Investigation of Intensity Parameters of Pr^{+3} Doped Metal-Organic Framework (MOFs)

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Abstract

Investigating the intensity parameters of Pr^{3+}-doped Metal-Organic Frameworks (MOFs) involves using the Judd-Ofelt theory to determine transition probabilities and radiative lifetimes from spectroscopic data, which helps characterize the material's optical properties. This process allows researchers to understand how the Pr^{3+} ions, introduced into the MOF's porous structure, interact with the framework, influencing luminescence and providing insights into potential applications, such as in luminescence-based temperature sensing or other optoelectronic devices.

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Introduction

One of the most interesting properties of metal–organic frameworks (MOFs) is luminescence behaviour. Rare-earth-based metal-organic frameworks (MOFs) are actively used in various fields of science and technology as luminescent sensors [1-5], LED components [6], luminescent probes for bioimaging [7], and luminescent thermometers [8]. MOFs are actively used as luminescent and electrochemical sensors for heavy metal ion detection in drinking and wastewater. Nanosized luminescent MOFs are able to penetrate the cell membrane and are therefore used in bioimaging as luminescent probes. The nano-sized rare-earth-based MOFs can be synthesized by several synthetic routes such as solvothermal, reverse microemulsion, surfactant-assisted, microwave, and ultrasonic methods [9-10]. In the current pursuit, Pr (III) chelates of Benzene-1,2-dicarboxylic were selected for study and their absorption spectra were recorded and analysed for various spectroscopic parameters.

Praseodymium exhibits characteristic f-f absorption spectrum which corresponds to transitions from the ground state multiplet to the excited state multiplet. These transitions have a fixed spectral position but their intensity and fine structure may vary with embedding matrix. The intensity of these multiplet-to-multiplet transitions has been successfully described by the Judd-Oflet theory [11-12]. According to Judd-Oflet theory, mixing between 4fn configuration and another configuration having opposite parity may be occurred by the crystal field potential and cause 4f-4f transitions to be allowed by the induced electric dipole. The spectra of Praseodymium consist of four peaks spectra with narrow bands with in the visible regions, representing the transition between $^3H_2$ (ground state) to $^1D_2$, $^3P_0$, $^3P_1$, $^3P_2$ (excited states).

The primary object of this investigation is to determine the Judd-Oflet* intensity parameters from the oscillator strength of absorption peaks and to examine how intensity parameters respond to the minor changes in the ligand environment. Using the Judd-Oflet intensity parameters Ω_λ (λ=2, 4, 6) and fluorescence spectra of the complexes, laser parameters like radiative lifetime of excited states, spontaneous emission probability, fluorescence branching ratio and stimulated emission cross section of optical transitions were also evaluated to examine the alteration in fluorescence properties in conjunction with that of structure of the complex.

Experimental

Reagents

Praseodymium (III) nitrate hexahydrate ($Pr(NO_3)_3 \cdot 6H_2O$) purchased from Sigma-Aldrich. 1,2-Benzenedicarboxylic acid (Phthalic acid), N, N-Dimethylformamide (DMF), and Ethyl alcohol were obtained from Sigma-Aldrich and used directly.

Synthesis

Stock solutions of 0.01 M ligand (Phthalic acid) and 0.01 M metal ions prepared by the solvothermal method. Initially, DMF (24 ml) and ethanol (12 ml) were mixed in a single beaker. Subsequently, in two separate beakers, Praseodymium (Pr) metal (0.75384 gm) and Phthalic acid ligands (0.66456 gm) were dissolved in DMF and ethanol solution. Both solutions kept for ultra sonification for 15-20 minutes and later mixed together. The resulting solution was subjected to ultrasonic treatment for 40 minutes. Additional DMF was incorporated as needed. A homogeneous solution was obtained after ultrasonication, which was then transferred to an autoclave and allowed to cool at room temperature for 24 hours at 120 °C. Upon removal from the autoclave, the mixture was thoroughly stirred and filtered using Whatman filter paper along with DMF and ethanol. Finally, the product was dried at 60 °C for 3 hours. Prepared MOFs shown in figure 1.

