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INFRARED LUMINESCENCE PROPERTIES OF THE Nd^{3+} IONS IN P_2O_5-CaO-SrO-BaO PHOSPHATE GLASSES

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Abstract

The optical properties of Nd^{3+} ions in phosphate glass have been investigated measuring absorption and luminescence spectra as well as

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fluorescence decay times. The neodymium doped glasses having composition $(45\text{-}x)P_2O_5$-25CaO-15SrO-15BaO, $(0 < x < 1)$ in Mol% were prepared by melt-quench technique. The amorphous nature of the glasses was confirmed by X-ray diffraction. The phenomenological Judd-Ofelt intensity parameters Ω_t were determined from the spectral intensities of absorption bands in order to calculate the radiative lifetimes, branching ratios, and stimulated emission cross-section of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$ transitions. The quantum efficiency factor of Nd^{3+} ion ($^4F_{3/2}$ level) was equal to 0.80. The decay from the $^4F_{3/2}$ level was a single exponential and shortening of lifetime was caused by low-order multiphonon relaxation and measured at LHeT lifetime is 334μs for 1.0 Mol% Nd-doped phosphate glass.

1. Introduction

Lanthanide phosphate glasses have been extensively investigated due to their transparency in a wide spectral range, from the ultraviolet to the infrared, which makes them suitable for the fabrication of optical fibers. Besides the ease of preparation, high concentrations of lanthanide and transition metal ions can be incorporated into the matrix. The optimum material composition has mechanical stability, is resistant to humidity, and largest concentrations of transition metal-ions can be incorporated as dopants compared to the other glasses [12, 13]. With the rapid development of diode-pumped solid-state laser technology, research on more efficient new laser materials has gained most importance. In this subject area, trivalent neodymium is widely studied ion in a variety of glasses and crystals under 808 and 885nm laser diode excitation to develop high peak-power solid state lasers in the near infrared (NIR) region at 1.0-1.5 μm [1, 6]. Therefore, it has become a hot subject of current research to study the spectroscopic properties of rare-earth ions in different phosphate glass and to compare the results obtained theoretically as well as experimentally. Theoretical analysis of spectroscopic properties of Nd^{3+} ions in many glasses have been widely studied by using the Judd-Ofelt theory [15, 21]. By changing the host

glass compositions, the spectroscopic parameters of Nd^{3+} ions that are used to estimate the laser performances of the glass can be modified. Several authors have recently studied the properties of phosphate glasses Nd^{3+} doped [3, 9, 10]. In this paper, third of a series, the optical properties of Nd^{3+} doped P_2O_5-CaO-SrO-BaO glasses have been elucidated for their potential application as laser material. The Judd-Ofelt formalism has been applied to the measured optical absorption intensities in order to determine the intensity parameters, like spontaneous emission probability, branching ratio, and radiative lifetimes for $^4F_{3/2}$ level. Further, complete knowledge of various radiative spectroscopic properties is essential for design and development of optical glass materials for device applications.

2. Experimental Details

A series of phosphate glasses based on P_2O_5-CaO-SrO-BaO composition were used in this study. Bulk samples were produced by standard methods in an atmosphere-controlled dry box. The following are Nd^{3+} ion-doped calcium-strontium-barium-phosphate glasses that were developed for the present work along with reference glass:

$45P_2O_5$-25CaO-15SrO-15BaO host glass (Mol%);

$44.9P_2O_5$-25CaO-15SrO-15BaO-$0.1Nd_2O_3$ (Mol%);

$44.75P_2O_5$-25CaO-15SrO-15BaO-$0.25Nd_2O_3$ (Mol%);

$44.5P_2O_5$-25CaO-15SrO-15BaO-$0.5Nd_2O_3$ (Mol%).

The starting materials were analytical grade of P_2O_5, CaO, SrO, BaO oxides, and Nd_2O_3 oxide was purity 99.99% (Aldrich, Germany). All weighed chemicals were powdered finely and mixed thoroughly before each batch (20g) was melted in a corundum crucible at 850ºC for 20 min in dry argon. These melts were poured onto a cold brass plate and then

pressed by another plate. The obtained glasses were in circular designs having 2-2.5cm in diameter with a thickness of about 0.3cm and with good transparency. The density of each glass sample was measured by the Archimedes's principle by using Xylene as immersing liquid.

