

# Optical Properties of Nd<sup>3+</sup> Doped Phosphate Glasses at <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> Hypersensitive Transitions

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## ABSTRACT

The lasing transition <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> for Nd<sup>3+</sup> doped phosphate glass centered around 1.05 – 1.07 μm is referred as hypersensitive transition. The radiative properties such as effective line width ( $\Delta\lambda_{eff}$ ), radiative transition probability ( $A_R$ ), branching ratio ( $\beta_R$ ), radiative lifetime ( $\tau_R$ ), quantum efficiency ( $\eta$ ) and stimulated emission cross section have been obtained for several phosphate and fluorophosphate glass contained Nd<sup>3+</sup>. The experimental and calculated oscillator strength were used to analysis Judd-Ofelt parameters ( $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ ) also to predict the quality of factor  $\chi$ . The phosphate glass material with the approximately 69P<sub>2</sub>O<sub>5</sub>-15Na<sub>2</sub>O-15K<sub>2</sub>O-1Nd<sub>2</sub>O<sub>3</sub> composition at <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> transition is suitable for laser medium. The enhanced radiative transition probability as well as branching ratio and stimulated emission cross section in this glass are 3694 s<sup>-1</sup>, 52% and 8.67 x 10<sup>-20</sup> cm<sup>2</sup> respectively. As in commercial laser, the magnitudes of the emission cross section in this study achieved in the range 4.0-5.0 x 10<sup>-20</sup> cm<sup>2</sup>.

Keywords: phosphate glass, Nd<sup>3+</sup>, lasing transition

## INTRODUCTION

Phosphate glass is one of the most famous glasses among glasses as host matrix medium gain Nd<sup>3+</sup> of ion laser. It is well known due to phosphate glass able to contain higher concentrations of Nd<sup>3+</sup> ions and still have excellent uniformity relative to other oxide glasses. In other hand, phosphate glass present high strength, low concentration self-quenching, low ESA, low thermal expansion coefficient, long fluorescence lifetime and good optical thermal behavior [1]. Studies on phosphate glass laser transitions at the <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> level have produced larger emission cross section, slight emission line-width, higher gain, higher energy storage capacity and minimum optical losses at a wavelength ~1.06 μm for several applications [2]. Phosphate glass laser contain Nd<sup>3+</sup> has produced high peak power (~10<sup>14</sup>W), high energy output system (10<sup>6</sup>J) (for nuclear fusion research)[3], optical amplifiers, photosensitivity, optical storage and Faraday rotators[4]. Performances of the Nd<sup>3+</sup> doped phosphate glass are obtained by calculation, measurement, characterization and analysis results. The optical parameters of the laser medium were observed such as absorption wavelength peak, energy band and absorption cross section. These parameters used to determine the intensity parameters ( $\Omega_2$ ,  $\Omega_4$ ,  $\Omega_6$ ), oscillator strength, line-width wavelength

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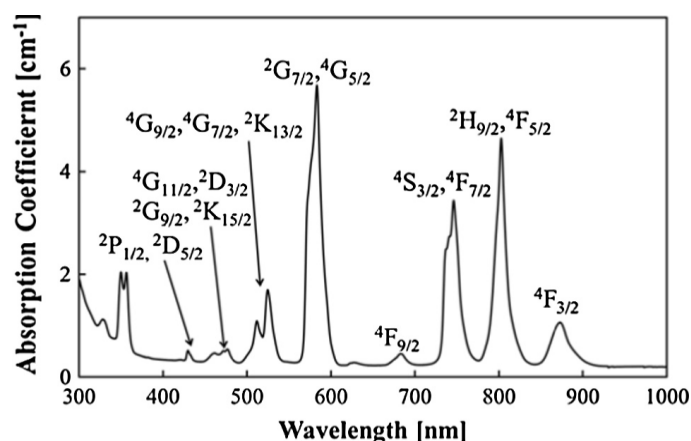
effective, stimulated emission cross section, fluorescence lifetime, and quantum efficiency of the radiative. In other hand, non-radiative transition process and quenching effect in the surrounding of  $\text{Nd}^{3+}$  ions should be important for observation. G.A. Kumar et al [5] explained that to achieve higher quantum efficiency on laser intensity, the non radiative process by multiphonon relaxation should be minimized.

P. Godlewska et al [6] carried out an investigation on the optical absorption and luminescence properties of  $\text{Nd}^{3+}$  ion in variety of phosphate glasses including diphosphate, orthophosphate, and metaphosphate. Among the phosphate group, metaphosphate glasses are the most attractive host due to longer Nd-Nd distance appears and higher luminescence lifetime. Alleged that this kind of phosphate indicating high active-particles concentration to decrease of the self-quenching of luminescence. The Emission transition in  $\text{Nd}^{3+}$  doped phosphate glasses produces three transitions in the NIR range where the  $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$  transition is the strongest emission than the others. However, the wavelength peak of the hypersensitive transition is not exactly the same for each different glass compositions, such as  $\text{NaH}_2\text{PO}_4\text{H}_2\text{O}-\text{H}_3\text{BO}_3-\text{BaF}_2-\text{NdF}_3$  [7] reported that the emission wavelength peak at 1057 nm,  $55\text{P}_2\text{O}_5-17\text{K}_2\text{O}-11\text{MgO}-9\text{Al}_2\text{O}_3-6\text{BaF}_2-2\text{Nd}_2\text{O}_3$  at 1053 nm [2],  $60\text{P}_2\text{O}_5-13\text{ZnO}-5\text{Al}_2\text{O}_3-20\text{La}_2\text{O}_3-2\text{Nd}_2\text{O}_3$  at 1060 nm [8],  $69\text{P}_2\text{O}_5-15\text{Na}_2\text{O}-15\text{Li}_2\text{O}-1\text{Nd}_2\text{O}_3$  at 1069 nm [9],  $69\text{P}_2\text{O}_5-22.5\text{Na}_2\text{O}-7.5\text{Li}_2\text{O}-1\text{Nd}_2\text{O}_3$  at 1071 nm [9] and  $93\text{NaH}_2\text{PO}_4\text{H}_2\text{O}-5\text{BaF}_2-1\text{Nd}_2\text{O}_3$  at 1055 nm [10]. Generally, the high fluorescence properties of laser medium could be enhanced by determining the novelty of composition and structure of the host matrix glass. This paper investigates several the laser glass medium began from the glass former in phosphate, modifier, intermediate structure and variation of  $\text{Nd}^{3+}$  ion concentration. Moreover, study about the optical properties as a function of both concentration and structure composition had been explained in each section below.

