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# Optical Study of Rare Earth Lasing Material in Visible and Ir Region

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## Abstract

*The optical absorption spectra of complex of Neodymium in different solvents i.e water, Methanol ,Ethanol and Acetic Acid have been recorded in visible region (360-900 nm for $Nd^{3+}$) and in IR region (1100-2400 nm) using amino acid Alanine as primary ligand and Propane 1-3 diol as secondary ligand in ratio(1:2:1). The value of energies and intensities of various transitions have been calculated using Judd-ofelt relation is in good agreement with experimental result. The complex studied is found to be ionic in nature. The effect of various ligand on the position and intensity of the observed transition in different environments have been discussed in term of metal-ligand co-ordinate.*

**Keywords:** UV-Vis NIR Spectra, rare earth metals, amino acid, optical spectroscopy, Judd–Ofelt parameters.

## Introduction

The absorption spectra of complexed rare earth ions in the f-f transition have been studied by various workers[1-6]. Other spectroscopic studies have yielded information regarding the structure and composition of the complexes[7-10]. In this note, we report the electronic spectra of neodymium (III) with alanine and propane 1-3 diol. Various intensity parameters such as the Judd-Ofelt parameters ($T_2$ ,$T_4$ ,$T_6$) , the bonding parameters $b^{1/2}$, the Slater-Condon parameters ($F_2$ ,$F_4$ ,$F_6$), Racah ($E^1$, $E^2$, $E^3$), Lande parameters ($\zeta_{4f}$) and oscillator strength (P), the covalency of the complex have been calculated and discussed.

## Material and Methods

The neodymium (III) ternary complex was prepared by the method reported in literature[11]. The chemicals used were AR grade and the metals were 99.9% pure (Indian Rare Earth Ltd.). The complex was synthesized with alanine and propane 1-3 diol in molar ratio 1:2:1. The complex was crystallized under vacuum.

The absorption spectra of the complex was recorded on model uv-2601 spectrophotometer (rayleigh analytical instrument corp) in the 360-900 nm (visible region) and 1100-2400 nm (IR region) in different solvent. The energies recorded in terms of wavelength were converted into wavenumber.

**Evaluation of Parameters: Energy levels parameters:** The energy levels of various transitions were obtained experimentally as well as theoretically by using the relation.

$$E_j(F_k, \zeta_{4f}) = E_{oj}(F_k^0, \zeta_{4f}^0) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k}\Delta F_k + \frac{\partial E_j}{\partial \xi_{4f}}\Delta\zeta_{4f} \quad (1)$$

Where E is the zero order energy of the $j^{th}$ level.

**Intensity Parameter:** The experimental values of the Oscillator strength for the various transitions have been computed by using the relation.

$$P_{exp} = 4.6 \times 10^{-9} \times \varepsilon_m \times \Delta \quad (2)$$

Where $\varepsilon_m$ and $\Delta \nu_{1/2}$ are the molecular extinction coefficient and band width for transition respectively.

The experimentally observed values of oscillator strength for $Nd^{3+}$ complex along with their calculated values have been show in Table 3. The values of F2, F4 and F6 parameter were computed using Judd-ofelt relation[12] by partial multiple regression method and have been collection in table -2. The values of reduced matrix elements were collected from Carnall et al. The value in parenthesis indicates the corresponding molecular weight. It has been observed that the value of $T_2$ changes linearly with molecular weight of amino acid.

Using the Judd-Ofelt relation in terms of $T_\lambda$ parameters, we have

$$P_{calc} = [U^{(2)}]^2 T_2 + [U^{(4)}]^2 T_4 + [U^{(6)}]^2 T_6 \quad (3)$$

and matrix elements $[U^{(\lambda)}]^2$ represented by caenall et al[13].this supports the fact that the coordinating environment around the metal ions remains unaltered.

$$b^{1/2} = \left[\frac{1-\beta}{2}\right]^{1/2} \quad (4)$$

**Bonding parameters**: The parameters $b^{1/2}$ which is a measure of the partial covalency in a metal-ligarnd bond can be calculated from the relation.

