Spectroscopic investigations of Nd^{3+} ion in lead acetate glass

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MS received 4 January 1995; revised 27 December 1995

Abstract. Using the optical absorption spectra and the Judd–Ofelt theory, intensity parameters (Ω_λ) are calculated. Radiative lifetimes (T_R), branching ratios (β) and integrated absorption cross sections (Σ) are reported for certain excited levels of Nd^{3+} ion in lead acetate glass.

Keywords. Lead acetate glass; intensity parameters; radiative lifetimes; branching ratios; absorption spectra.

1. Introduction

The optical properties of Nd^{3+} ion in ZnF_2 based glasses were reported by Cases *et al* (1991). Cases and Chamarro (1991) reported the Judd–Ofelt analysis and multiphonon relaxation of rare-earth ions in fluorohafnate glasses. The radiative and non-radiative properties of silicate and phosphate glasses doped with neodymium have been reported by Izumitani *et al* (1982). Amaranath and Buddhudu (1991) reported certain luminescence properties of Nd^{3+} in mixed alkali fluoride glasses. Previously we have reported the electronic spectra of triply ionized neodymium ion in certain sulphate glasses (Lakshman and Ratnakaram 1988a). As a continuation of these studies, we report certain new results on Nd^{3+} doped lead acetate glass. The Judd–Ofelt theory (Judd 1962; Ofelt 1962) has been applied to study the transition probabilities of dopant rare-earth ion in the glass matrix. A brief summary of these physical and absorption properties and lifetime measurements of Nd^{3+} doped lead acetate glass is reported.

2. Experimental

Lead acetate of analar grade (BDH) was heated in a small pyrex vessel up to 340°C and dehydrated till it lost approximately one molecule of water per formula weight. Then a small quantity of the hydrocarbon was dissolved in the (0.1% by weight) lead acetate and the molten mass was kept at a temperature of 300°C for about 30 min and quickly pressed between the two brass disks spaced about 0.5 mm apart. The sample which was uniformly transparent was selected for optical studies. Rare-earth (Nd^{3+}) doped glasses were prepared by adding 0.1 mole% of Nd^{3+} ion in these glasses. An undoped lead acetate glass was used as a reference sample.

Absorption spectra of Nd^{3+} doped lead acetate glass were recorded at room temperature in the region of UV–VIS on Perkin–Elmer 551 spectrophotometer (figure 1). The wavelengths of bands were converted to vacuum wave numbers by employing NBS Wavenumber Tables (Coleman *et al* 1960).

The glass density was measured by employing Archimedes principle with xylene as the immersion liquid. The refractive index of the glass was determined on an Abbe refractometer with a sodium lamp.

Figure 1. Absorption spectrum of Nd^{3+} in lead acetate glass.

3. Results and discussion

The energy, E_J , of the J^{th} level may be written in Taylor's series (Wong 1961) expansion as

$$E_J = E_{0J} + \sum_{K=1}^3 \frac{dE_J}{dE^K} \Delta E^K + \frac{dE_J}{d\xi} \Delta \xi + \frac{dE_J}{d\alpha} \Delta \alpha + \dots,$$

where E_{0J} is the zero order energy of the J^{th} level and dE_J/dE^K , $dE_J/d\xi$ and $dE_J/d\alpha$ are partial derivatives. Using experimental energy levels for E_J and the numerical values of zero order energies and partial derivatives, a number of linear equations equal to the number of observed levels were formed and the delta values were calculated by using the least squares fitting method. The E^K , ξ_{4f} and α parameters were evaluated from

$$E^K = E_0^K + \Delta E^K,$$

$$\xi = \xi^0 + \Delta \xi,$$

and

$$\alpha = \alpha^0 + \Delta \alpha,$$

where E_0^K , ξ^0 and α^0 are the aquo ion parameters (Carnall 1979) with which the partial derivatives were evaluated. The Racah (E^1 , E^2 , E^3), spin-orbit (ξ_{4f}) and configuration interaction (α) parameters obtained for Nd^{3+} ion in lead acetate glass have been

Table 1. Experimental and calculated energies and oscillator strengths of Nd^{3+} doped lead acetate glass along with Racah (E^k), spin-orbit (ζ_{4f}), configuration interaction (α) and intensity (Ω_λ) (cm^2) parameters.