## DISCUSSIONS

### Absorption properties of $\text{Nd}^{3+}$ doped phosphate glasses

Before the emission and radiative properties were determined, the first was measured absorption spectra of  $\text{Nd}^{3+}$  ions in these phosphate glasses. In several papers reported that the shapes and position of the absorption transition from the ground state to excited state were almost the same. However, some papers also have slight differences in the amount of absorption band and the wavelength shift of the absorption peak positions due to variation of the glass composition. One form of the absorption spectrum of  $\text{Nd}^{3+}$  in phosphate glasses that has been reported was shown in Figure 1 [11]. In these spectrum obtained eight absorption wavelength peaks of 428, 465, 524, 582, 685, 744, 804, and 869 nm with the strongest absorption band occurs at 582 nm followed by 804 nm could be assigned to the transition of  $^4\text{I}_{9/2} \rightarrow ^2\text{G}_{5/2}$ ,  $^4\text{G}_{5/2}$  and  $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{9/2}$ ,  $^4\text{F}_{5/2}$  respectively.



**Figure 1.** Absorption bands of 0.5 mole% Nd<sup>3+</sup> doped phosphate glasses, LHG-8[11]

These absorption wavelength peaks were slightly different compared to the absorption bands of papers that have been reported previously [2,6,9,12]. The initial absorption of Nd<sup>3+</sup> doped lithium phosphate glass in visible range occurs of  $^4I_{9/2} \rightarrow ^4I_{11/2} + ^4D_{3/2} + ^4D_{5/2}$  transition around at 360 nm obtained by M. Seshadri et al [9]. The absorption peaks shifted caused by differences in the composition of the host glass matrix. Each composition of the modifier in the glass can changes the Nd<sup>3+</sup> structure of ion, therefore affect the positions of the energy and oscillator strength of each transitions as shown in **Table 1**.

### Oscillator Strength and Judd-Ofelt Parameters

The intensity of transition among J-manifolds  $^{2s+1}L_J$  for rare earth (RE) ions calculated by using of Judd-Ofelt theory. The absorption band and wavelength range of Nd<sup>3+</sup> doped phosphate glasses used to identify the radiative transition, such as probabilities transition, effective bandwidth, branching ratio and lifetime of  $^4F_{3/2} \rightarrow ^4I_{9/2}$ ,  $^4F_{3/2} \rightarrow ^4I_{11/2}$  dan  $^4F_{3/2} \rightarrow ^4I_{13/2}$  transitions. J-manifold transitions in RE ion are generated by induced electric dipole transitions, despite of the weak magnetic dipole transitions still occur in the band spectra [13]. The intensity parameters  $\Omega_\lambda$  ( $\lambda = 2, 4$  and  $6$ ) calculated from oscillator strength for electric dipole transition have been explained before [14].

The intensity produced by the absorption spectrum of Nd<sup>3+</sup> doped phosphate is strongly influenced by the condition of the host matrix. Some factors that affect the intensity were the chemical properties of metals, variation of the glass composition. On the other hand, the active ions-metal bond can be changed by the concentration of each compound that affects the intensity. The values of both oscillator strength of ground state  $^4I_{9/2}$  to excited state for seven higher intensity transitions summarized from several papers about Nd<sup>3+</sup> doped phosphate glasses shown in **Table 1**. The general hypersensitive transitions in the Nd<sup>3+</sup> doped phosphate glass i.e.  $^4I_{9/2} \rightarrow ^4G_{9/2}$ ,  $^4I_{9/2} \rightarrow ^4G_{7/2}$ ,  $^4I_{9/2} \rightarrow ^4G_{5/2}$ ,  $^2G_{7/2}$ ,  $^4I_{9/2} \rightarrow ^4F_{9/2}$ ,  $^4I_{9/2} \rightarrow ^4F_{7/2}$ ,  $^4I_{9/2} \rightarrow ^4F_{5/2}$ , and  $^4I_{9/2} \rightarrow ^4F_{3/2}$ . In Table 2 showed that the absorption transition  $^4I_{9/2} \rightarrow ^4G_{5/2}$ ,  $^2G_{7/2}$  centered on around of 582-586 nm expressed as hypersensitive transitions due to the oscillator strength at this transition is bigger than that all of absorption transitions.