In case of Nd, $b^{1/2}$ is positive indicating that the complexes are ionic. The nephelauxetic ratio β together with $F_2$ ,$F_4$ ,$F_6$ for the Nd(III) complex has been shown in table-2.

In figure-1 we have shown the variation of optical density with wavelength in all solvents for $Nd^{3+}$ complex in visible region (360-900 nm). In figs 2-5, the variations of optical density with wavelength in infrared region (1000-2000 nm) have been shown for different solvents i.e. water, methanol, ethanol, acetic acid.

**Table-1**
**observed and calculated values of energy levels for $Nd^{3+}$ complex in different solvent.**

| Levels | water | | Methanol | | Ethanol | | Acetic Acid | |
|---|---|---|---|---|---|---|---|---|
| | Cal. $cm^{-1}$ | Obs. $cm^{-1}$ | Cal. $cm^{-1}$ | Obs. $cm^{-1}$ | Cal. $cm^{-1}$ | Obs. $cm^{-1}$ | Cal. $cm^{-1}$ | Obs. $cm^{-1}$ |
| $^2P_{1/2}$ | 23419.02 | 23419.20 | 23360.55 | 23364.48 | 23360.55 | 23364.48 | 23306.24 | 23310.02 |
| $^4G_{11/2}$ | 21675.46 | 21739.13 | 21631.10 | 21739.13 | 21631.10 | 21739.13 | 21637.88 | 21739.13 |
| $^2G_{9/2}$ | 21293.12 | 21367.52 | 21215.37 | 21276.59 | 21215.37 | 21276.59 | 21210.92 | 21276.59 |
| $^4G_{9/2}$ | 19672.55 | 19569.47 | 19600.84 | 19531.25 | 19600.84 | 19531.25 | 19594.69 | 19531.25 |
| $^4G_{7/2}$ | 19323.31 | 19193.85 | 19230.19 | 19120.45 | 19230.19 | 19120.45 | 19211.05 | 19083.96 |
| $^4G_{5/2}$ | 17363.39 | 17361.11 | 17270.55 | 17241.37 | 17270.55 | 17241.37 | 17241.65 | 17211.70 |
| $^4F_{9/2}$ | 14842.15 | 14727.54 | 14816.71 | 14705.88 | 14816.71 | 14705.88 | 14820.82 | 14705.88 |
| $^4F_{7/2}$ | 13386.90 | 13513.51 | 13353.46 | 13440.86 | 13353.46 | 13440.86 | 13350.68 | 13440.86 |
| $^4F_{5/2}$ | 12551.44 | 12594.45 | 12511.26 | 12531.32 | 12511.26 | 12531.32 | 12505.36 | 12531.32 |
| $^4F_{3/2}$ | 11531.83 | 11560.69 | 11477.11 | 11520.73 | 11477.11 | 11520.73 | 11458.36 | 11507.47 |
| rms eviation | 82.9620 | | 74.4306 | | 74.4306 | | 77.5118 | |

**Table 2**
**Computed value of Slater- Condon parameters and Landes parameters β and $b^{1/2}$ for $Nd^{3+}$ complexes in different solvent.**

