Spectral properties of Nd^{3+} ion in new fluorophosphates glasses: Judd-Ofelt intensity parameters

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ABSTRACT

Judd-Ofelt parameters for Nd^{3+} ions in a new series of (Mg, Ba)F_2-based fluorophosphate glass (the MBBA system) are determined from the intensities of the integrated absorption bands of the Nd^{3+} ion in the MBBA system. The intensity parameters, Ω_2, Ω_6, and Ω_4 for f-f transitions of Nd^{3+} ions are found to be -1.02, 10.82, and 4.27 (x10^{20} cm^2), and 1.19, 3.95 and 3.11 in the MBBA/NdI and MBBA/NdII systems, respectively. The measured lifetime τ_f is 168 μs for the MBBA/NdI system, while the Judd-Ofelt analysis expects a radiative transition lifetime A_{rad} for $^4F_{3/2}$ to be 316 μs, resulting in a fluorescence quantum efficiency of 47%. The results are compared with those reported in the literature for other fluorophosphate glasses and show that $^4F_{3/2}$ to $^4I_{11/2}$ transition has the most potential for laser application with a peak fluorescence at 1056nm.

Keyword: *Judd-Ofelt parameters, Oscillator strength, Fluorophosphates glasses, Quantum efficiency*

1. INTRODUCTION

A new series of (Mg, Ba)F_2-based fluorophosphate glass (the MBBA system) doped with Nd^{3+} has been introduced for lasers and optical amplifier applications in the broadband UV to IR spectral range. The absorption spectra at room temperature in the spectral range 400-950 nm are obtained. The experimental oscillator strengths are determined from the areas under the absorption bands. Using the standard Judd-Ofelt theory [1, 2], intensity parameters Ω_t (t=2,4,6) for f-f transitions of Nd^{3+} ions are determined as well as radiative transition probabilities, branching ratios for each band. The

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lifetime is also measured. The results are compared with those of other glasses described in the literature.

2. EXPERIMENTAL ARRANGEMENT

2.1 Glass synthesis

Starting materials for the glass system are obtained in reagent-grade quality (City Chemicals). The dopant material Nd_2O_3 (Spectrum Materials) has purity better than 99.99 %. The ingredients of the glasses were weighed with 0.001 % accuracy and mixed thoroughly. These raw materials were melted in a vitreous carbon crucible in an Ar-atmosphere at 1200-1250°C. Two glass systems have been prepared, named MBBA/NdI (Nd^{3+} ion concentration $2.50 \times 10^{+20}$ cm^{-3}) and MBBA/NdII (Nd^{3+} ion concentration $6.26 \times 10^{+20}$ cm^{-3}). The samples were annealed at 50-100°C below the transition temperature to remove internal stress. The samples were examined with a polariscope (Rudolph Instruments) to assure that all residual stress is removed. Samples for optical and spectroscopic measurements were cut to dimensions 15 x 10 x 2 mm^3 and polished.

2.2 Optical and spectroscopic measurements

The refractive index of the samples was measured using an Abbe refractometer (ATAGO). The absorption spectra were recorded at room temperature in the range of 400-1700 nm with a Perkin-Elmer photo spectrometer (Lambda 900). The resolution is set to 1 nm. Emission spectra are obtained by exciting the samples with 808 nm radiation from a 1W CW Laser Diode (Coherent). The fluorescence radiation is then recorded over the range 850-1400 nm using a monochromator (Acton SpectraPro 300) and a Ge-photodiode (Thorlabs). The laser radiation incident to the sample is passed through an optical chopper (Stanford Research) enabling the use of a lock-in amplifier (Ametek 5105) to recover and amplify the electronic signal from the detector. The lifetime of the excited state is determined with a Q-switched Nd:YAG laser pumping an OPO (Continuum Surelite) tuned to 808 nm (idler). The duration of the pulses is 5 ns. The fluorescent radiation is detected using a Si pin photodiode (Thorlabs) and an interference filter (Edmund Scientific). The signal is recorded with a fast oscilloscope (LeCroy 9350) and fitted to an exponential.