X-ray diffraction measurements were performed to confirmation of amorphous state of studied glasses (plate samples). The XRD data were collected using a Panalytical X'Pert PRO MPD PW 3040/60 diffractometer with a Theta-Theta geometry and parallel beam technique, using $CoK_{\alpha 1}$ radiation (U = 45kV, i = 3mA, step size $0.01^{\circ}2\Theta$, counting time 100s, with detector X'Celerator -using real time multiple strip detection technology and quasi-parallel beam diffracted by the X-ray mirror for Co radiation (PW 3088/66)).

An Abbe refractometer was used to measure the refractive index at Na (589.3nm) lamp wavelength. The VIS-NIR absorption spectra were measured by UV-VIS-NIR Cary-Varian 2300 double-beam spectrophotometer. Luminescence spectra and luminescence decay curves were recorded following a short pulse excitation provided by an optical parametric oscillator (OPO) pumped by a third harmonic of an I Nd:YAG laser. Resulting luminescence signal was filtered by using a monochromator GDM-1000, detected by a Hamamatsu R928 photomultiplier or InSb detector and recorded with an oscilloscope Tektronix TDS3052. The emission spectra have been corrected from the equipment answer. The relative error in the measurement of fluorescence lifetime is estimated to be ±2%. All optical measurements were carried out between liquid helium and room temperatures.

3. Results and Discussion

The XRD diffraction pattern of phosphate glass doped with neodymium ion (Figure 1) displayed a broad peak corresponding to the diffusion X-ray scattering on the fully amorphous phase.

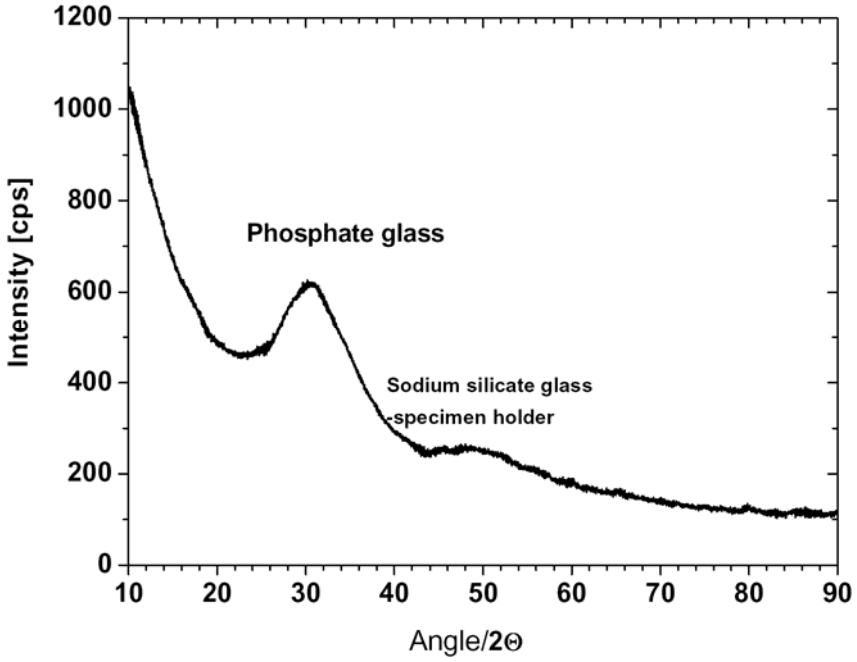

Figure 1. X-ray diffraction pattern of phosphate glass doped with 1mol% of Nd^{3+} ions.

The radiative transition probabilities for excited levels of Nd^{3+} have been calculated by using the standard Judd-Ofelt theory [7, 14], the experimental oscillator strengths for transitions from the ground $^4I_{9/2}(Nd^{3+})$ level to excited levels were determined by numerical integration of the corresponding absorption bands. For each transition, the calculated oscillator strength is given by the equation

$$\int (J;\, J')_{\text{calc.}} = \frac{8\pi^2 mc(n^2+2)^2}{3h\lambda(2J+1)9n} \times \sum_{t=2,4,6} \Omega_t (\langle 4f^N J \| U^{(t)} \| 4f^N J' \rangle)^2, \quad (1)$$

where m is the mass of the electron, c is velocity of light, h is the Planck constant, and λ is the mean wavelength of the transition. In performing the analysis, the measured refractive index n = 1.58(1) of the host glass, and reduced matrix elements $U^{(t)}$ taken from Carnall et al. [2] were

applied. The parameters $\Omega_{2,4,6}$ implicitly contain radial integrals, perturbation denominators, and odd-symmetry terms of the crystalline field. As such, they are intrinsically positive. The experimental oscillator strengths $f_{\text{exp.}}$ are found by measurement of the integrated absorption coefficient for each of the various transitions and using the expression

$$\int (J;\ J')_{\text{exp.}} = \frac{mc^2}{lN\pi e^2} \int \frac{2.303 OD(\lambda)\, d\lambda}{d\lambda^2}, \tag{2}$$

where c is the speed of light, m and e are the mass and charge of the electron, respectively, l (in cm) and N (as ions/cm^3) are the sample thickness and the number of active ions per unit volume, and $OD(\lambda)$ is the optical density.