| | Water | Methanol | Ethanol | Acetic Acid |
|---|---|---|---|---|
| $F_2$ ($cm^{-1}$) | 335.2795 | 335.3143 | 335.3143 | 334.2308 |
| $F_4$ ($cm^{-1}$) | 50.8693 | 49.7363 | 49.7363 | 49.4757 |
| $F_6$($cm^{-1}$) | 5.4422 | 5.4796 | 5.4796 | 5.4412 |
| $\zeta_{4f}$ ($cm^{-1}$) | 872.9012 | 883.5057 | 883.5057 | 890.5244 |
| $E^1$($cm^{-1}$) | 5123.971 | 5103.476 | 5103.476 | 5079.824 |
| $E^2$($cm^{-1}$) | 24.5296 | 24.9402 | 24.9402 | 24.8769 |
| $E^3$($cm^{-1}$) | 495.4567 | 492.1150 | 492.1150 | 490.952 |
| $F_4/F_2$ | 0.1517 | 0.1483 | 0.1483 | 0.1480 |
| $F_6/F_2$ | 1.6231E-02 | 1.6341E-02 | 1.6341E-02 | 1.6279E-02 |
| $E^1/E^3$ | 10.3419 | 10.3705 | 10.3705 | 10.3468 |
| $E^2/E^3$ | 4.9509E-02 | 5.0679E-02 | 5.0679E-02 | 5.0670E-02 |
| $\beta'$ | 1.0124 | 1.0125 | 1.0125 | 1.0092 |
| b1/2 | 7.8865E-02 | 7.9197E-02 | 7.9197E-02 | 6.8090E-02 |

$F_2 = 331.567\ cm^{-1}$ $F_4 = 49.056\ cm^{-1}$ $F_6 = 5.170\ cm^{-1}$ $\xi_{4f} = 906.00\ cm^{-1}$

**Table 3**
**Observed and calculated value of Oscillator strength for $Nd^{3+}$ complexes in different solvent**

| Levels | water | | Methanol | | Ethanol | | Acetic Acid | |
|---|---|---|---|---|---|---|---|---|
| | Cal. x10$^{-6}$ | Obs. x10$^{-6}$ | Cal. x10$^{-6}$ | Obs. x10$^{-6}$ | Cal. x10$^{-6}$ | Obs. x10$^{-6}$ | Cal. x10$^{-6}$ | Obs. x10$^{-6}$ |
| $^2P_{1/2}$ | 0.5288 | 0.1347 | 0.3898 | 0.1614 | 0.2685 | 0.1101 | 0.4349 | 0.0613 |
| $^4G_{11/2}$ | 0.1948 | 0.688 | 0.1660 | 0.6182 | 0.1149 | 0.4509 | 0.1692 | 0.7626 |
| $^2G_{9/2}$ | 0.6369 | 0.1684 | 0.5101 | .0998 | 0.3521 | 0.0608 | 0.5447 | 0.0817 |
| $^4G_{9/2}$ | 1.5513 | 3.2776 | 1.3068 | 4.1187 | 0.9029 | 2.6183 | 1.3616 | 2.7979 |
| $^4G_{7/2}$ | 2.7081 | 3.2077 | 2.4761 | 4.2381 | 1.7005 | 3.1322 | 2.6566 | 3.3743 |
| $^4G_{5/2}$ | 10.4165 | 10.4346 | 13.6750 | 14.1621 | 9.2918 | 9.6361 | 14.8305 | 15.0033 |
| $^4F_{9/2}$ | 0.6727 | 0.4530 | 0.6010 | 0.7884 | 0.4165 | 0.8171 | 0.5976 | 0.8970 |
| $^4F_{7/2}$ | 6.9714 | 6.4841 | 6.2910 | 6.7574 | 4.3647 | 4.5610 | 6.1679 | 5.9442 |
| $^4F_{5/2}$ | 6.5778 | 7.2393 | 5.7028 | 5.9279 | 3.9494 | 4.2908 | 5.7618 | 6.3323 |
| $^4F_{3/2}$ | 1.9818 | 1.1814 | 1.5227 | 1.4987 | 1.0505 | 0.8775 | 1.6537 | 1.2006 |

