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Spectroscopy and Nonradiative Phenomena of Rare Earths in Glasses: Future Applications

RENATA REISFELD*

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

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The radiative transition probabilities of rare earth ions in glasses can be calculated from the measured intensity parameters and calculated transition matrix elements using the Judd–Ofelt theory. The Judd–Ofelt parameters in oxide, fluoride and chalcogenide glasses were obtained for a variety of rare earth ions. These intensity parameters depend on the chemical bonding between the rare earths and the glass matrix and the viscosity of the medium. The non-radiative transition probabilities are calculated using a phenomenological theory, experimentally measured fluorescence lifetimes and quantum efficiencies. The nonradiative transition probabilities show an exponential dependence on the phonon energy of the network-forming material. Experimental results according to this theory show that Er(III) has the highest quantum efficiency in fluoride glasses. Technological implementation of the above theory will be discussed for glass lasers, sources for fiber waveguides and luminescent solar concentrators.

Introduction

The interest in spectroscopy of rare earths in the condensed phase is increasing continuously especially in connection with laser research [1, 2] and related applications. In oxide glasses there is an almost complete tabulation to date of radiative and non-radiative transition rates. In the newly developed fluoride and chalcogenide glasses the non-radiative losses are smaller than in oxide glasses because of the low multiphonon relaxation corresponding to the low phonon frequency of the glass constituents. Thus in recent years fluoride glasses, which are good candidates for fiber optic waveguides due to their high transparency in the ultraviolet, visible and infrared regions and chalcogenide glasses having good transparency in part of the visible and infrared, have been studied. The present paper summarizes our knowledge of these radiative and non-radiative processes in oxide and nonoxide glasses. Ideas are suggested on how these glasses can be used practically in luminescent solar concentrators [3] and in fiber optical communications [4], in addition to their conventional use as lasers.

Radiative Transitions

The radiative transition probabilities of the rare earths in glasses may be calculated using the Judd–Ofelt treatment. The radiative transition probabilities of the rare earths are composed mainly of the electric-dipole contribution and to a much lesser extent by the magnetic-dipole contribution [5].

The spontaneous emission rate is

$$A(aJ:bJ') = \frac{64\pi^4\nu^3}{3hc^3(2J+1)}\left[\frac{n(n^2+2)^2}{9}S_{ed} + n^3S_{md}\right] \tag{1}$$

where S_{md} is the magnetic dipole line strength.

$$S_{md}(aJ:bJ') = \frac{e^2\hbar^2}{4m^2c^2}|\langle f^N[\gamma SL]J\|\vec{L}+2\vec{S}\|f^N[\gamma'S'L']J'\rangle|^2 \tag{2}$$

$$S_{ed}(aJ:bJ') = e^2\sum_{\lambda=2,4,6}\Omega_\lambda|\langle f^N[\gamma SL]J\|U^{(\lambda)}\|f^N[\gamma'S'L']J'\rangle|^2 \tag{3}$$

The Ω_λ parameters are obtained from the absorption spectra. The matrix elements have been calculated from the reduced matrix elements of Nielson and Koster [6] and the 3j and 6j symbols [7] as described by Wybourne [8].

By using this method radiative transition probabilities were calculated for the following rare earths in a number of glasses: Pr(III) [9], Nd(III) [10], Sm(III) [11], Eu(III) [12, 13], Dy(III) [9], Ho(III) [14–16]. Er(III) [4, 17–19] and Tm(III) [16, 20].

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*Enrique Berman Professor of Solar Energy.

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TABLE I. Intensity Parameters of Nd(III) in Various Hosts in the Unit 10^{-20} cm^2.

Host materials	Ω_2	Ω_4	Ω_6
$3Al_2S_3 \cdot La_2S_3$	9.45	4.84	6.54
$3Ga_2S_3 \cdot La_2S_3$	6.65	4.39	4.67
YAG	0.20	2.70	5.00
Y_2O_3	8.55	5.25	2.89
$YAlO_3$	1.24	4.68	5.85
ED-2	3.30	4.70	5.20
Borate	4.10	3.40	4.30
Silicate	4.00	3.30	2.50
Phosphate	3.50	3.90	5.80
Germanate	5.80	3.30	2.90

TABLE II. Intensity Parameters of Ho(III) in Various Hosts in the Unit 10^{-20} cm^2.