$S' L' J'$	E_{exp} (cm^{-1})	E_{cal} (cm^{-1})	$f_{\text{exp}} \times 10^6$	$f_{\text{cal}} \times 10^6$	Parameters
$^4F_{3/2}$	11544	11397	2.836	5.219	$E^1 = 3797.5 \text{ cm}^{-1}$
$^4F_{5/2} + ^2H_{9/2}$	12528	12650	15.291	14.240	$E^2 = 12.68 \text{ cm}^{-1}$
$^4F_{7/2} + ^4S_{3/2}$	13510	13673	18.425	19.236	$E^3 = 487.3 \text{ cm}^{-1}$
$^4F_{9/2}$	14788	14644	3.782	4.456	$\zeta_{4f} = 897.8 \text{ cm}^{-1}$
$^2H_{11/2}$	16047	—	0.931	—	$\alpha = -7.56 \text{ cm}^{-1}$
$^4G_{5/2}$	17236	17244	41.082	41.340	$T_2(\text{Cm}) = 2.144 \times 10^{-9}$
$^4G_{7/2}$	19006	18946	16.110	14.278	$T_4(\text{Cm}) = 0.954 \times 10^{-9}$
$^4G_{9/2}$	19487	19524	14.007	1.409	$T_6(\text{Cm}) = 2.334 \times 10^{-9}$
$^2G_{9/2} + ^2K_{15/2}$	20915	—	1.135	—	$\Omega_2 = 14.749 \times 10^{-20}$
$2D_{3/2} + 4G_{11/2}$	21733	—	1.785	—	$\Omega_4 = 6.562 \times 10^{-20}$
RMS deviation:		± 210		± 7.528	$\Omega_6 = 16.056 \times 10^{-20}$ $n = 1.502$

presented in table 1. The experimental and calculated energy positions and root mean square deviation of Nd^{3+} ion in lead acetate glass are presented in table 1. The experimental energy values of the transitions $^4I_{9/2} \rightarrow ^2H_{11/2}$, $^4I_{9/2} \rightarrow ^2G_{9/2} + ^2K_{15/2}$ and $^4I_{9/2} \rightarrow ^2D_{3/2} + ^4G_{11/2}$, are not included in the above least squares fitting because of their uncertainty in the energy measurement.

The intensities of the spectral lines are measured in terms of oscillator strengths using the following equation (Carnall 1979)

$$f_{\text{meas}} = 4.32 \times 10^{-9} \int \varepsilon(\nu) d\nu,$$

where $\varepsilon(\nu)$ is the molar extinction coefficient at the wavenumber $\nu (\text{cm}^{-1})$. According to Judd–Ofelt theory the oscillator strength of a band is theoretically estimated by the formula

$$f_{\text{cal}} = [T_2 \|U^2\|^2 + T_4 \|U^4\|^2 + T_6 \|U^6\|^2] \nu,$$

where T_2 , T_4 and T_6 are the Judd–Ofelt intensity parameters and $\|U^2\|^2$, $\|U^4\|^2$ and $\|U^6\|^2$ are the squares of the unit tensor operators. As these squared reduced matrix elements $\|U^\lambda\|^2$ are very insensitive to the environment, we have taken the $\|U^\lambda\|^2$ elements given by Ratnakaram (1987) for sulphate glass.