**Table-4**
**Compute value of $T_\lambda$ – parameters and $T_4 / T_6$ for $Nd^{3+}$ complex in different solvent**

| | Water | Methanol | Ethanol | Acetic Acid |
|---|---|---|---|---|
| $T_2 \times 10^{10}$ | 1.9197 | 4.8998 | 3.2972 | 5.2858 |
| $T_4 \times 10^{10}$ | 5.6974 | 4.1346 | 2.8459 | 4.6799 |
| $T_6 \times 10^{10}$ | 7.4293 | 6.8061 | 4.7237 | 6.6295 |
| $T_4 / T_6$ | 0.7668 | 0.6074 | 0.6024 | 0.7059 |
| rms deviation | 7.2194E-07 | 10.9441E-07 | 7.5357E-07 | 6.3120E-07 |

**Table-5**
**Refractive index value observed for Complex $Pr^{3+}$ in different solvents**

| Complex | Solvent | Refractive index |
|---|---|---|
| $Nd(Al)_2P$ | water | 1.356 |
| | Methanol | 1.357 |
| | Ethanol | 1.375 |
| | Acetic Acid | 1.391 |

**Table-6**
**Observed value of omega parameters complex $Pr^{3+}$ in different solvents**

| | Water | Methanol | Ethanol | Acetic Acid |
|---|---|---|---|---|
| $\Omega_2 x10^{20}$ | 1.4656 | 3.7382 | 2.4849 | 3.9397 |
| $\Omega_4 x10^{20}$ | 4.3497 | 3.1545 | 2.1448 | 3.4882 |
| $\Omega_6 x10^{20}$ | 5.6719 | 5.1926 | 3.5599 | 4.9413 |