**Table 1.** Absorption transitions (from the ground state  $^4I_{9/2}$  to excited state), and oscillator strength for  $x$  Nd<sup>3+</sup> (mole%) doped phosphate glass

Initial glass	$^{4}\text{I}_{9/2} \rightarrow ^{4}\text{G}_{9/2}, ^{4}\text{G}_{7/2}, ^{4}\text{G}_{5/2}, ^{2}\text{G}_{7/2}, ^{4}\text{F}_{9/2}, ^{4}\text{F}_{7/2}, ^{4}\text{F}_{5/2}, ^{4}\text{F}_{3/2}$														
	$x\text{Nd}^{3+}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$
PKFBAN[1]	1.0	2.8	1.9	4.1	3.2	19.0	19.0	0.4	0.5	6.8	7.4	7.4	6.8	1.6	2.0
PKMAFN[2]	2.0	4.0	2.6	4.9	4.6	28.3	28.3	0.8	0.7	10.0	9.7	8.6	9.1	2.9	2.7

Initial glass	$^4I_{9/2} \rightarrow$	$^4G_{9/2}$		$^4G_{7/2}$		$^4G_{5/2}, ^2G_{7/2}$		$^4F_{9/2}$		$^4F_{7/2}$		$^4F_{5/2}$		$^4F_{3/2}$	
	$xNd^{3+}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$	$f_{exp}$	$f_{cal}$
PKMABFN[2]	2.0	4.5	2.7	5.6	4.8	28.8	28.8	0.9	0.7	10.3	9.4	7.9	9.2	3.1	3.0
KumarA[5]	2.0	7.6	8.0	11.1	10.0	47.1	50.0	3.3	2.8	14.4	15.0	14.0	11.5	3.4	3.8
KumarB[5]	1.0	3.6	3.1	7.3	7.8	27.1	30.0	2.3	2.0	8.4	8.0	8.9	10.0	2.5	2.0
KumarC[5]	1.0	3.0	2.5	7.3	8.0	26.4	28.0	2.5	2.0	8.9	9.0	8.4	7.6	2.8	3.0
G.AKumar A[7]	2.0	5.7	-	5.4	-	17.2	-	3.5	-	7.4	-	5.7	-	2.6	-
G.AKumar B[7]	2.0	7.7	-	6.2	-	16.8	-	2.6	-	8.7	-	6.8	-	2.3	-
G.AKumar C[7]	2.0	6.2	-	5.5	-	15.1	-	2.7	-	8.1	-	7.7	-	2.6	-
PKMFAN[12]	1.0	2.7	1.5	3.2	2.6	16.1	16.1	0.8	0.4	5.2	5.6	5.6	5.2	1.2	1.5
PKSFAN[12]	1.0	3.6	2.2	4.9	3.6	20.7	20.9	0.7	0.6	7.8	8.1	8.0	8.0	2.3	2.2
J.H. Choi[15]	1.0	2.6	1.5	5.8	5.9	12.5	12.5	0.7	0.5	6.6	6.4	6.8	7.2	2.9	3.1
A.S.Rao A[16]	1.0	1.6	5.1	6.2	7.6	49.6	49.5	1.5	1.5	19.8	18.6	20.5	18.6	3.7	4.4
A.S.Rao B[16]	1.0	2.9	5.2	6.5	7.9	50.8	50.7	1.5	1.6	20.9	19.0	21.0	19.0	4.0	4.7
A.S.Rao C[16]	1.0	1.5	5.3	6.5	8.1	52.8	52.6	1.3	1.6	21.7	19.2	21.7	19.2	3.7	4.7
RAO A[17]	1.0	1.5	2.7	6.2	9.4	52.8	51.5	1.4	1.6	21.3	22.2	19.9	19.4	3.7	3.8
RAO B[17]	1.0	1.6	1.9	6.5	5.7	50.7	51.8	1.5	1.5	21.7	22.5	21.0	20.5	4.0	3.8
RAO C[17]	1.0	1.5	0.9	6.4	7.0	52.7	52.5	1.7	1.7	21.5	21.0	20.8	20.7	3.7	3.5
PKBAN[18]	1.0	4.9	3.3	6.3	5.9	35.2	35.2	0.9	0.9	12.4	12.1	10.9	11.6	3.9	3.6
PKBFAN[18]	1.0	5.2	3.3	6.6	5.6	25.2	25.2	0.7	0.8	10.8	10.9	10.9	11.1	3.8	3.9
PKBAFN[18]	1.0	4.7	2.9	5.7	5.0	27.6	27.7	0.7	0.8	9.8	10.3	10.4	10.0	2.7	3.2
PKSAN[19]	1.0	3.1	2.2	4.6	3.7	24.0	24.0	0.7	0.6	9.1	8.8	7.4	8.0	2.5	2.1
PKSAFN[19]	1.0	3.3	2.4	44.8	4.2	25.6	25.6	0.6	0.6	9.2	8.4	7.1	8.2	2.4	2.6
PKSABFN[19]	1.0	3.4	2.3	5.0	4.0	24.6	24.7	0.6	0.9	9.0	8.4	7.2	8.0	2.2	2.4

In general, experiment nor theoretical oscillator strength value almost similar except of KUMAR's initial glass that have distinction around  $3 \times 10^{-6}$  [5]. The highest of the oscillator strength value for hypersensitive transition achieved by A.S. RAO and RAO initial glasses with glass composition of  $50(NaPO_3)_6-10Zn_3(PO_4)_2-10BaF_2-9AlF_3-20KF$  and  $40(NaPO_3)_6-10BaF_2-9ZnF_2-B_2O_3-20KF$  respectively [16,17]. The oscillator strength magnitudes also used to determine of the best of intensity parameters  $\Omega_\lambda$  ( $\lambda=2,4,6$ ) by fitting of the standard least-square values in both theoretical and experimental oscillator strength. Judd-Ofelt parameters of  $Nd^{3+}$  in various glasses phosphate are compared in **Table 2**. As presented by S.S. Babu et al [2,20],  $\Omega_2$  parameter defines the covalence bonding of metal-ligand, in other words the  $\Omega_2$  value is increase by lowered the symmetry of  $Nd^{3+}$  ion ligand field. Whereas,  $\Omega_4$  and  $\Omega_6$  parameters were identified as the rigidity of host matrix.