3. RESULTS AND DISCUSSION

3.1 Absorption properties and Judd-Ofelt parameters

Fig. 1 shows the optical absorption spectra of Nd^{3+} ions in (Mg, Ba)F_2-based fluorophosphates in the 400-950nm range. An identified band in absorption spectrum corresponds to the transitions from $^4I_{9/2}$ state to various excited state. The peak positions were taken to be the barometers of the absorption bands. The eight major band energies in the MBBA/NdI and MBBA/NdII systems are determined from the absorption measurements. The absorption coefficient and mean wavelength can be used to predict the radiative transition probabilities, the branching ration and the radiative lifetime of the transitions from $^4F_{3/2}$ state to $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ states using the Judd-Ofelt theory. When Nd^{3+} concentration increases, the absorption peaks of Nd^{3+} ions in (Mg, Ba)F_2-based fluorophosphates remain similar in their spectral features, showing little difference in peak width and relative intensity. The wavelength of the absorption peaks does not shift with respect to Nd^{3+} ion concentration [3]. The measured oscillator strengths f_{med} at each absorption wavelength can be calculated from the integrated optical absorption spectra through the following expression:

$$f_{med} = \frac{mc^2}{\pi e^2 N} \int \frac{\alpha(\lambda)}{\lambda^2} d\lambda \qquad (1)$$

where c is light velocity, N is the Nd^{3+} ion concentration (ion/cm^3). e and m are the charge and the mass of the electron, respectively. $\alpha(\lambda)$ (=2.303D_o(λ)/d) is the measured optical absorption coefficient at a particular absorption wavelength λ and d is the sample thickness.

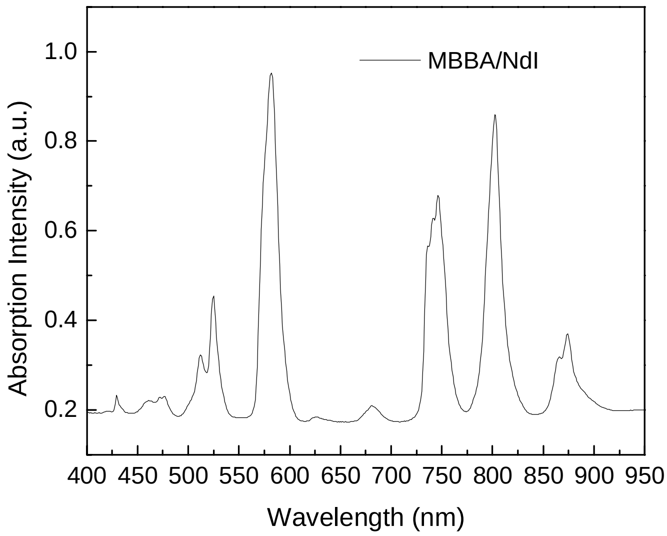

Fig 1. Optical absorption spectra of Nd $^{3+}$ ion in the MBBA/NdI system

The theoretical oscillator strengths f_{cal} are derived by using the Judd-Ofelt theory. The magnetic dipole transitions, which give only negligible contribution to the transition bands of Nd^{3+}, are not considered. Theoretical oscillator strengths $f(J, J')$ of the $J \rightarrow J'$ transition at the mean frequency ν is given for an electric dipole transition by Eq.(2)

$$f_{cal} = \frac{8\pi^2 mc\nu(n^2+2)^2}{27hn(2J+1)} \times \sum_{t=2,4,6} \Omega_t \left| <(S,L)J \left\| U^t \right\| (S',L')J' \right|^2 \qquad (2)$$

where Ω_t is the Judd-Ofelt intensity parameters and h is Plank constant. The reduced matrix elements, $<\|U^{(t)}\|>$, are found to be almost invariant to the environment and we have used the values given by Carnall et al. [4]. The values of reduced matrix elements and the mean wavelength of the chosen absorption bands of Nd^{3+} with respect to absorption bands were tabulated in Table 1.

Table 1. Values of reduced matrix elements for the chosen absorption of Nd^{3+} in the MBBA system

$(S,L)J$: $^4I_{9/2}$ → $(S',L')J'$:	$(U^{(2)})^2$	$(U^{(4)})^4$	$(U^{(6)})^6$	Mean wavelength (nm) MBBA system
$^4F_{3/2}$	0	0.2293	0.0549	874
$^4F_{5/2}$, $^2H_{9/2}$	0.0102	0.2451	0.5124	802
$^4F_{7/2}$, $^4S_{3/2}$	0.0010	0.0449	0.6597	746
$^4F_{9/2}$	0.0009	0.0092	0.0417	681
$^4G_{5/2}$, $^2G_{7/2}$	0.9736	0.5941	0.0673	582
$^2K_{13/2}$,$^4G_{7/2}$, $^4G_{9/2}$	0.0664	0.2180	0.1271	525
$^2K_{15/2}$,$^4G_{9/2}$, $(^2D, ^2P)_{3/2}$, $^2G_{91/2}$	0.001	0.0441	0.0364	476
$^2P_{1/2}$, $^2D_{5/2}$	0	0.0367	0	433

Judd-Ofelt parameters Ω_t, however, exhibit the influence of the host materials on the transition probabilities because they contain the crystal field parameters, interconfigurational radial integrals and energy denominators. Thus, the summation is taken over eight bands used to calculate Judd-Ofelt parameters Ω_t. The values of the measured oscillator strengths f_{med} and the theoretical oscillator strengths f_{cal} are listed in Table 2.