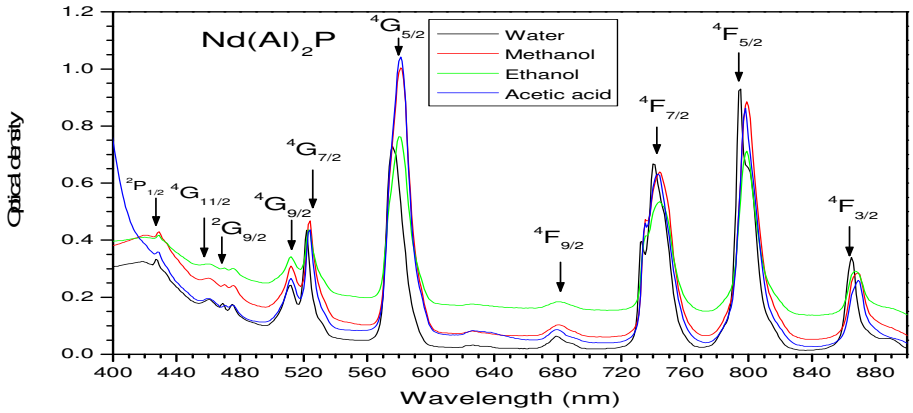


**Figure-1**
**Variation of optical density with wavelength for $Pr^{3+}$ complex in different solvent.**

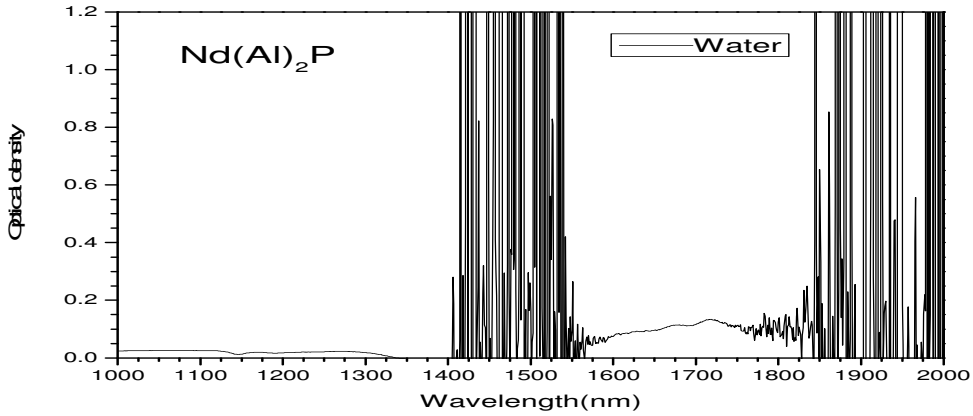


**Figure-2**
**A variation of optical density with wavelength in infrared region for water solve**

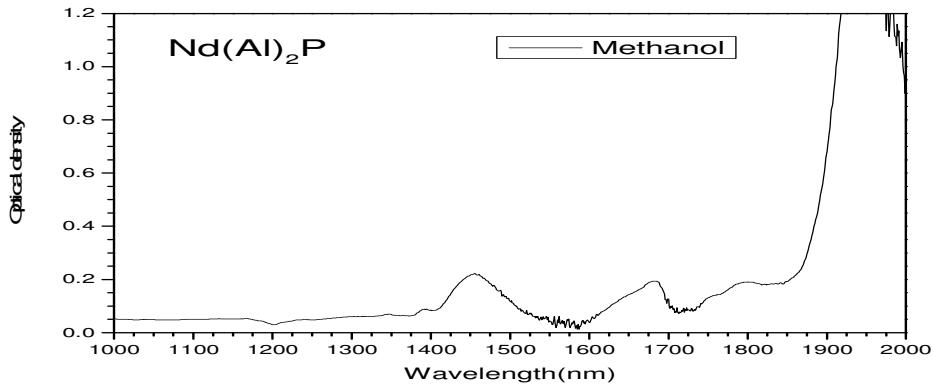


**Figure-3**
**A variation of optical density with wavelength in infrared region for methanol solvent.**

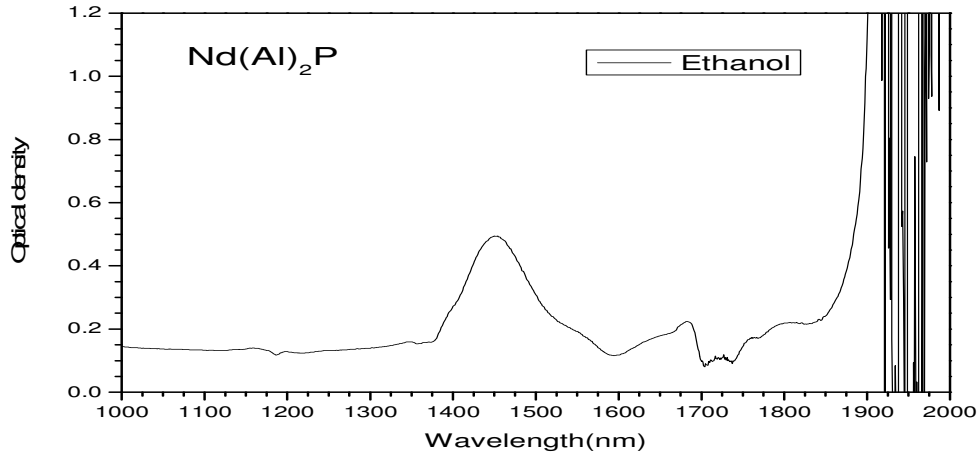


**Figure-4**
**A variation of optical density with wavelength in infrared region for Ethanol solvent.**

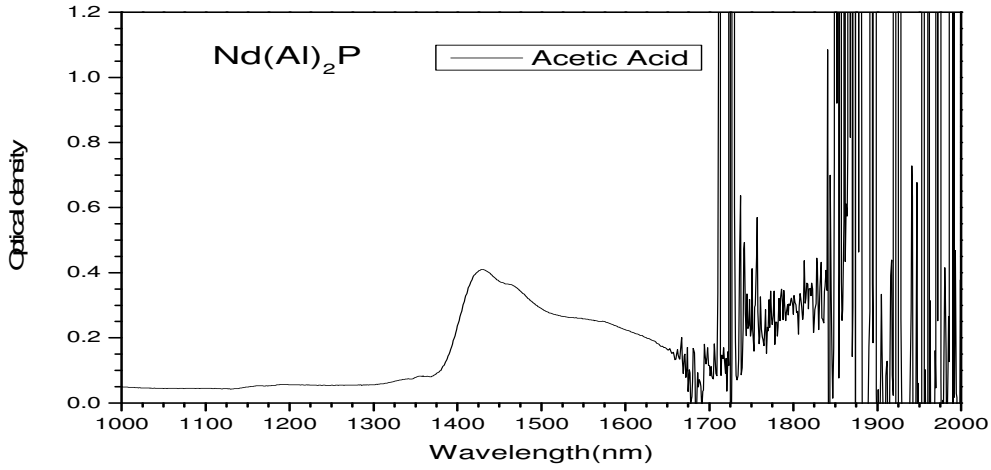


**Figure-5**
**A variation of optical density with wavelength in infrared region for acetic acid solvent**

## Results and Discussion

In table-1 we have shown the observed energy (have been converted into wave numbers) as well as calculated values of energy levels using above equation for $Nd^{3+}$ complex in different solvents. Here we find that calculated value of energy level parameters matches with observed value.

We have calculated values of Slater-Condon parameters $F_2$ , $F_4$ and $F_6$ Lande's parameters $\zeta_{4f}$ , nephelauxetic ratio β, and bonding parameters $b^{1/2}$ in different solvents and have been collected in table 2. The value matches with free ion value. From table-2 we also observe that parameter values are roughly same in different environments.

Ten peaks in case of $Nd^{3+}$ complexes have been observed . The difference of energy value between observed and calculated is very small supports the formation of complex well. The variation of wave length with optical density for $Nd^{3+}$ have been shown in graph in visible region. We have also observed the Infra-red spectra in range 1000-2000 nm for $Nd^{3+}$ complex in all solvents.

In table 3- We have reported the calculated value of Oscillator strength for $Nd^{3+}$ complex in different solvents which is in good agreement with observed value. The observed and calculated values of oscillator strength for hypersensitive[14] transition i.e. $^4G_{5/2}$ is almost same in all solvents. The values of reduced matrix elements have been taken from Carnall et al. For hypersensitive transition in case of $Nd^{3+}$ the value of oscillator strength observed is max i.e highest among all transition in all solvents.