Equation (1) accounts for electric dipole line strengths only. Magnetic dipole line strengths were found to be less than 1% of electric dipole line strengths and were not included in the fitting procedure. By fitting the theoretical oscillator strength given by Equation (1) to the experimental oscillator strengths given by Equation (2) through a least-squares analysis, the Ω_t parameters were derived. The quality of the fit can be expressed by the magnitude of the root-mean-square (*rms*) deviation, defined by $\sum (f_{\text{exp.}} - f_{\text{calc.}})^2$. The room temperature absorption spectrum as well as calculated oscillator strengths for Nd^{3+} in phosphate glass are shown in Figure 2 and in Table I.

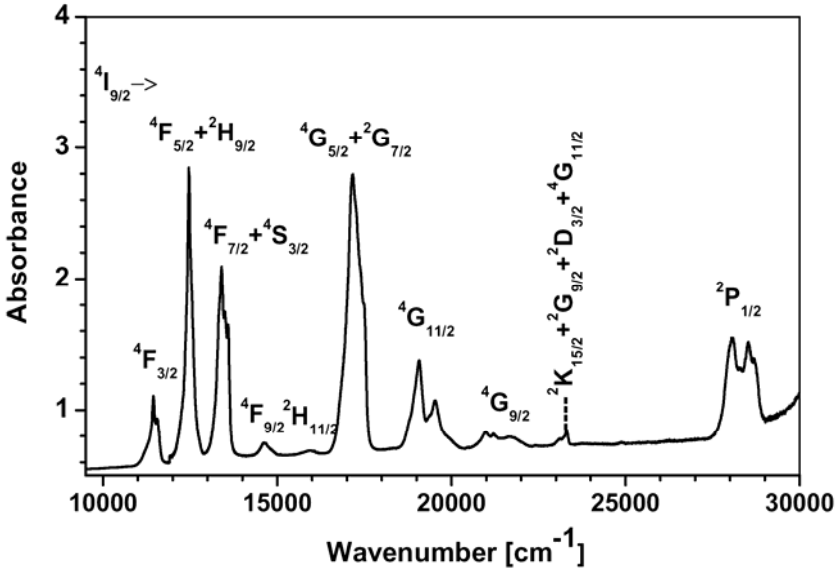

Figure 2. Absorption spectrum of Nd^{3+} in phosphate glass; c = 1.0mol%, T = 300K.

Table I. Measured and calculated oscillator strengths for Nd^{3+} ions in phosphate glass ($44.5P_2O_5$-25CaO-15BaO-15SrO-$0.5Nd_2O_3$). Transitions are from $^4I_{9/2}$ ground state to the levels indicated

Levels	Energy	Oscillator strength	Oscillator strength
	$\sigma[cm^{-1}]$	$f_{exp.}x[10^{-6}]$	$f_{calc.}x[10^{-6}]$
$^4F_{3/2}$	11345	1.17	1.17
$^4F_{5/2} + {}^2H_{9/2}$	12440	4.09	3.84
$^4F_{7/2} + {}^4S_{3/2}$	13400	4.02	4.02
$^4F_{9/2}$	14632	0.28	0.29
$^2H_{11/2}$	15854	0.08	0.06
$^4G_{5/2} + {}^4G_{7/2}$	17364	9.21	9.21
$^2K_{13/2} + {}^4G_{7/2} + {}^4G_{9/2}$	19381	3.35	3.89
$^2K_{15/2} + {}^2G_{9/2} + {}^2D_{3/2} + {}^4G_{11/2}$	21614	0.93	1.14
$^2P_{1/2}$	23178	0.21	0.32
rms deviation = $1.07 \pm 0.14 \times 10^{-6}$			
J-O parameters			
$\Omega_2 = 2.17 \pm 0.14 \times (10^{-20} cm^2)$			
$\Omega_4 = 2.46 \pm 0.05 \times (10^{-20} cm^2)$			
$\Omega_6 = 3.07 \pm 0.02 \times (10^{-20} cm^2)$			

