± 1.8	5.5 ± 0.7	[17]

to the hypersensitive transitions. Indeed, the intensities of these transitions show large variations with the ligand type. However, the discussion can go beyond the results obtained by the study of the hypersensitive transitions, although the range of the experimental values of the Ω_2 parameter (describing hypersensitivity) is much larger than the range of the experimental values of the parameters Ω_4 and Ω_6. It should be noted that a correlation between the intensity of the f–f transitions and the chemical nature of the lanthanide complex is more difficult to establish than a correlation between spectroscopic and structural properties for d-group transition metal complexes, because the f orbitals are much better shielded from the environment than the d orbitals. The compositional dependence of the Ω_λ intensity parameters has been studied extensively in vitreous matrices, because a glass offers the advantage of a large compositional space. An overview of these studies can be found in a recent review by Görller-Walrand and Binnemans [3]. Stokowski *et al* [4] already mentioned that although small compositional changes of a few per cent may significantly change the characteristic temperatures of the glass (the glass transition temperature, crystallization temperature and melting temperature) and other physical properties, these changes cause in general only small variations in the intensity parameters. These changes are often within the experimental uncertainties. In this letter we consider the sensitivity of the Judd–Ofelt intensity parameters towards compositional changes of lanthanide-doped glasses. In particular, we want to judge whether it makes sense to determine parameter sets for lots of glass samples with closely related compositions in order to investigate trends in these parameters.

The most complete compilation of Ω_λ intensity parameters found in the literature is that given by Görller-Walrand and Binnemans [3]. However, the majority of the papers cited in this work do not report the errors on the parameters. This is a pity, because the error on the parameters is in general large and can be up to 10–20%. The large errors involved in the determination of these parameters also explain why such large differences are found between the parameter sets obtained by different authors on the same glass matrix. The differences in the parameter sets are partially due to the fact that the values of the parameters depend on the transitions chosen for the fitting procedure (if the standard least-squares fitting procedure is chosen). As an example, we summarize in table 1 the intensity parameters for Pr^{3+} in the fluorozirconate glass ZBLAN. For Pr^{3+}-doped glasses, the spread of the parameter values is large, because of the problems of the Judd–Ofelt theory as regards describing the spectroscopic properties of the trivalent praseodymium ion well. Comparison between fits is only possible if the chi-squared method is used to determine the parameters [5].

Binnemans *et al* [6] give Judd–Ofelt parameters for Nd^{3+}-doped fluorophosphate glasses of the type $75NaPO_3$–$24AF$–$1NdF_3$ (A = Li, Na, K) and of the type $75NaPO_3$–$24AF_2$–$1NdF_3$ (A = Ca, Sr, Ba, Zn, Cd) (see table 2). If we compare the Judd–Ofelt parameters for the different Nd^{3+}-doped fluorophosphate glasses, no large variations are found. Moreover,

Table 2. Judd–Ofelt intensity parameters of neodymium-doped fluorophosphate glasses (taken from reference [6]).

Glass composition	$\Omega_2/10^{-20}$ cm^2	$\Omega_4/10^{-20}$ cm^2	$\Omega_6/10^{-20}$ cm^2
$75NaPO_3$–$24LiF$–$1NdF_3$	3.44 ± 0.36	4.14 ± 0.42	6.28 ± 0.32
$75NaPO_3$–$24NaF$–$1NdF_3$	3.19 ± 0.29	3.73 ± 0.34	5.55 ± 0.26
$75NaPO_3$–$24KF$–$1NdF_3$	3.61 ± 0.30	3.81 ± 0.35	5.83 ± 0.27
$75NaPO_3$–$24CaF_2$–$1NdF_3$	2.78 ± 0.31	4.16 ± 0.36	5.56 ± 0.24
$75NaPO_3$–$24SrF_2$–$1NdF_3$	2.39 ± 0.34	4.02 ± 0.40	6.10 ± 0.30
$75NaPO_3$–$24BaF_2$–$1NdF_3$	2.41 ± 0.28	3.27 ± 0.32	5.19 ± 0.25
$75NaPO_3$–$24ZnF_2$–$1NdF_3$	3.75 ± 0.40	4.05 ± 0.47	5.99 ± 0.36
$75NaPO_3$–$24CdF_2$–$1NdF_3$	3.19 ± 0.27	3.88 ± 0.31	5.73 ± 0.24
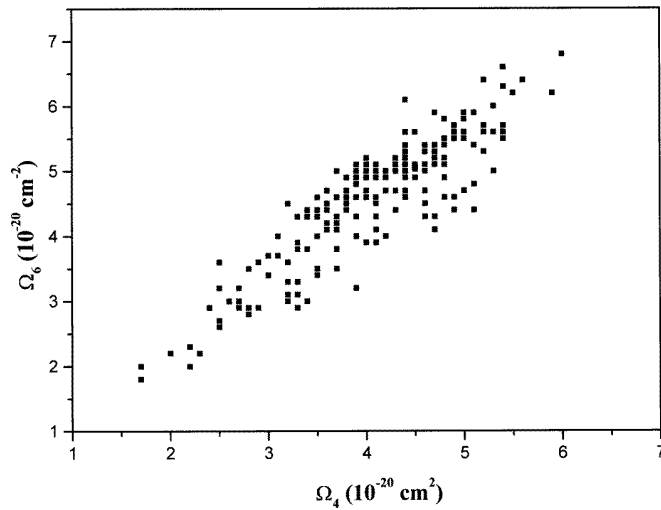
Figure 1. The correlation between the Ω_4 and the Ω_6 intensity parameters for Nd^{3+}-doped glasses (the data were taken from reference [4]).