**Table 2.** Judd-Ofelt parameters ( $\times 10^{-20}$ ) and spectroscopic quality factor ( $\Omega_4/\Omega_6$ ) of the excellent concentration of  $Nd^{3+}$  (x) doped phosphate glasses based

Glasses compositions	$xNd^{3+}$ (mole%)	Parameters			
		$\Omega_2$	$\Omega_4$	$\Omega_6$	$\chi$
55.5P <sub>2</sub> O <sub>5</sub> -14K <sub>2</sub> O-6KF-14.5BaO-9Al <sub>2</sub> O <sub>3</sub> [1]	1.0	4.92	3.67	5.26	0.70
46.6P-16.7K-13.8Mg-8.4A-3.45AlF-2Nd[2]	2.0	7.66	5.15	6.99	0.73
55P <sub>2</sub> -17K <sub>2</sub> -11Mg-9Al <sub>2</sub> -6BaF-2Nd[2]	2.0	7.34	5.97	6.69	0.89
68P <sub>2</sub> O <sub>5</sub> -20Na <sub>2</sub> SO <sub>4</sub> -10BaF <sub>2</sub> [5]	2.0	3.6	8.7	6.4	1.35
68NaH <sub>2</sub> PO <sub>4</sub> H <sub>2</sub> O-20H <sub>3</sub> BO <sub>3</sub> -10BaF <sub>2</sub> -2NdF <sub>2</sub> [7]	2.0	2.78	5.00	7.04	0.71
60P <sub>2</sub> O <sub>5</sub> -13ZnO-5Al <sub>2</sub> O <sub>3</sub> -20La <sub>2</sub> O <sub>3</sub> [8]	2.0	4.53	3.67	4.02	0.91
69P <sub>2</sub> O <sub>5</sub> -15Na <sub>2</sub> O-15Li <sub>2</sub> O[9]	1.0	4.32	3.66	6	0.61
69P <sub>2</sub> O <sub>5</sub> -15Na <sub>2</sub> O-15K <sub>2</sub> O[9]	1.0	7.68	8.96	11.71	0.76
88NaH <sub>2</sub> PO <sub>4</sub> H <sub>2</sub> O-5LiF-5BaF <sub>2</sub> [10]	2.0	2.47	7.0	7.55	0.92
55P <sub>2</sub> O <sub>5</sub> -17K <sub>2</sub> O-12SrO-6SrF <sub>2</sub> -9Al <sub>2</sub> O <sub>3</sub> [12]	1.0	5.24	4.30	5.81	0.74
0.1Al(PO <sub>3</sub> ) <sub>3</sub> -0.1Ba(PO <sub>3</sub> ) <sub>2</sub> -0.4(Mg-Ba)F <sub>2</sub> [15]	2.0	1.83	4.73	4.19	1.13
50(NaPO <sub>3</sub> ) <sub>6</sub> -10Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> -10BaF <sub>2</sub> -9AlF <sub>3</sub> -20KF[16]	1.0	18.83	8.16	15.86	0.51
40(NaPO <sub>3</sub> ) <sub>6</sub> -10BaF <sub>2</sub> -9ZnF <sub>2</sub> -B <sub>2</sub> O <sub>3</sub> -20NaF[17]	1.0	22.41	4.43	17.83	0.29

Glasses compositions	$x\text{Nd}^{3+}$ (mole%)	Parameters			
		$\Omega_2$	$\Omega_4$	$\Omega_6$	$\chi$
$\text{P}_2\text{O}_5+\text{K}_2\text{O}+\text{BaO}+\text{Al}_2\text{O}_3$ [18]	1.0	9.23	7.0	8.74	0.8
$58.5\text{P}_2\text{O}_5-17\text{K}_2\text{O}-14.5\text{SrO}-9\text{Al}_2\text{O}_3$ [19]	1.0	6.74	3.86	6.35	0.61
$20\text{Al}(\text{PO}_3)_3-60\text{MgF}_2-20\text{NaF}-1\text{NdF}_3$ [21]	1.0	4.63	2.55	6.79	0.37
$\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ [22]	1.3	3.53	6.57	5.12	1.28
$40(\text{NaPO}_3)_6-9\text{ZnF}_2-20\text{B}_2\text{O}_3-10(\text{BaF}_2-\text{KF}-\text{LiF})$ [23]	1.0	22.47	6.78	11.25	0.60

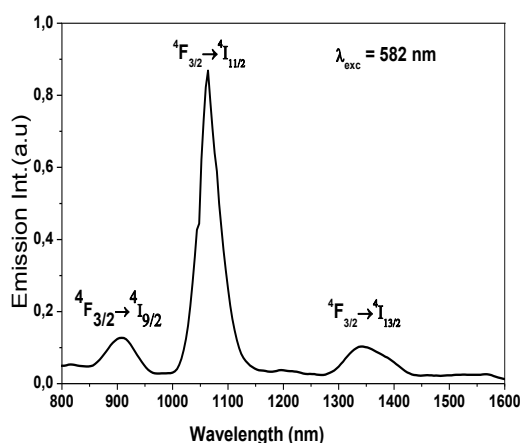
The  $\Omega_2$  parameter for  $40(\text{NaPO}_3)_6-9\text{ZnF}_2-20\text{B}_2\text{O}_3-10(\text{BaF}_2-\text{KF}-\text{LiF})$  or Glass-C [23] and  $40(\text{NaPO}_3)_6-10\text{BaF}_2-9\text{ZnF}_2-\text{B}_2\text{O}_3-20\text{NaF}$  or RAO-B [17] glasses are observed to be relatively higher than other glasses. The  $\Omega_2$  magnitude is influenced by the values of the oscillator strength were higher in hypersensitive transition. The higher  $\Omega_2$  magnitude at Glass-C and RAO-B reflects of asymmetry and covalency bond at  $\text{Nd}^{3+}$  ions were strong [2]. This phenomenon also explains that in this glasses has a higher *nephelauxetic* effect caused by the asymmetry of the crystal field and the changes in the energy difference between the 4f configurations [20,24].