Using the conventional method defined above, the *rms* deviation of the fitted values is equal to 1.07×10^{-6} for Nd^{3+}. These values increase to 1.21×10^{-6} when minimizing the fractional deviations defined by $\sum[(f_{exp.} - f_{calc.})/f_{calc.}]^2$ [5, 16]. The phenomenological Judd-Ofelt parameters for Nd^{3+} ions in studied phosphate glass are found to be

$\Omega_2 = 2.17 \pm 0.14, \Omega_4 = 2.46 \pm 0.05, \Omega_6 = 3.07 \pm 0.02,$ in $[10^{-20}\,\mathrm{cm}^2]$ units. They are comparable to those reported by Reisfeld and Jorgensen [18] for Nd^{3+} in other phosphate glasses by using the modified Judd-Ofelt technique. It is interesting to note (see Table I) that the trends of magnitude Ω_t parameters for Nd^{3+} doped phosphate glass are found to be $\Omega_6 > \Omega_4 > \Omega_2$. Due to the zero value of certain reduced matrix elements $< \|U^{(t)}\| >^2$, the emission intensity from the $^4F_{3/2}$ level of Nd^{3+} ions can be uniquely characterized by the ratio of intensity parameters Ω_4 / Ω_6, which is known as spectroscopic quality factor χ. If χ is smaller than unity, the intensity of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is stronger than the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition in that host. The χ value for P_2O_5-CaO-SrO-BaO glass is found to be 0.80, which is comparable to other oxide glasses [18]. The Judd-Ofelt Ω_t parameters can now be applied to Equation (3) to calculate the radiative transition probabilities for electric dipole transitions between an excited states and the lower lying level of Nd^{3+}

$$A(J, J') = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3} \times \frac{n(n^2+2)^2}{9} \sum_{t=2,4,6} \Omega_t (\langle 4f^N J \| U^{(t)} \| 4f^N J' \rangle)^2. \quad (3)$$

The radiative lifetime of an excited level is calculated from the inverse of a sum of $A(J, J')$ values calculated over all terminal levels

$$\tau_{\mathrm{rad}} = \frac{1}{\sum A(J, J')}. \quad (4)$$

The luminescence branching ratios β were calculated according to the formula

$$\beta = \frac{A(J, J')}{\sum A(J, J')}, \quad (5)$$

which indicates the relative intensities of transitions from excited level to all terminal levels. The results of these calculations for Nd^{3+} in the phosphate glass are given in Table II. The wavelength (λ) of respective transitions were determined from absorption and luminescence spectra. The emission spectra doped with 1.0Mol% of Nd^{3+} in phosphate glass at LHeT, 77K and room temperature, were shown in Figure 3 as a representative example.

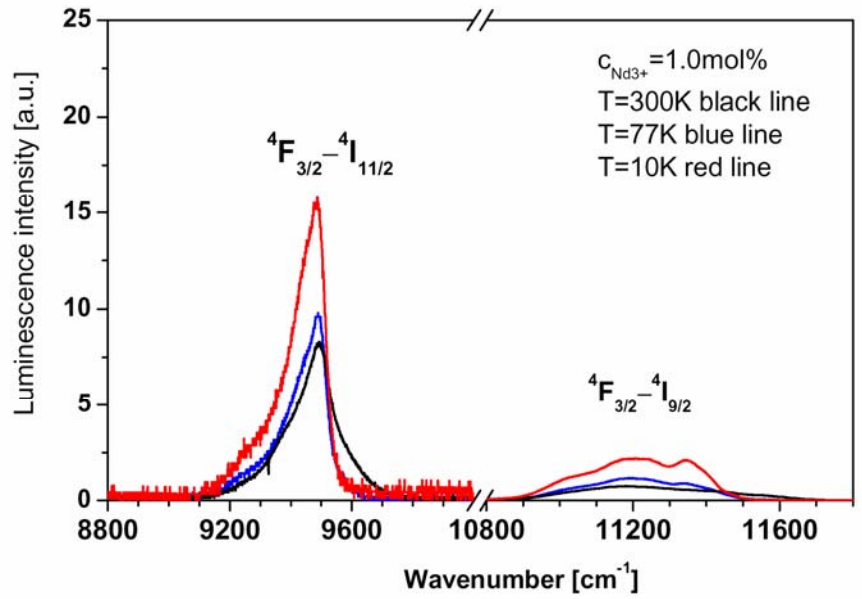

Figure 3. Luminescence spectra of Nd^{3+} ions doped in phosphate glass; c = 1.0 mol%, measured at T = 300K, T = 77K, and T = 10K.