Figure 1: MOFs prepared using solvothermal method

The absorption spectra of the sample solutions were recorded at the room temperature in the range of 400-800 nm using Systronic-119 spectrophotometer with a scan speed 600 nm/min.

Theory

The effective Hamiltonian of rare earth metal ion under the influence of a ligand field is composed of four terms

$$H = H_c + H_e + H_m + H_L$$

$$H = \sum_{i=j}^{N}\left(-\frac{h^2}{2m_e}\Delta^2{}_i - \frac{Ze^2}{4\Pi\varepsilon_0}\right) + \sum_{i>k=1}^{N}\frac{e^2}{4\Pi\varepsilon_0 r_{ik}} + \sum_{i=k}^{N}\frac{Ze^2\hbar^2}{8\Pi\varepsilon_0 C^2 m_e{}^2 r_i{}^3}\vec{S}_i\,\vec{l}_i + \sum_{i=1}^{N}\sum_{l=1}^{M}\frac{Ze^2}{d_{il}} \quad (1)$$

Here, first term H_c represents the undisturbed Hamiltonian (central field approximation), the second term H_e represents columbic interactions which were calculated by Slater [13], shortly, Codon [14] and Racah [15-17] using tensor operated methods and are expressed in terms of Slater Codon (F_2, F_4, F_6) and Racah parameters (E_1, E_2, E_3). The third term H_m gives spin orbit interactions, expressed as Lande parameter (ζ_{4f}). The final term H_L is the ligand field Hamiltonian (configuration interaction) which is expressed as interaction parameters (α) [18-20].

Result and Discussions

Oscillator Strength

The absorption spectra of Praseodymium chelate in the wave length range of 400-800 nm at room temperature containing phthalic acid is given in figure 2.

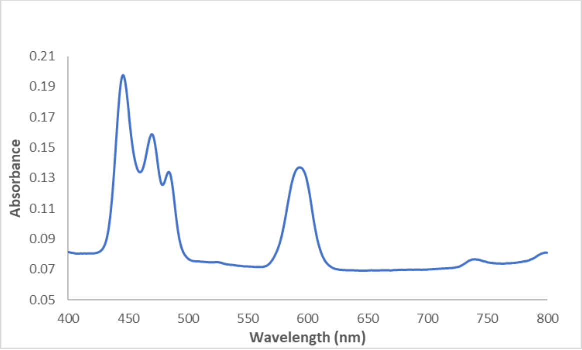

Figure 2: Absorption spectra of Pr(III) doped in Phthalic Acid

The solution spectra have been analyzed by resolving each band into Gaussian curve shape to enable evaluation of oscillator strength. The bands for different transitions have been identified by comparing the values of energies with corresponding energy level in free metal-ion. The oscillator strength values which are a measure of intensities of specific electronic transitions or degree, to which a specific transition is allowed, show marked dependence on the cation environment. The four distinct bands in the visible region can be attributed to the excitation from the ground state ($^3H_4$) to various excited states ($^1D_2$, $^3P_0$, $^3P_1$, $^3P_2$). Band sum & Mean value of wavelength calculated using python program from UV absorption spectra. Obtained values are given in table 1.

Table 1: Band sum & Mean value of wavelength obtained from UV absorption spectra.

Transition	Band Sum#	Mean Wavelength*
$^1D_2$-$^3H_4$	4.4754	444.94
$^3P_0$-$^3H_4$	2.9882	469.39
$^3P_1$-$^3H_4$	1.8838	487.60
$^3P_2$-$^3H_4$	10.7828	564.20

*Average wavelength of transition in nm

#integrated absorption of manifold (band sum) in units 10^{-20} cm^2-nm.