The distribution of  $\Omega_\lambda$  parameters generated are different one others and depends on host ligand even though have the same of  $\text{Nd}^{3+}$  ion concentration. As shown at **Table 2** is found  $\Omega_2 > \Omega_4 > \Omega_6$  form [9,10],  $\Omega_2 > \Omega_6 > \Omega_4$  [2,13,18,19,21,25,26],  $\Omega_6 > \Omega_2 > \Omega_4$  [1,23] and  $\Omega_4 > \Omega_6 > \Omega_2$  [5,10,17]. The larger value of  $\Omega_2$  for both types reflects on the higher sensitivity of each glass. In addition, the  $\Omega_6$  parameter is found higher in [1,10,9,21] glasses than that phosphate glasses indicating a higher of the rigidities of the host matrix due to distance between  $\text{Nd}^{3+}$  ions and the ligands increase [9,25]. The spectroscopic quality factor has been determined by using equation  $\chi = \Omega_4/\Omega_6$  to predict the branching ratios,  $\beta_R$  at lasing transitions. In **Table 2** listed the  $\chi$  values of the several  $\text{Nd}^{3+}$  doped phosphate glass compositions and the values are varied each glass. Generally, the spectroscopic quality factor in **Table 2** obtained smaller than one except [10,18,22]. The lower  $\chi$  values indicate that advantageous of intensity for the  $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$  lasing transition but instead of  $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$  [26].

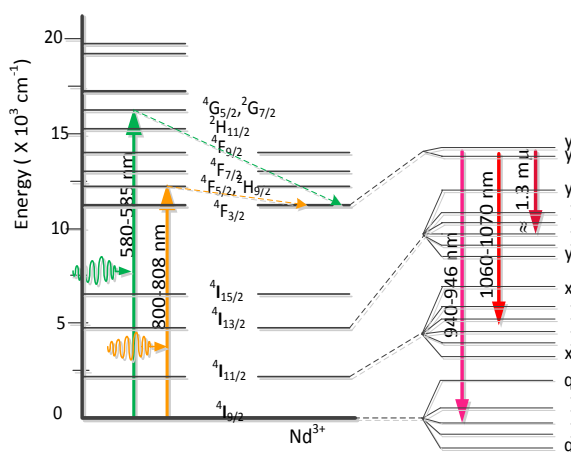
### Radiative properties of $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transition

The emission spectra shape and values of the  $\text{Nd}^{3+}$  doped glass excited by 582 nm at wavelength range 800-1600 nm is shown in **Fig. 2**. In **Fig. 3** also shown the energy level of  $\text{Nd}^{3+}$  transitions that excited from ground state absorption  $^4\text{I}_{9/2}$  to upper state  $^4\text{G}_{5/2}$ ,  $^2\text{G}_{7/2}$  or  $^4\text{F}_{5/2}$ ,  $^2\text{H}_{9/2}$  then extended to relaxation state  $^4\text{F}_{3/2}$  by the non-radiative.

The radiative emission properties of  $\text{Nd}^{3+}$  in phosphate host glasses were predicted by using absorption bands and  $\Omega_\lambda$  parameters as presented at **Table 4**. The values of the excitation wavelength required to investigation of lasing wavelength peak ( $\lambda_p$ ) and prediction of effective line-width ( $\Delta\lambda_{eff}$ ), radiative transition probability ( $A_R$ ), branching ratio ( $\beta_R$ ), radiative lifetime ( $\tau_R$ ), quantum efficiency ( $\eta$ ) by using expressions [15,27].



**Fig. 2.** Emission spectra of Nd<sup>3+</sup> doped glasses excited by 582 nm



**Fig. 3.** Energy level of Nd<sup>3+</sup> doped glass transitions [28,29]

There are three transitions occurs in the emission spectra of Nd<sup>3+</sup> doped phosphate glasses that consistent begins from <sup>4</sup>F<sub>3/2</sub> manifold leading to <sup>4</sup>I<sub>9/2</sub>, <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> levels respectively. However, some authors have reported four transitions including the <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition [4,9]. In **Table 3** it showed specially the radiative transition for <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> level providing the range of wavelength peaks at 1051-1070 nm. The main radiative hypersensitive transition fits with the commercial laser wavelength by N21, N31, LG-770; LG-750 and LGN in **Table 1** are glass compositions in references [1,2]. Whereas, laser commercial wavelength which conducted by LHG-5 and LHG-6 has already matched with glass compositions in reference [12].