Host materials	Ω_2	Ω_4	Ω_6
$3Al_2S_3 \cdot La_2S_3$	8.09	3.85	1.40
$3Ga_2S_3 \cdot La_2S_3$	2.31	2.81	1.08
Phosphate glass	5.60	2.70	1.87
Calibo glass	6.83	3.15	2.53
Tellurite glass	6.92	2.81	1.42
LaF_3	1.16	1.38	0.88

It was shown by Riseberg and Weber [21] and Reisfeld *et al.* [22] that the matrix elements of the majority of rare earth ions are only slightly dependent on the environment in which they are situated, the main factor responsible for the intensity of various transitions being the three parameters. The Ω_λ parameters for the various rare earths in oxide and non-oxide glasses were calculated in our laboratory. The radiative transition probabilities were obtained using these values [23]. The intensity parameters for Sm(III) are given in ref. [5], for Eu(III) reference 12, for Tm(III) reference 19, for Nd(III) in Table I, see also references 24 and 25 for Ho(III) in Table II and for Er(III) in Table III and reference 26. The induced emission cross section σ_p may be calculated from the radiative transition rates by the following equation as proposed by Krupke [27] for Nd(III)

$$\sigma_p \Delta\bar{\nu} \equiv \int \sigma(\bar{\nu}) d\bar{\nu} = \frac{\lambda_p^2}{8\pi c n^2} A[(^4F_{3/2}):(^4I_{11/2})] \qquad (4)$$

where $\lambda = 1/\bar{\nu}$; λ_p is the wavelength of the fluorescence peak (1.06 μ) and $\Delta\bar{\nu}$ is the effective fluorescence linewidth determined from integration of the fluorescence line shape.

As already mentioned, the positions of the spectra of the rare earth ions which are due to intraconfigurational f–f transitions in amorphous materials are only slightly dependent on the host; however, a small shift of the free-ion levels to lower energies, the nephelauxetic effect, can be observed as a result of covalency between the rare earths and the matrix. This is evident especially in chalcogenide glasses [16] as exemplified by the emission of $^4F_{3/2} \rightarrow {^4I_{11/2}}$ of Nd(III) which is shifted from 1.06 μ in Ed-2 glass to 1.077 μ in chalcogenide glass [28].

Non-radiative Transitions

The multiphonon relaxation between the electronic levels of rare earths in glasses may be adequately described by a single frequency model in a weak coupling scheme by [29]

$$W_{NR} = \beta \exp(-\alpha\Delta E)[n(\omega,T) + 1]^p \ldots . \qquad (5)$$

TABLE III. Ω_t Parameters for Erbium(III) in Different Environments [26] in the Unit 10^{-20} cm^2.

System	Ω_2	Ω_4	Ω_6
$46PbF_2-22ZnF_2-30GaF_3-2LaF_3$ glass	1.54	1.13	1.19
Er(III) hydrated ion solution	1.59	1.95	1.90
$Y_{0.5}Zr_{0.5}O_{1.75}$ fluorite-type crystal	2.92	0.78	0.57
$ErCl_3 \cdot 6H_2O$ in CH_3OH	3.2	3.2	0.8
$2ErF_3-57ZrF_4-34BaF_2-4AlF_3-3LaF_3$ glass	3.26	1.85	1.14
$3Al_2S_3-La_2S_3$ glass	3.74	4.33	0.90
Y_2O_3 C-type crystal	4.59	1.21	0.48
$NaPO_3$ glass	9.9	4.3	7
Borate glass	11.3	3.6	2.2
Molten $LiNO_3$ + KNO_3	15.8	1.8	1.4
$ErCl_3(AlCl_3)_x$ vapour	25.8	2.7	2.0

TABLE IV. Parameters of Nonradiative Relaxations [29].

The host	β sec^{-1}	α cm	$\hbar\omega$ cm^{-1}	ϵ
GLS, ALS	1×10^6	2.9×10^{-3}	350	0.36
Tellurite	6.3×10^{10}	4.7×10^{-3}	700	0.037
Germanate	3.4×10^{10}	4.9×10^{-3}	900	0.013
Phosphate	5.4×10^{12}	4.7×10^{-3}	1200	0.0037
Borate	2.9×10^{12}	3.8×10^{-3}	1400	0.0049
BeF_2	9×10^{11}	6.3×10^{-3}	500	0.042
$LaCl_3$	1.5×10^{10}	13.0×10^{-3}	260	0.037
$LaBr_3$	1.2×10^{10}	19.0×10^{10}	175	0.037
LaF_3	6.6×10^8	5.6×10^{-3}	350	0.14
Y_2O_3	2.7×10^8	3.8×10^{-3}	550	0.12
SrF_2	3.1×10^8	4.0×10^{-3}	360	0.20
$Y_3Al_5O_{12}$	9.7×10^7	3.1×10^{-3}	700	0.045
$YAlO_3$	5×10^9	4.6×10^{-3}	600	0.063
LiYF	3.5×10^7	3.8×10^{-3}	–	–

where β and α are constants characteristic of a given glass, ΔE is the energy gap to the next lower level, ω is the stretching frequency of the glass-forming units and $p = \Delta E/\hbar\omega$ is the number of phonons which must be emitted in order to conserve energy in the transition. α is connected with the electron phonon coupling constant ϵ

$$\alpha = -\ln(\epsilon)/\hbar\omega \tag{6}$$

Parameters for non-radiative relaxation of rare earths in glasses are given in Table IV.