In table 5- We have reported the value of refractive index for $Nd^{3+}$ complex which is in the increasing order as is the increasing order of molecular weight of the solvents. The values of refractive index have also been obtained which are in increasing order i.e. Water – 1.356, Methanol- 1.357, Ethanol- 1.375, Acetic Acid- 1.391

In table 6- We have reported the value of omega parameters for $Nd^{3+}$ in different solvents.

## Conclusion

RMS deviation between calculated and observed value is very low which actually supports the validity of relation used in case of $Nd^{3+}$ complex. It has been found that calculated and observed value of energy is roughly same in all the solvent. It has been clearly observed from the low value of rms deviation as well. From table 1 we also find that the value of energy levels calculated for Neodymium matches with observed value which clearly indicates that the formation of complex is perfect.

The value of β slightly greater than 1 indicates that complexes are ionic in nature. The decrease in value of $F_2$ from that of free ion may support the complexation. This decrease shows that on complexation the contraction of 4f- orbital is reduced with the increase of atomic number of metal ion. The values of all parameters for $^4G_{5/2}$ levels are maximum because of hypersensitive transition.

In table 4- We have reported $T_\lambda$ parameters and the ratio of $T_4$/ $T_6$ in almost constant in all solvent and low value of rms deviation confirms the formation of complex. We observe that the ratio of $T_4$ /$T_6$ is low in each metal. The complex under study have ratio ($T_4$ /$T_6$) lies between 0.19-0.28 supporting that they have oxygen / nitrogen –donor liquids. Also it has been observed that value of $T_4$ and $T_6$ remains nearly invariant in above table.

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