**Table 3.** Excitation wavelength ( $\lambda_{exc}$ ), wavelength peak ( $\lambda_p$ ), effective bandwidth ( $\Delta\lambda_{eff}$ ), radiative transition probabilities ( $A_R$ ), stimulated emission cross section ( $\sigma_e$ ), branching ratio ( $\beta_R$ ), radiative lifetime ( $\tau_R$ ) and experimental lifetime ( $\tau_{exp}$ ) for the hypersensitive Nd<sup>3+</sup> doped Phosphate glasses at <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> emission transition

Phosphate Glass Compositions	<sup>4</sup> F <sub>3/2</sub> → <sup>4</sup> I <sub>11/2</sub> transition							
	$\lambda_{ex}$ (nm)	$\lambda_p$ (nm)	$\Delta\lambda_{eff}$ (nm)	$A_R$ (s <sup>-1</sup> )	$\sigma_e(\lambda_p) \times 10^{-20}$ (cm <sup>2</sup> )	$\beta_R$	$\tau_R$ (μs)	$\tau_{exp}$ (μs)
55.5P <sub>2</sub> O <sub>5</sub> -14K <sub>2</sub> O-6KF-14.5BaO-9Al <sub>2</sub> O <sub>3</sub> [1]	-	1053	27.97	2870	3.67	-	348	286
46.6P-16.7K-13.8Mg-8.4A-3.45AlF-2Nd[2]	355	1053	29.5	-	4.40	0.64	-	196
55P <sub>2</sub> -17K <sub>2</sub> -11Mg-9Al <sub>2</sub> -6BaF-2Nd[2]	355	1053	30.7	-	4.46	0.65	-	210
68P <sub>2</sub> O <sub>5</sub> -20Na <sub>2</sub> SO <sub>4</sub> -10BaF <sub>2</sub> [5]	807	1055	21	1608	5.9	0.58	250	168
78NaH <sub>2</sub> PO <sub>4</sub> H <sub>2</sub> O-10H <sub>3</sub> BO <sub>3</sub> -10BaF <sub>2</sub> -2NdF <sub>2</sub> [7]	807	1057	27.5	1563	3.7	0.531	271	160
68NaH <sub>2</sub> PO <sub>4</sub> H <sub>2</sub> O-20H <sub>3</sub> BO <sub>3</sub> -10BaF <sub>2</sub> -2NdF <sub>2</sub> [7]	807	1057	28.5	1825	4.4	0.536	276	180
58NaH <sub>2</sub> PO <sub>4</sub> H <sub>2</sub> O-30H <sub>3</sub> BO <sub>3</sub> -10BaF <sub>2</sub> -2NdF <sub>2</sub> [7]	807	1057	29.3	1871	4.7	0.547	320	200
60P <sub>2</sub> O <sub>5</sub> -13ZnO-5Al <sub>2</sub> O <sub>3</sub> -20La <sub>2</sub> O <sub>3</sub> [8]	819	1060	28.4	1034	-	0.49	320	117
69P <sub>2</sub> O <sub>5</sub> -15Na <sub>2</sub> O-15Li <sub>2</sub> O[9]	514	1069	36.23	1833	3.73	0.52	-	79
69P <sub>2</sub> O <sub>5</sub> -30Na <sub>2</sub> O [9]	514	1069	39.37	2463	5.48	0.52	-	61
69P <sub>2</sub> O <sub>5</sub> -15Na <sub>2</sub> O-15K <sub>2</sub> O[9]	514	1070	41.5	3694	8.67	0.52	-	40
69P <sub>2</sub> O <sub>5</sub> -15Na <sub>2</sub> O-15CaO[9]	514	1069	38.9	2337	4.78	0.52	-	52



Phosphate Glass Compositions	${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition							
	$\lambda_{ex}$ (nm)	$\lambda_p$ (nm)	$\Delta\lambda_{eff}$ (nm)	$A_R$ (s <sup>-1</sup> )	$\sigma_e(\lambda_p) \times 10^{-20}$ (cm <sup>2</sup> )	$\beta_R$	$\tau_R$ (μs)	$\tau_{exp}$ (μs)
69P <sub>2</sub> O <sub>5</sub> -22.5Na <sub>2</sub> O-7.5Li <sub>2</sub> O[9]	514	1071	37.59	1810	3.99	0.52	-	82
69P <sub>2</sub> O <sub>5</sub> -15Na <sub>2</sub> O-7.5Li <sub>2</sub> O-7.5K <sub>2</sub> O [9]	514	1070	36.76	2809	3.95	0.52	-	51
69P <sub>2</sub> O <sub>5</sub> -22.5Na <sub>2</sub> O-7.5K <sub>2</sub> O[9]	514	1069	36.23	1874	3.90	0.52	-	74
93NaH <sub>2</sub> PO <sub>4</sub> H <sub>2</sub> O-5LiF [10]	807	1055	26.3	-	6.7	0.55	350	160
93NaH <sub>2</sub> PO <sub>4</sub> H <sub>2</sub> O-5BaF <sub>2</sub> [10]	807	1055	26.4	-	3.5	0.54	377	170
88NaH <sub>2</sub> PO <sub>4</sub> H <sub>2</sub> O-5LiF -5BaF <sub>2</sub> [10]	807	1055	26.5	-	3.52	0.55	358	170
55P <sub>2</sub> O <sub>5</sub> -17K <sub>2</sub> O-12MgO-6MgF <sub>2</sub> -9Al <sub>2</sub> O <sub>3</sub> [12]	355	1056	40.4	-	1.81	0.63	491	200
55P <sub>2</sub> O <sub>5</sub> -17K <sub>2</sub> O-12SrO-6SrF <sub>2</sub> -9Al <sub>2</sub> O <sub>3</sub> [12]	355	1054	32.6	-	3.29	0.64	326	211
0.1Al(PO <sub>3</sub> ) <sub>3</sub> -0.1Ba(PO <sub>3</sub> ) <sub>2</sub> -0.4(Mg-Ba)F <sub>2</sub> [15]	800	1058	32	3238	2.68	0.44	358	185
58.5P <sub>2</sub> O <sub>5</sub> -17K <sub>2</sub> O-14.5SrO-9Al <sub>2</sub> O <sub>3</sub> [19]	355	1051	27.95	-	4.05	0.52	319	172
55.5P <sub>2</sub> O <sub>5</sub> -17K <sub>2</sub> O-14.5SrO-8Al <sub>2</sub> O <sub>3</sub> -4AlF <sub>3</sub> [19]	355	1051	23.72	-	5.08	0.50	290	188
55.5P <sub>2</sub> O <sub>5</sub> -17K <sub>2</sub> O-11.5SrO-9Al <sub>2</sub> O <sub>3</sub> -6BaF <sub>2</sub> [19]	355	1051	23.51	-	4.72	0.5	306	194
20Al(PO <sub>3</sub> ) <sub>3</sub> -60MgF <sub>2</sub> -20NaF-1NdF <sub>3</sub> [21]	800	1054	28.5	1801	4.51	0.365	-	271
Na <sub>2</sub> O-Al <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub> [22]	880	1057	-	1500	3.1	0.44	295	59
K <sub>2</sub> O-BaO-Al <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> [22]	880	1057	-	1200	2.3	0.45	376	43
ZnO-Li <sub>2</sub> O-P <sub>2</sub> O <sub>5</sub> [22]	880	1057	-	1600	3.2	0.45	284	54