Substituting f_{meas} for f_{cal} and using $\|U^\lambda\|^2$ and the wavenumbers ν of the respective bands, the Judd–Ofelt parameters T_2 , T_4 and T_6 are derived by the least squares method. The experimental and calculated oscillator strengths for Nd^{3+} ion in lead acetate glass are given in table 1. Here too, we have not included the intensities of the bands $^2H_{11/2}$, $^2G_{9/2} + ^2K_{15/2}$ and $^2D_{3/2} + ^4G_{11/2}$ in the above fitting procedure. As the two bands $^4F_{5/2}$, $^2H_{9/2}$ and $^4F_{7/2}$, $^4S_{3/2}$ are overlapped, the respective $\|U^\lambda\|^2$ values are combined for these two bands, and they have been used in the T_2 , T_4 and T_6 measurements (Krupke 1966).

Using these T_2 , T_4 , and T_6 parameters, Ω_2 , Ω_4 and Ω_6 parameters are determined using the formula

$$\Omega_\lambda = \frac{3h}{8\pi^2 mc} \frac{9n}{(n^2 + 2)^2} (2J + 1) T_\lambda,$$

where n is the refractive index of the glass, $(2J + 1)$ the degeneracy of the ground state of the ion and the other symbols have their usual meaning. The T_λ and Ω_λ parameters obtained for Nd^{3+} ion in lead acetate glass are presented in table 1. Generally the Ω_2 parameter depends on surrounding environment and Ω_6 depends on vibrational modes.

From these intensity parameters (Ω_λ) the radiative properties of the excited levels ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$, ${}^4I_{13/2}$, ${}^4I_{11/2}$ and ${}^4I_{9/2}$ have been determined. The radiative transition probabilities of certain excited levels ${}^4G_{9/2}$, ${}^4G_{7/2}$, ${}^4G_{5/2}$, ${}^2H_{11/2}$, ${}^4F_{9/2}$, ${}^4F_{5/2}$ and ${}^4F_{3/2}$ are obtained from the following equations (Lakshman and Ratnakaram 1988b)

$$A = \frac{64\pi^4 \nu^3}{3h(2J + 1)} \left[\frac{n(n^2 + 2)^2}{9} \cdot S_{\text{ed}} + n^3 S_{\text{md}} \right],$$

where S_{ed} is the electric dipole linestrength,

$$S_{\text{ed}} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \|U^\lambda\|^2,$$

and S_{md} is the magnetic dipole linestrength,

$$S_{\text{md}} = \frac{e^2 h^2}{16\pi^2 m^2 c^2} (\psi J \| L + 2S \| \psi' J')^2.$$

The branching ratio (β) is obtained from the relation

$$\beta\% = \frac{A}{A_T} \times 100.$$

The radiative lifetime of the excited states is obtained from

$$\tau_R = A_T^{-1}.$$

Integrated absorption cross-sections (Σ) are measured using the relation (Lakshman and Ratnakaram 1988b)

$$\Sigma = \frac{1}{\nu^2} \cdot \frac{A}{8\pi c n^2}.$$

Table 2 gives the average energy (ν), electric dipole linestrengths (S_{ed}), magnetic dipole linestrengths (S_{md}), radiative transition probabilities (A), branching ratios (β) and integrated absorption cross-sections (Σ) for the excited levels ${}^4F_{9/2}$, ${}^4F_{5/2}$ and ${}^4F_{3/2}$ of Nd^{3+} ion in lead acetate glass.

It has been computed that the radiative lifetimes for excited levels ${}^4G_{9/2}$, ${}^4G_{7/2}$, ${}^4G_{5/2}$, ${}^2H_{11/2}$, ${}^4F_{9/2}$, ${}^4F_{5/2}$ and ${}^4F_{3/2}$ are 90, 32, 27, 4975, 129, 113 and 163 (all values are in $\mu\text{-sec}$) respectively.

Table 2. Electric dipole line strengths (S_{ed}), magnetic dipole line strengths (S_{md}), radiative transition probabilities (A), branching ratios (β) and integrated absorption cross-sections (Σ) for Nd^{3+} ion in lead acetate glass.