Table 2. The values of the measured (f_{med}) and the theoretical (f_{cal}) oscillator strengths of Nd^{3+} in MBBA system

Excited Level $(S',L')J'$	Position λ(nm)	f_{med} (x10^{-6})	f_{cal} (x10^{-6})	f_{med} (x10^{-6})	f_{cal} (x10^{-6})
		MBBA/NdI		MBBA/NdII	
$^4F_{3/2}$	874	11.56	12.00	4.27	4.76
$^4F_{5/2}$, $^2H_{9/2}$	802	19.38	23.28	11.63	12.41
$^4F_{7/2}$, $^4S_{3/2}$	746	18.57	17.12	11.78	11.57
$^4F_{9/2}$	681	8.66	1.57	2.47	0.95
$^4G_{5/2}$, $^2G_{7/2}$	582	38.03	38.20	24.73	24.80
$^2K_{13/2}$,$^4G_{7/2}$, $^4G_{9/2}$	525	24.22	21.02	11.36	9.91
$^2K_{15/2}$,$^4G_{9/2}$, $(^2D, ^2P)_{3/2}$, $^2G_{91/2}$	476	3.07	5.18	0.92	2.37
$^2P_{1/2}$, $^2D_{5/2}$	433	3.62	3.59	0.86	1.31

In order to evaluate the validity of the intensity parameters, the deviation parameter was obtained by the root-mean-square δ_{rms}

$$\delta_{rms} = \left[\frac{\sum (f_{cal} - f_{med})^2}{N_{param} - N_{trans}} \right] \qquad (3)$$

where N_{param} is the number of spectral bands analyzed and N_{trans} are 3 in this case, which is the parameter number sought. The values of δ_{rms} imply the good fitting between the measured f_{med} and the theoretical f_{cal} oscillator strengths. The deviation parameters, δ_{rms}, is equal to 4.4 and 1.2 (x10^{-6}) for the MBBA/NdI and the MBBA/NdII system, respectively.
The Judd-Ofelt parameters Ω_t for Nd^{3+} ions in the MBBA systems are presented in Table 3. The best set of Ω_t parameters was determined by a standard least-square fitting of the theoretical oscillator strength values to the measured values. It is remarkable to note that the order of the Ω_t parameters in general is $\Omega_2 < \Omega_4 < \Omega_6$, but the trends in fluorophosphates glasses do not always correspond to the general trends. For the MBBA systems, the trend for the Ω_t parameters is $\Omega_2 < \Omega_6 < \Omega_4$. The tendency of intensity parameters in the MBBA system is in agreement with those reported by Kumar [5] and comparable with those of other fluorophosphates glasses [6, 7]. It implies that the efficiency for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is weak and enhanced for the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition [6]. Emission intensity could be also characterized by the Ω_4 and Ω_6 parameters. The parameter, Ω_2, exhibits the dependence on the covalency between rare earth ions and ligands anions, since Ω_2 reflect the asymmetry of the local environment at the Nd^{3+} ion site.

Table 3 Calculated Judd-Ofelt papameters for Nd^{3+} in MBBA system

Judd-Ofelt parameters	Ω_2 (X10^{20} cm^2)	Ω_4 (X10^{20} cm^2)	Ω_6 (X10^{20} cm^2)	$\chi = \Omega_4/\Omega_6$	Reference
FP20	4.71	1.61	1.62	2.30	[7]
Fluoroborophosphate (Glass C, D)	2.9	5	7	0.68	[6]
	2.47	7	0.93	0.9	
MBBA/NdI	-1.02	10.82	4.27	2.54	Current research on MBBA system
MBBA/NdII	1.19	3.95	3.11	1.27	

The ratio χ (=Ω_4/Ω_6), defined as a the spectroscopic quality parameter, is found to be 2.54 and 1.27 for the MBBA/NdI and the MBBA/NdII, respectively. The decrease of χ with Nd^{3+} ion concentration arises from the dramatic decrease of Ω_4. It implies that the efficiency for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is weak with Nd^{3+} ion concentration. It will be supplemented in the view of branching ration below. The χ values in MBBA systems imply the less intense in laser transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ in being compared with those of other host materials reported.