Stimulated emission cross section for the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition can be calculated by equation [15]:

$$\sigma_{em} = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}} A \left[ \left( {}^4F_{3/2} \right) \left( {}^4I_{11/2} \right) \right] \quad (5)$$

Where  $c$  is the speed of light in vacuums and  $n$  is the refractive index. The variation of emission cross section for several phosphate glasses which contained with Nd<sup>3+</sup> were listed in **Table 3**. The smallest value at  $1.81 \times 10^{-20}$  cm<sup>2</sup> of the emission cross section produced by 55P<sub>2</sub>O<sub>5</sub>-17K<sub>2</sub>O-11MgO-6MgF<sub>2</sub>-9Al<sub>2</sub>O<sub>3</sub> glass composition[12], whereas the highest value obtained at  $8.67 \times 10^{-20}$  cm<sup>2</sup> by 69P<sub>2</sub>O<sub>5</sub>-15Na<sub>2</sub>O-15K<sub>2</sub>O glass composition [9] with the Nd<sup>3+</sup> ion concentrations doped are 1.0 mole% respectively. The distribution of the emission cross section for Nd<sup>3+</sup> doped phosphate glasses are shown in **Fig. 6**. Generally, the laser medium candidate based on Nd<sup>3+</sup> doped phosphate glasses showed that the average magnitude distribution of the emission cross section are approximately  $4.0 \times 10^{-20}$  cm<sup>2</sup> to  $5.0 \times 10^{-20}$  cm<sup>2</sup>. In the case of phosphate glasses as a laser medium candidate, the radiative parameters and performance of the laser can be improved by using fluorophosphate glass as host matrix [2,5,7,10,19].

The calculated branching ratio in **Table 3** for  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition can be fitted with the quality factor  $\chi$ , explain about efficiency of lasing transition. The magnitudes range of branching ratio in this discussion showed minimum at 36.5% and maximum at 65% which generally achieved approximately at 50%. The radiative transition probability and radiative lifetime of  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  manifold for Nd<sup>3+</sup> lasing have been shown and compared among phosphate glasses in **Table 3**. The longest radiative lifetime for this study transition is shown by 55P<sub>2</sub>O<sub>5</sub>-17K<sub>2</sub>O-12MgO-6MgF<sub>2</sub>-9Al<sub>2</sub>O<sub>3</sub>-1Nd<sub>2</sub>O<sub>3</sub> composition with quantum efficiency at

40.73%. The radiative lifetime is influence the radiative decay rate caused by differences of the crystal-field environment at the  $\text{Nd}^{3+}$  site and non-radiative decay rate caused by multiphonon relaxation [12].

## CONCLUSION

The  $\text{Nd}^{3+}$  ions doped phosphate and fluorophosphate glasses have been discussed that started from host matrix composition, ions concentration, oscillator strength, Judd-Ofelt parameters and radiative transitions. The content of neodymium ions in phosphate glasses to be applied as a laser medium is 1.0 mole%. The quenching effect of 1.0 mole%  $\text{Nd}^{3+}$  ion luminescence obtained is smaller due to the lower concentration of  $\text{OH}^-$ . The utilization of fluorophosphate, alkali oxide and alkaline oxide are also recommended as a mixture of glass material to improve the radiative properties of the laser. In this investigation has found some increase in the laser performance such as the high stimulated emission cross section, long radiative lifetime fluorescence and wider the bandwidth generated by  $\text{Nd}^{3+}$  doped fluorophosphate glasses. The magnitudes were produced by this glass has also been adapted to commercial laser medium and almost the same even to be better than the commercial lasers. Judd-Ofelt analysis declared that most of the relationship between  $\Omega_\lambda$  parameters indicates on  $\Omega_2 > \Omega_6 > \Omega_4$  for  $\text{Nd}^{3+}$ : phosphate glasses but the trends do not always occur to general trends especially for phosphate glasses. The radiative properties of the  $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$  transition for  $\text{Nd}^{3+}$ : phosphate glasses potential lasing which found to be higher at 69P<sub>2</sub>O<sub>5</sub>-15Na<sub>2</sub>O-15K<sub>2</sub>O-1Nd<sub>2</sub>O<sub>3</sub> composition. In this glass has enhanced the radiative transition probability as well as branching ratio and stimulated emission cross section are 3694 s<sup>-1</sup>, 52% and 8.67 x10<sup>-20</sup> cm<sup>2</sup> respectively.