In general the non-radiative relaxation of rare earths follows an exponential dependence on the energy gap [29, 30] when the number of phonons is more than two.

Application of the multiphonon theory in glasses requires the knowledge of the structural units forming the glass. Similar to the electronic spectra in glasses the vibrational frequencies show inhomogeneous broadening, due to the variation of sites. Table IV shows the average frequencies of the network formers. The vibrations involving the network formers are lower by a factor of 2 to 4. The lack of symmetry in a glass and the molecular character of high-energy vibration were taken into account [29] in developing the theory of multiphonon relaxation in glass by using higher-order terms in the perturbation theory.

The multiphonon decay rate from a given level to the next lower level decreases with the lowering of energy of the stretching frequencies of the glass former. Since a large number of phonons is needed in fluoride glasses and more so in chalcogenide glasses in order to reach the same energy gap the non-radiative relaxations are smallest in these hosts.

Non-oxide Glasses

The non-radiative relaxations in chalcogenide and fluoride glasses have motivated preparation and optical studies of these glasses in recent years in view of their potential in luminescent materials having high quantum efficiencies. These glasses have also low absorption in the infrared part of the spectrum because of the high order multiphonon absorption in this region and lower than for the oxide glasses.

Rare earth sulfides form glasses with Ga_2S_3 and Al_2S_3 if appropriate conditions are observed. Such glasses were prepared by Flahaut and his group who have studied in detail the phase diagrams of these materials [31]. The glass of composition $3Al_2S_3{:}La_2S_3$ (ALS) is transparent from 1500 cm^{-1} to 25000 cm^{-1} and the glass of composition $3Ga_2S_3{:}La_2S_3$ (GLS) from 1500 cm^{-1} to 20000 cm^{-1} and may play an important role in fiber optical waveguides.

Laser emission cross-sections of the 1077 nm and 1370 nm emissions of Nd(III) in $3Ga_2S_3{:}0.85\,La_2S_3{:}0.15Nd_2S_3$ (GLS) and $3Al_2S_3{:}0.872\ La_2S_3{:}0.128\ Nd_2S_3$ (ALS) were obtained from the calculated matrix elements in the glasses, experimentally measured intensity parameters, emission half-widths and lifetimes. The laser threshold power for side-pumping in the chalcogenide glasses is much lower than for ED-2 glass.

The peak cross-section of Nd(III) in GLS is 7.95×10^{20} cm^2 at 1077 nm and 3.60×10^{-20} cm^2 at 1320 nm; 8.20×10^{-20} cm^2 at 1077 nm and 4.10×10^{-20} cm^2 at 1370 nm in ALS, as compared to 2.90×10^{-20} cm^2 at 1060 nm and 0.72×10^{-20} cm^2 at 1300 nm for ED-2 glass [32].

A new family of fluoride glasses was obtained in 1975 by Poulain *et al.* [33]. They are called fluorozirconate glasses containing large amounts (above 50 mole %) of ZrF_4 (which can be replaced by HfF_4 or ThF_4) along with lesser amounts of alkaline-earth, rare earth or uranium(IV) fluorides. Miranday *et al.* [34, 35] prepared another type of new fluoride glass based on PbF_2 and 3d-group fluorides.

The spectroscopic and fluorescent properties of Nd(III)-containing fluorozirconate glasses have been reported by Weber in work with the Lucas–Poulain group [36].

Possible Technological Applications

In addition to the wide use of rare earths, especially Nd(III) in laser glasses, two other potential applications are light sources for fiber optics and luminescent solar concentrators.

Since the undoped materials are excellent candidates for fiber optic waveguides due to their high transmittance in the infrared and their chemical stability, it is suggested that erbium-doped materials having the desired laser emission wavelengths, which can be selected from Table V ref. [4], be used as light sources for fiber optic systems. They could be integrated into one waveguide providing integrated fiber optic systems.

Luminescent Solar Concentrators

A different practical use of rare earths in combination with other ions can be found in luminescent solar concentrators LSC. The performance of such devices has been described in refs. [3] and [32].

The first attempt to use neodymium for solar collectors was made by Levitt and Weber [37] who measured devices consisting of Owen-Illinois ED-2 neodymium-doped laser glass. The efficiency of this glass for solar collection is rather low because of the low absorption of Nd(III) in this glass. This problem can be circumvented by incorporating Nd(III) into tellurite glasses. Calculated plate efficiencies of Nd(III) in tellurite glasses based on optical measurements of the absorption and emission spectra and the quantum efficiency of Nd(III) in these glasses are 12%, 3 times higher than in conventional silicate glasses [38, 39].

