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Optical transition intensities of trivalent lanthanide ions in zinc and lead metaphosphate glasses

Gianluigi Ingletto*
Istituto di Biochimica, Facoltá di Medicina Veterinaria, Universitá di Parma, via del Taglio, Cornocchio, 43100 Parma (Italy)

Marco Bettinelli, Lorenzo Di Sipio, Francesco Negrisolo
Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Universitá di Padova, via Loredan 4, 35131 Padua (Italy)

and Carla Aschieri
ICTR-CNR, Area della Ricerca di Padova, Corso Stati Uniti, 35020 Padua (Italy)

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Abstract

The Judd–Ofelt intensity parameters of the lanthanide ions Pr^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+} in $Zn(PO_3)_2$ and $Pb(PO_3)_2$ glasses were evaluated from the absorption spectra. With the exception of Pr^{3+}, the Ω_2 parameter is significantly lower in $Pb(PO_3)_2$ than in $Zn(PO_3)_2$, as previously found for the Nd^{3+} ion, due to a weaker mixing with the opposite parity configurations. The monotonic dependence of Ω_6 on the number of f electrons suggests that the mechanism responsible for the spectral intensities is mainly due to static distortions. The intensity parameters are in general higher than for other common oxide glasses.

Introduction

The optical properties of trivalent lanthanide ions in glasses can be remarkably influenced by the presence of a high concentration of Pb^{2+} ion in the random network. In particular, the intensities of the optical transitions are in some cases anomalously depressed. In a recent paper [1] we reported that the Judd–Ofelt intensity parameters Ω_2, Ω_4 and Ω_6 for Ho^{3+} ions in a glass of molar composition 38% PbO–62% SiO_2 appear to be the lowest found to date for this ion in oxide glasses. Weber *et al.* [2, 3] investigated the optical properties of metaphosphate $M(PO_3)_2$ glasses (M=Mg, Ca, Sr, Ba, Zn, Cd, Pb) doped with Nd^{3+}. Their results show that the $Pb(PO_3)_2$ glass exhibits the smallest values of the intensity parameters if compared to the other divalent-ion metaphosphate glasses, and in particular the Ω_2 parameter has the smallest value for any oxide glass. We recently reported and discussed the optical absorption and emission spectra of Eu^{3+} in Pb, Zn and Ba metaphosphate glasses [4].

It is interesting to extend these studies to the investigation of the optical properties of other trivalent lanthanide ions in $M(PO_3)_2$ glasses, in order to understand if the depression of the transition intensities in $Pb(PO_3)_2$ is a general phenomenon for all the Ln^{3+} ions. We concentrate our attention on the metaphosphate glasses because they are relatively easy to prepare and show several interesting chemical and physical properties, which make them attractive as hosts for luminescent ions.

In this communication we report on the optical transition intensities of the lanthanide ions Pr^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+} in the metaphosphate glasses $Pb(PO_3)_2$ and $Zn(PO_3)_2$. The Judd–Ofelt intensity parameters are derived for all the doping ions and their values in the two hosts are compared and discussed.

Experimental

The molar compositions of the glasses under investigation were $Pb(PO_3)_2$ 97.5%–$Ln(PO_3)_3$ 2.5% and $Zn(PO_3)_2$ 97.5%–$Ln(PO_3)_3$ 2.5%. The lead metaphosphate glass was prepared by mixing ap-

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*Author to whom correspondence should be addressed.

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propriate quantities of PbO and $(NH_4)_2HPO_4$ (both Carlo Erba RPE) and Ln_2O_3 (Riedel-De Haën reagent grade) in a ceramic crucible and melting the composition for 2 h at 900 °C. The zinc metaphosphate glass was prepared mixing appropriate quantities of ZnO (Carlo Erba RPE), $(NH_4)_2HPO_4$ and the lanthanide oxide in a sintered alumina crucible, and melting the composition for 2 h at 1250 °C. The glasses doped with Pr^{3+} were always prepared starting from Pr_6O_{11}. The melts were quenched onto a copper plate and annealed for 12 h at temperatures close to the softening point of the glasses. Samples were cut to a 0.3–1.0 cm thickness and carefully polished for the optical measurements.

Electronic absorption spectra were measured at 293 K in the ultraviolet, visible and near infrared regions using a Perkin-Elmer Lambda 15 and a Perkin-Elmer Lambda 9 recording spectrophotometers, with air in the reference beam and a spectral bandwidth of 1 nm.

Results and discussion

The 293 K absorption spectra of the Ln^{3+} doped lead metaphosphate and zinc metaphosphate glasses are composed of sets of inhomogeneously broadened f–f transitions and of a steeply rising edge at low wavelengths, starting at about 390 nm for the lead metaphosphate glasses and at about 350 nm for the zinc metaphosphate glasses.