if we take the errors on the parameters into account, it is acceptable to say that the Ω_4 and the Ω_6 parameters are the same for all of these fluorophosphate glasses. The choice of the cation (Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+} or Cd^{2+}) has virtually no influence on these parameters. Even the more sensitive Ω_2 parameter varies only relatively slightly.

We analysed statistically the Ω_λ parameters of Nd^{3+}-doped samples reported by Stokowski *et al* [4]. A total number of 211 glass samples were considered. A correlation analysis of the Ω_λ parameters reveals a strong positive linear relationship between the Ω_4 and Ω_6 parameters (see figure 1), i.e. glasses with large values for the Ω_4 parameter also have large values for the corresponding Ω_6 parameter. This is an indication that the Ω_4 and Ω_6 parameters are not independent. Empirically, we find the relationship: $\Omega_6 = 1.12\,\Omega_4$. Therefore, we may say that $\Omega_6 \simeq \Omega_4$. No good correlation was found between the Ω_2 parameter and the Ω_4 (or Ω_6) parameter, so the Ω_2 parameter and the Ω_4 parameter are to a large extent independent. Therefore, in a good approximation the intensities of the transitions of Nd^{3+} in glasses can be described by only two independent parameters Ω_2 and Ω_4. The values of Ω_2 (range: $(0.1–7) \times 10^{-20}$ cm^2) cover a comparable range to the values of Ω_4 (range: $(1.7–6.0) \times 10^{-20}$ cm^2). The Ω_2 is thus less host dependent than can be expected from its status as the parameter describing hypersensitivity. Compare this range for the Ω_2 parameters with the total range for Nd^{3+} ions—ranging between 0.082×10^{-20} cm^2 (in the $Lu_3ScGa_3O_{12}$:Nd^{3+} crystal [7]) and 275×10^{-20} cm^2 (in NdI_3 vapour [8]). The

Ω_4 parameter covers the range from 0.41×10^{-20} cm^2 (for the BaF$_2$:Nd^{3+} crystal [9]) to 11.9×10^{-20} cm^2 (for Nd(DBM)$_3\cdot$H$_2$O powder [10]), although an exceptionally high value, 16.38×10^{-20} cm^2, for Ω_4 has been reported for the 49Li$_2$CO$_3$–50H$_3$BO$_3$–1Nd$_2$O$_3$ glass [11]. It should be noticed that the rule $\Omega_4 \approx \Omega_6$ is only valid for Nd^{3+} ions in glasses; the rule is not valid for Nd^{3+}-containing coordination compounds.

The glasses can be divided into different classes according to their values of the Ω_λ parameter. For instance, the f–f transitions tend to have lower intensities in fluoride than in oxide. It is difficult to draw sharp boundaries between the different classes, because of the small spread of the parameter values.

In conclusion we may state that the Judd–Ofelt intensity parameters are *not* sensitive enough to reflect small variations in the composition of lanthanide-doped glasses. If the intensity parameters are determined for lanthanide ions in different glass samples with only small compositional changes, the intensity parameters often vary significantly. However, these variations are not always due to a difference in glass composition, but mostly to the large errors inherent for these parameters. Therefore, we strongly advise not only the reporting of parameter values, but also the reporting of the errors on these parameters. Only in this way will it be possible to see whether the parameter variations are statistically relevant or not. We do not want to ignore the importance of the Judd–Ofelt parameters in intensity studies. They are very suitable for predicting the radiative relaxation in lanthanide ions and the hypersensitive transitions can be used to study for instance the metal–ligand interaction in complexes. But we want to warn against the use of the Judd–Ofelt theory beyond its limits. Additionally, we showed that for Nd-doped glasses $\Omega_6 \simeq \Omega_4$.

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