Table 2: Line strength and life time analysis of Pr doped MOFs

Transition	Matrix elements			S	S	Life time
	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$	(Experiment)	(Theoretical)	
$^1D_2$-$^3H_4$	0.00290	0.01920	0.06180	0.62373	0.62373	0.42391
$^3P_0$-$^3H_4$	0.00000	0.17190	0.00000	0.39477	0.31844	0.97486
$^3P_1$-$^3H_4$	0.00000	0.17080	0.00000	0.23958	0.31640	1.09985
$^3P_2$-$^3H4$	0.00000	0.03330	0.12470	1.18513	1.18513	0.45489

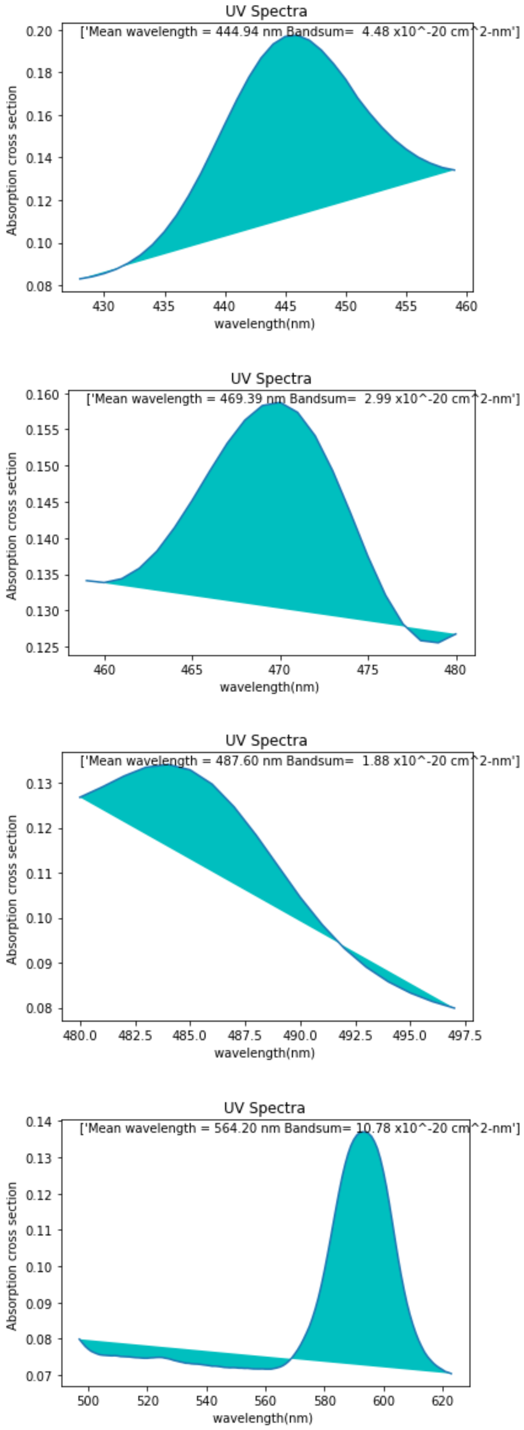

Figure 3: Mean wavelength and band sum calculated for four different transitions.

Intensity Parameters

Line strength and life time analysis of Pr doped MOFs are reported in table 2. The effect of host matrix on local environment for a given rare earth ion can be elucidated using the Judd-Oflet theory by studying changes in the experimentally fitted Judd-Oflet intensity parameters [Ω_λ (λ=2, 4, 6)]. Obtained values of Judd-Ofelt parameters are given below-

Judd-Ofelt Parameters

Ω_2= 10.83, Ω_4= 1.85 and Ω_6= 9.01

Standard Error in Judd-Ofelt Parameters

Ω_2= 0.00 Ω_4 = 0.01and Ω_6= 0.0

Root Mean Square Error

RMS= 0.04421

It has been shown that among the three intensity parameters the Ω_2 is very sensitive to the structural details and chemical environment of the ligand environment.

Conclusion

We have investigated the intensity parameters of Pr^{3+}-doped Metal-Organic Frameworks (MOFs) involves using the Judd-Ofelt theory to determine transition probabilities, and radiative lifetimes from spectroscopic data, which helps characterize the material's optical properties. This process allows researchers to understand how the Pr^{3+} ions, introduced into the MOF's porous structure, interact with the framework, influencing luminescence and providing insights into potential applications, such as in luminescence-based temperature sensing or other optoelectronic devices.

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