Reisfeld and Kalisky [4] have shown that a combination of UO_2^{2+} with Nd(III) or Ho(III) in glasses extends the spectral sensitivity range of LSCs as a result of the efficient energy transfer from the 20500 cm^{-1} excited level of the uranyl ion. Both energy transfer and direct excitation to the Nd(III) levels provide the well-known laser transition [1] $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1060 nm), with a branching ratio around 0.5, as well as the transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (880 nm) to the ground state. The latter transition is resonant and repopulates the $^4F_{3/2}$ level, and thus little energy is lost by reabsorption. Both transitions lie in the spectral range in which the silicon solar cells have high spectral sensitivity.

A different method of sensitizing Nd(III) and Yb(III) emissions by the Cr(III) ion has been described recently [41–43]. The absorption spectrum of Cr(III) in glasses (and crystals) consists of two broad bands covering most of the solar spectrum with peaks at 450 nm ($^4A_2 \rightarrow {}^4T_1$) and at 650 nm ($^4A_2 \rightarrow {}^4T_2$).

Glasses provide low field Cr(III) sites in which the zero-phonon $^4T_2$ level lies below the zero-phonon ^2E state. In these low field cases the room temperature Cr(III) emission from $^4T_2$ consists of a broad unstructured band centred in the near IR. Quantum yields for luminescence are low in glass hosts; for example the highest quantum yield of Cr(III) found to date in a silicate glass is 11–17% [44].

The best efficiencies of 23% for $^4T_2 \rightarrow {}^4A_2$ are obtained for lithium lanthanum phosphate (LLP) glasses [43]. The explanation for the non-radiative transitions of Cr(III) in glasses is still being investigated. The theory of multiphonon relaxation which holds for rare earth ions cannot be applied to Cr(III).

Our present studies [43, 45] show that the probability of energy transfer from Cr(III) to Nd(III) in LLP may be higher than that of the non-radiative transfer within the Cr(III) system. This is probably the reason for the good laser performance of such glasses, as reported recently by Härig et al. [46]. The integrated lifetime at room temperature is 24.6 μs, indicative of the proximity of $^4T_2$ and ^2E states in the LLP glass [47].

Cold Glasses

The glasses so far discussed were prepared by melting the rare earth oxides, sulfides or fluorides with the glass ingredients. Quite recently we have proposed doping glasses with rare earths by the adsorption of the hydrated or complexed rare earth ions on porous glasses at room temperature.

The relative intensities of fluorescence of the various rare earth ions adsorbed on Vycor porous glass or fumed silica from aqueous solutions are [48]

$$Tb > Eu > Dy > Tm > Pr > Ho > Er$$

By following the behavior of the hypersensitive transitions of Eu(III) in these glasses an indication of a chemical bond between Eu(III) and the glass was found.

A different approach of introducing rare earth ions into vitreous solidified gel glasses [49] also enables the use of rare earth complexes in glasses without destroying the organic ligand [50].

Site-Selectivity of Rare Earths in Glasses

The dopant ions in glasses reside in a variety of environments and experience different perturbing local fields. Thus instead of identical electronic energy levels, there is a distribution of spectroscopic parameters which depend on the host glass composition resulting in different radiative and non-radiative transition probabilities. These variations are evident in absorption and fluorescence spectra as inhomogeneously broadened lines when conventional light sources are used. The decay times of fluorescence from excited states of different sites normally exhibit a non-exponential behavior unless fast diffusion of energy between the different sites equilibrates between the various sites, as evidenced by a simple exponential decay.

Laser-induced fluorescence line narrowing (FLN) enables in some cases the excitation of a subset of ions having the same energies. In the absence of accidental coincidence of electronic levels, a tunable pulsed laser can be used for determining the electronic levels and transition probabilities of a selected subset of the total ensemble of sizes. The intraconfigurational 4f–4f transitions of rare earth ions are especially suitable in this type of investigation because of small electron phonon coupling. The degree of selectivity of the FLN technique depends on the ratio of homogeneous to inhomogeneous widths [51], which is of the order of 10^{-3} for rare earths at low temperatures.

Site-selective spectroscopy is especially suitable for Eu(III) in which the $^5D_0 \rightarrow {}^5F_0$ transition is between non-degenerate levels and the number of lines obtained correspond to the different sites in which Eu(III) is situated.

The difference between glasses and crystals can be observed in selectively exciting the crystalline or glassy phase of Eu(III) in phosphotungstate vitreous ceramics [52].

In conclusion, the theoretically-obtained spectroscopical data of rare earths in vitreous media can be valuable in the designing of new materials in fields such as lasers, fiber optics and luminescent solar concentrators.

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