Transition	Wave number (cm^{-1})	S_{ed}/e^2 $\times 10^{22}$	S_{md}/e^2 $\times 10^{22}$	$A(\text{s}^{-1})$	β	$\Sigma(10^{-18})$ (cm^{-1})
${}^4F_{9/2} \rightarrow {}^4I_{7/2}$	971	175.3	28.43	0.4	0	0.26
${}^4S_{3/2}$	1177	4.1	0	0	0	0.01
${}^4F_{5/2}$	1994	163.1	0	2.8	0	0.42
${}^2H_{9/2}$	3160	312.8	15.88	22.7	0.003	1.34
${}^4F_{3/2}$	3247	178.5	0	13.3	0.002	0.74
${}^4I_{15/2}$	8575	1097.3	0	1511.3	0.19	12.08
${}^4I_{13/2}$	10750	979.5	0	2657.9	0.34	13.52
${}^4I_{11/2}$	12696	639.5	0.15	2859.3	0.37	10.42
${}^4I_{9/2}$	14644	99.7	0.09	684.5	0.09	1.87
${}^4F_{5/2} \rightarrow {}^2H_{9/2}$	1166	30.4	0	0.17	0	0.07
${}^4F_{3/2}$	1253	106.7	33.68	1.03	0	0.38
${}^4I_{15/2}$	6581	371.8	0	385.78	0.04	5.23
${}^4I_{13/2}$	8756	758.5	0	1853.70	0.21	14.21
${}^4I_{11/2}$	10702	168.0	0	749.66	0.08	3.84
${}^4I_{9/2}$	12650	792.2	0	5838.00	0.66	21.44
${}^4F_{3/2} \rightarrow {}^4I_{15/2}$	5328	51.8	0	42.78	0.007	0.88
${}^4I_{13/2}$	7503	319.3	0	736.50	0.12	7.69
${}^4I_{11/2}$	9449	761.4	0	3507.75	0.57	23.09
${}^4I_{9/2}$	11397	228.8	0	1849.65	0.30	8.37

Table 3. Comparison of certain radiative properties of Nd^{3+} ion in lead acetate glass with other glasses.

	Phosphate ^a	Borate ^a	Germanate ^a	Tellurite ^a	Lead acetate (Present work)
${}^A\text{Total} ({}^4F_{3/2})\text{sec}^{-1}$	2888	2386	2299	4193	6136
$\beta({}^4F_{3/2}; {}^4I_{9/2})$	0.43	0.42	0.46	0.45	0.30
$\beta({}^4F_{3/2}; {}^4I_{11/2})$	0.48	0.49	0.45	0.46	0.57
$\beta({}^4F_{3/2}; {}^4I_{13/2})$	0.09	0.09	0.08	0.08	0.12
$\beta({}^4F_{3/2}; {}^4I_{15/2})$	0.005	0.005	0.004	0.004	0.007
$\tau \text{ rad} ({}^4F_{3/2})\mu\text{sec}$	346	419	435	239	163

^aReisfeld and Jorgensen (1977)

Table 3 gives the comparison of radiative properties of Nd^{3+} ion in lead acetate glass with some other glasses. From the table it is observed that ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is having larger branching ratio than the other glasses, therefore it can be used as laser transition.

4. Conclusions

The spectral intensities of all the bands of Nd^{3+} ion in lead acetate are very high. From tables 2 and 3 it is observed that the branching ratios for the excited levels which starts

from ${}^4F_{3/2}$ are very high in lead acetate glass when compared with other glasses. Among all these transitions ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ has highest branching ratio. On the basis of above results, we conclude that lead acetate glass has highest optical efficiency.

Acknowledgements

The author thanks Prof. N Prabhakar Rao, Prof. V Padmanabha Sarma and Prof. J Lakshmana Rao in the execution of the above work.

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