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## REFERENCES

- [1] Jayasankar, C.K., Balakrishnaiah, R., Venkatramu, V., Joshi, A.S., Speghini, A., and Bettinelli, M., *J. Alloys Compd.*, **2008**, 451, 697-701.
- [2] Babu, S.S., Babu, P., Jayasankar, C. K., Joshi, A. S., Speghini, A., and Bettinelli.. M., *J. Non-Cryst. Solids.*, **2007**, 353, 1402-1406.
- [3] Campbell, J.H., Suratwala, T. I., *J. Non-Cryst. Solids*, **2000**, 263-264, 318-341.
- [4] Ajith Kumar, G., Biju, P.R. Venugopal, C., and Unnikrishnan, N.V. *J. Non-Cryst. Solids*, **1997**, 221(1), 47-58.
- [5] Kumar, G.A., Martinez, A., and Rosa, E.D., *J. Lumin.*, **2002**, 99, 141-148.
- [6] Rajagukguk, J., Kaewkhao, J., Djamal, M., Hidayat, R., Suprijadi., and Ruangtawee, Y., *J. Mol. Struct.*, 2016, 1121, 180-187.
- [7] Kumar, G.A., Rosa, E.D.L., Martinez, A., Unnikrishnan, N.V., and Ueda, K., *J. Phy. Chem. Solids*, **2003**, 64, 69-76.
- [8] Bouderbala, M., Mohmoh, H., Bahtat, A., Bahtat, M., Ouchetto, M., Duretta, M., and Elouadi, B., *J. Non-Cryst. Solids.*, **1999**, 259, 23-30.
- [9] Seshadri, M., Rao, K.V., Rao, J.L. Rao, K.S.R.K. Ratnakaram, Y.C., *J. Lumin.*, **2010**, 130, 536-543.
- [10] Kumar, G.A., Cruz, E.D.R., Uede, K., Martinez, A., and Garcia, O.B. *Opt. Mater.*, **2003**, 22, 201-213.



- [11] Nogata, K., Suzuki, T., and Ohishi, Y. *Opt. Mater.*, **2013**, 35, 1918–1921.
- [12] Vijaya, R., Venkatramu, V., Babu, P. Moorthy, L.R., and Jayasankar, C.K. *Mater. Chem. Phys.*, **2009**, 117, 131-137.
- [13] Binnemans, K., and Walrand, C.G., *J. Phys: Condens. Matter.*, **1998**, 10, 167–170.
- [14] Djamal, M., Rajagukguk, J., Hidayat, R., and Kaewkhao, Enhanced 1057 nm luminescence peak and radiative properties of laser pump Nd<sup>3+</sup>-doped sodium borate glasses, Proceeding of 4<sup>th</sup> International Conference on Instrumentation, Communications, Information Technology, and Biomedical Engineering (ICICI-BME), 2015 ; pp 248-253.
- [15] Choi, J.H., Margaryan, A., Margaryan, A., and Shi, F.G., *J. Lumin.*, **2005**, 114, 167-177.
- [16] Rao, A.S., Rao, B.R.V., Prasad, M.V.V.K.S., Kumar, J.V.S., Jayasimhadri, M., Rao, J.L. and Chakradhar, R.P.S., *Phys. B.*, **2009**, 404, 3717-3721
- [17] Rao, A.S., Ahammed, Y.N., Reddy, R.R., and Rao, T.V.R., *Opt. Mater.*, **1998**, 10, 245-252
- [18] Balakrishnaiah, R., Babu, P., Jayasankar, C.K., Joshi, A.S., Speghini, A., and Bettinelli, M. *J. Phys.: Condens. Matter.*, **2006**, 18, 165-179.
- [19] Kumar, K.U., Babu, P., Jang, K.H., Seo, H.J., Jayasankar, C.K., and Joshi, A.S. *J. Alloys Compd.*, **2008**, 458, 509–516.
- [20] Jorgensen, C.K., and Reisfeld, R. *J. Less-Common Met.*, **1983**, 93, 107-112
- [21] Tian, Y., Zhang, J., Jing, X., and Xu, S. *Spectrochim. Acta A.*, **2012**, 98, 355-358
- [22] Mehta, V., Aka, G., Dawar, A.L. and Mansingh, A. *Opt. Mater.*, **1999**, 12, 53-63
- [23] Rao, A.S., Rao, J.L., Ahammed, Y.N., Reddy, R.R., and Rao, T.V.R. *Opt. Mater.*, **1998**, 10, 129-135
- [24] Ebendorff-Heidepriem, H., Ehrt, D., Bettinelli, M., and Speghini, A. *J. Non-cryst. solids*, **1998**, 240(1), 66-78.
- [25] Tanabe, S., Takahaea, K., Takahashi, M., and Kawamoto, Y. *J. Opt. Soc. Am. B.*, **1995**, 12, 786.
- [26] Zhao, W., Zhou, W., Song, M., Wang, G., Du, J., Yu, H., and Chen, J. *Opt. Mater.*, **2011**, 33, 647–654.
- [27] Moorthy, L. R., Rao, T.S., Jayasimhadri, M., Radhapathy, A., and Murthy, D.V.R. *Spectrochim. Acta. A*, **2004**, 60, 2449–2458.
- [28] Tian, Y., Zhang, J., Jing, X., and Xu, S. *Spectrochim. Acta. A.*, **2012**, 98, 355–358.
- [29] Semwal, K., and Bhatt, S.C., *Int. J. Phy.*, **2013**, 1, 15–21.