The Judd–Ofelt intensity parameters Ω_2, Ω_4 and Ω_6 were calculated from the experimental oscillator strengths of the f–f absorption transitions after subtracting the magnetic dipole contributions [5], using a multiple least-squares fitting routine. The calculations made use of the reduced matrix elements published by Carnall *et al.* [6] and of the literature values of the refractive indices $n_D = 1.5400$ for the $Zn(PO_3)_2$ glass [2] and $n_D = 1.71$ for the $Pb(PO_3)_2$ glass [3].

The data relative to the band assignment, the experimental (P_{exp}) and calculated (P_{calc}) oscillator strengths, the root-mean square deviations of P_{exp} and P_{calc} are retained by the authors and are available on request. The intensity parameters Ω_2, Ω_4 and Ω_6 for the two glasses are reported in Tables 1 and 2.

The root-mean squares (r.m.s.) deviations in general correspond to 10–20% of the experimental average oscillator strengths, with some exceptions. In the case of Sm^{3+}, significant deviations have often been observed and this has been ascribed to the reduced matrix elements $U^{(\lambda)}$ [5], that have been calculated on the basis of not well defined or sometimes uncertain [7] energy levels. For the Sm^{3+} ion, moreover, the Ω_2 value is in practice undefined, because the $U^{(2)}$ matrix elements are not significantly different from zero for all the transitions.

TABLE 1. Judd–Ofelt parameters Ω_λ for Ln^{3+} ions in the $Zn(PO_3)_2$ glass

Ion	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)
Pr^{3+}	10.0 ± 3.4	2.0 ± 3.8	7.0 ± 1.1
Nd^{3+a}	5.1 ± 0.2	4.4 ± 0.3	4.7 ± 0.2
Sm^{3+}	5.7 ± 5.0	6.7 ± 1.4	2.0 ± 1.5
Eu^{3+b}	7.4 ± 1.6	2.3	1.3
Dy^{3+}	11.7 ± 0.3	1.3 ± 0.3	1.8 ± 0.3
Ho^{3+}	8.8 ± 0.3	2.3 ± 0.6	2.0 ± 0.8
Er^{3+}	9.9 ± 0.2	1.6 ± 0.3	1.8 ± 0.4
Tm^{3+}	5.5 ± 1.0	1.4 ± 0.5	0.8 ± 0.2

[a]Taken from ref. 2. [b]Taken from ref. 4.

TABLE 2. Judd–Ofelt parameters Ω_λ for Ln^{3+} ions in the $Pb(PO_3)_2$ glass

Ion	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)
Pr^{3+}	14.8 ± 3.2	9.7 ± 1.2	26.9 ± 1.2
Nd^{3+a}	2.6 ± 0.2	3.5 ± 0.3	4.3 ± 0.1
Sm^{3+}	1.7 ± 5.1	4.0 ± 1.2	2.2 ± 1.2
Eu^{3+b}	4.3 ± 0.5	3.1 ± 0.9	2.0
Dy^{3+}	9.8 ± 1.9	0.9 ± 1.9	4.4 ± 2.1
Ho^{3+}	7.9 ± 0.2	2.9 ± 0.4	2.2 ± 0.5
Er^{3+}	6.3 ± 0.2	2.0 ± 0.3	1.1 ± 0.3
Tm^{3+}	4.9 ± 2.7	0.3 ± 2.4	1.3 ± 0.6

[a]Taken from ref. 3. [b]Taken from ref. 4.

In the case of the spectrum of the Tm^{3+} ion in $Pb(PO_3)_2$, quite high differences between P_{exp} and P_{calc} are observed and attributed to the low number of bands available for the fit, because of the presence of the onset of the strong absorption of the matrix in the UV region that hides the lowest wavelength Tm^{3+} transitions.

For what concerns the Dy^{3+} ion in $Pb(PO_3)_2$, it is possible to note that the Ω_2 value is determined only from the ${}^6H_{13/2} \rightarrow {}^6H_{9/2} + {}^6F_{11/2}$ transition at 7800 cm^{-1}, but no transition in the visible region is characterized by a $U^{(2)}$ value different from zero. This fact implies a different mixing with the opposite-parity transitions for the low and high energy states and consequent difficulties in the application of the Judd–Ofelt theory.

It is well known that the Judd–Ofelt parametrization scheme does not apply to Pr^{3+} when the transitions ${}^3H_4 \rightarrow {}^3F_3 + {}^3F_4$ and ${}^3H_4 \rightarrow {}^3P_2$ [8] are fitted at the same time. In the case of the spectra of Pr^{3+} in $Zn(PO_3)_2$ and $Pb(PO_3)_2$, it has been possible to reproduce the experimental oscillator strengths, including in the fitting the ${}^3H_4 \rightarrow {}^3F_3 + {}^3F_4$ transition and neglecting the $^3H_4 \rightarrow {}^3P_2$ one, that lies at the highest energy and therefore can steal more intensity from transitions to the $4f^15d^1$ configuration.