3.2 Radiative transition probabilities and Branching ratio

These Judd-Ofelt parameters obtained from the fitting between the measured f_{med} and the theoretical f_{cal} oscillator strengths can be also applied to calculate the line strength corresponding to the transitions from the initial J manifold and the final J' manifold. The radiative transition probabilities, are given in Eq. (4), were obtained with the line strength for the excited $^4F_{3/2}$ to $^4I_{J'}$ manifold ($^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$) for Nd^{3+}.

$$A_{ra}[(S,L)J;(S',L')J'] = \frac{64\pi^4}{3h(2J+1)\lambda^3}[\frac{n(n^2+2)^2}{9}]S_{ed} \qquad (4)$$

where $n(n^2+2)^2/9$ is the local field correction for Nd^{3+} in the initial J manifold. J' is the final manifold. n is the refractive index at the wavelength of the transition. S_{ed} is the electric dipole line strengths which are expressed:

$$S_{ed} = e^2 \sum_{t=2,4,6} \Omega t \left| \left\langle (S,L)J \left\| U^{(t)} \right\| (S',L')J' \right\rangle \right|^2 \qquad (5)$$

The emission branching ratio for transitions originating from initial manifold can be obtained from the radiative transition probabilities A_{rad} by using Eq. (6) below:

$$\beta_R[(S,L)J;(S',L')J'] = \frac{A[(S,L)J;(S',L')J']}{\sum_{S',L',J'} A[(S,L)J;(S',L')J']} \qquad (6)$$

where the summation is over all terminal manifolds. Theoretically computed radiative properties of Nd^{3+} in MBBA system including electric line strength, radiative transition probabilities, branching ratio are listed in Table 4.

Table 4. Electric line strengths, radiative transition probabilities, branching ratios of Nd^{3+} ion in MBBA system

$^4F_{3/2}$	λ (nm)	S_{ed} (x10^{-20} cm^2)	$A_{rad}(s^{-1})$	β(%)	S_{ed} (x10^{-20} cm^2)	$A_{rad}(s^{-1})$	β(%)
		MBBA/NdI			MBBA/NdII		
$^4I_{13/2}$	1328	0.91	247.16	7.81	0.66	180.79	5.71
$^4I_{11/2}$	1056	3.27	1783.53	56.35	1.83	1001.04	31.63
$^4I_{9/2}$	895	1.22	1690.25	35.84	1.08	1017.28	32.14

The radiative lifetimes τ_{rad} are related to the total radiative transition probabilities A_{rad} of all transitions from the initial J manifold to the final J' manifold. It, therefore, involves the effective average over site-to-site variation of Nd^{3+} ion environment in host materials. The total radiative transition probabilities A_{rad} for three transitions in MBBA system are summed up to obtain the radiative lifetime τ_{rad} of 3164.90 s^{-1} of the $^4F_{3/2}$ metastable state using Eq. (7).

$$\tau_{rad} = \left\{ \sum_{S',L',J'} A[(S,L)J;(S',L')J'] \right\}^{-1} \qquad (7)$$

Radiative quantum efficiency is defined as $\eta=(\tau_f/\tau_{rad})$. The measured lifetime τ_f is the lifetime from fluorescence decay due to all relaxation process. The measured lifetime τ_f is found to be 168 μs for the MBBA/NdI, while the Judd-Ofelt analysis expects radiative transition probabilities A_{rad} for $^4F_{3/2}$ to be 316 μs, resulting in the fluorescence quantum efficiency of 47%.

4. CONCLUSION

The radiative transition probabilities A_{rad}, lifetime τ_f, and branching ratios β have been determined for major excited states in order to evaluate the potential of Nd^{3+} ions in new (Mg, Ba)F_2-based fluorophosphates glass (MBBA system). The values of measured f_{med} and the theoretical f_{cal} oscillator strength of Nd^{3+} in MBBA system have been calculated and the best set of Ω_t intensity parameters was determined by a standard least-square fitting and entirely analyzed. The values of Ω_2, Ω_6, and Ω_4 for the MBBA/NdI, MBBA/NdII system have been found to be -1.02, 10.82, and 4.27 (x10^{20} cm^2), and 1.19, 3.95 and 3.11, respectively. The quality factors χ have been found to be 2.54 and 1.27 for the MBBA/NdI and the MBBA/NdII system, respectively. The measured lifetime τ_f has been found to be 168 μs, while the Judd-Ofelt analysis expected a radiative transition probability A_{rad} for $^4F_{3/2}$ state to be 316 μs for the MBBA/NdI system. The quantum efficiency of 47% was obtained. The spectra properties including the quantum efficiency and high gain shows potentials on the MBBA systems for laser applications.

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