We note that Ω_2 and Ω_4 depend in a random way on n, whereas Ω_6 decreases in a roughly monotonic way when n increases. The Ω_6 values for Nd^{3+} ($n = 3$) and Eu^{3+} ($n = 6$), which are included for completeness in the Tables, have been taken from Weber *et al.* [2, 3] and Capobianco *et al.* [4]. This observation suggests that the intensity mechanism is prevalently static, in agreement with the presence of distorted coordination sites for the Ln^{3+} ions. The behaviour of Ω_6 (owing to its dependence on the radial wavefunctions of the configurations involved in the mixing) is predicted to be monotonic with n, when the intensity mechanism is static, and to show a minimum in correspondence to Gd^{3+} or Eu^{3+} when the spectral intensity is due to a vibronic mechanism [8, 9]. Our conclusions agree with what was found for self-activated $Ln(PO_3)_3$ glasses [10].

A comparison of the intensity parameters for the two glass hosts shows that the values for Ω_2, which are especially sensitive to the environment, as they are mainly derived from the hypersensitive transitions, are consistently higher in $Zn(PO_3)_2$ than in $Pb(PO_3)_2$. This agrees with the results of Weber *et al.* [2, 3], who suggested that the high Pb^{2+} polarizability and the directional and covalent nature of the Pb–O bonding induce a weaker crystal field on the Nd^{3+} ion and, therefore, a reduced mixing with the opposite-parity electronic configurations that are responsible for the spectral intensities.

We also point out that in the emission spectra of Eu^{3+} in metaphosphate glasses [4], the intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, which is related to the Judd–Ofelt parameter Ω_2, decreases in the series $Zn(PO_3)_2 > Ba(PO_3)_2 > Pb(PO_3)_2$. This behaviour is explained taking into account that the larger modifier ion (Ba^{2+}, ionic radius 1.56 Å) causes a larger distance between the phosphate chains which constitute the random network of these glasses and therefore produces a weaker field around the lanthanide impurity than for $Zn(PO_3)_2$. In the case of the $Pb(PO_3)_2$ glass, the decrease in the intensity ratio with respect to $Ba(PO_3)_2$ cannot be accounted for by the ionic radii (Pb^{2+}, ionic radius 1.43 Å), but by the fact that Pb^{2+} is more strongly bound to the oxygen, which reduces the covalency of the Eu–O bond. Moreover, both the values of the crystal field parameter B_{20}, which is particularly sensitive to the electrostatic interactions, and of the average crystal field strength parameter S [11] are lower for Eu^{3+} in the lead than in the zinc and barium metaphosphate glasses [4], therefore confirming the suggestion by Weber *et al.* for the case of Nd^{3+} [3]. The present results show that these conclusions apply also to the other Ln^{3+} ions under investigation.

A remarkable exception is the Pr^{3+} ion, as all the Ω_λ parameters show a reversed trend, being distinctly higher in the $Pb(PO_3)_2$ matrix than in $Zn(PO_3)_2$. The parity allowed $4f \rightarrow 5d$ transitions are much lower for Pr^{3+} than for the other Ln^{3+} ions, so the $4f \rightarrow 4f$ transitions are strongly mixed with them. The higher values of Ω_λ for $Pb(PO_3)_2$ could be explained by a decrease in energy in this host of the lower states belonging to the $4f^15d^1$ configuration, due to a strong nephelauxetic effect or to a strong crystal field acting on the 5d orbitals.

Conclusions

From our experimental results it appears that the intensity of the transitions is due especially to the mixing of the states belonging to the $4f^n$ configuration with the opposite-parity states induced by a static crystal field in distorted sites. The comparison of the Ω_2 values for $Zn(PO_3)_2$ and $Pb(PO_3)_2$ (with the exception of the Pr^{3+} ion) confirm the presence, in the case of the $Pb(PO_3)_2$ matrix, of a smaller mixing with the opposite-parity configurations, due to the presence of the highly polarizable Pb^{2+} ions and the directionality of the Pb–O covalent bond.

The dependence of Ω_λ on the number of f electrons shows a prevailing static nature for the perturbation responsible for the band intensity, rather than a vibronic mechanism.

The evaluation of the Judd–Ofelt intensity parameters allows the prediction of radiative transition probabilities, lifetimes and branching ratios for emitting excited states and the estimation of important optical properties, such as the stimulated emission cross section for the laser transitions [12–14]. The fact that the intensity parameters Ω_λ for the luminescing Ln^{3+} ions are in general higher in these hosts than in other oxide glasses [15], together with the chemical stability and relatively easy preparation, due to the low melting temperature, could make these materials interesting in the field of optical devices, especially when doped with the IR emitting Er^{3+}, Ho^{3+} and Tm^{3+} ions.

Supplementary material

Copies of the tables containing the band assignments, the experimental and calculated oscillator strengths and their r.m.s. deviations were provided for the referees and are available from the authors.

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