The effective bandwidth of the emission spectra can be estimated by using the relation

$$\Delta\lambda_{\text{eff}} = \int \frac{I(\lambda)d\lambda}{I_{\max.}}, \tag{6}$$

where $I(\lambda)$ is the measured luminescence intensity at wavelength λ and $I_{\max}$ is the peak luminescence intensity. Generally, the bandwidth is

mainly caused by the splitting of the levels of different transitions and the site to site variation of the ligand field around Nd^{3+} ions in glass, i.e., the inhomogeneous broadening. The peak stimulated emission cross-section, $\sigma_e(\lambda_p)$, is an essential parameter to predict the laser performance of the glass and can be determined by using the expression

$$\sigma_e(\lambda_p) = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{\text{eff}}} A(J, J'), \tag{7}$$

where λ_p is the wavelength of the luminescence peak and $\Delta\lambda_{\text{eff}}$ is the line width obtained from Equation (6). The observed values of $\Delta\lambda_{\text{eff}}$ and σ_e were collected in Table II, all these parameters were well within the ranges commonly reported for Nd^{3+} doped laser glasses [17, 20].

Table II. Calculated values of the radiative transition rates *A,* luminescence branching ratios β, effective bandwidth $\Delta\lambda_{\text{eff}}$, and peak stimulated emission cross-section σ_e for excited state $^4F_{3/2}$ of Nd^{3+} ions in studied phosphate glass, T = 293K

Transition from the $^4F_{3/2}$ level	Energy [cm^{-1}]	A [s^{-1}]	τ_{rad} [μs]	τ_{exp} [μs]	β	$\Delta\lambda_{\text{eff}}$ [nm]	σ_e [$\times 10^{20} cm^2$]
$^4I_{9/2}$	11345	644			0.23	40.1	1.15
$^4I_{11/2}$	9231	1840			0.65	27.5	3.90
$^4I_{13/2}$	7247	328			0.12		
$^4I_{15/2}$	5197	12			0.00		
		$\sum A =$ 2824	354	284			

The decay of the luminescence from $^4F_{3/2}$ state of Nd^{3+} have been measured by monitoring the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition and is shown in Figure 4.

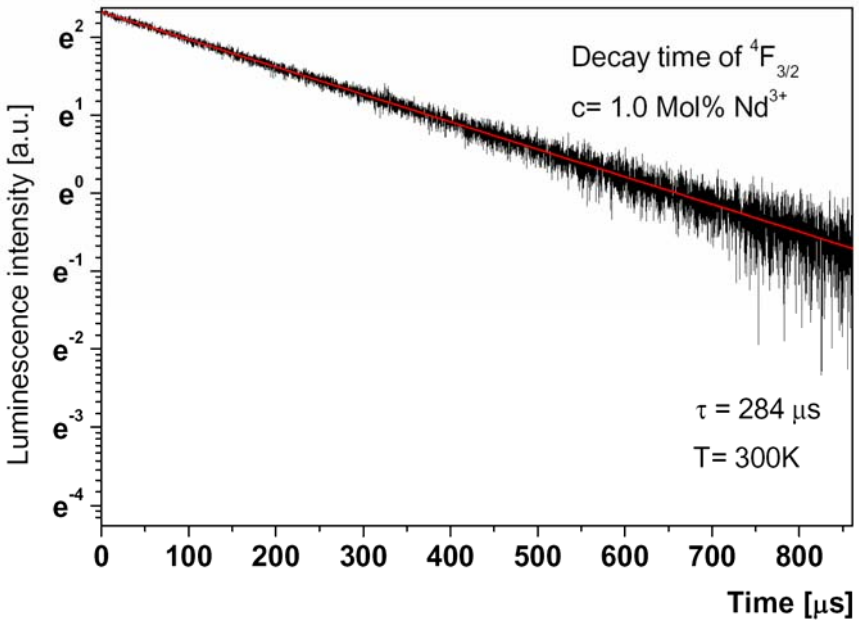

Figure 4. Luminescence decay from the $^4F_{3/2}$ level of Nd^{3+} ions c = 1.0Mol%, T = 293K in phosphate glass.

The decay curve is single exponential. From the decay curve, fluorescence lifetime have been determined by finding the first e-folding time of the decay intensity. The τ_{exp} values of 0.2-1.0Mol% Nd^{3+} doped phosphate glass are found to be $284 \pm 5\mu s$, which give the quantum efficiency τ_{exp}/τ_{rad} equal to 0.80. The τ_{exp} of the 0.2-1.0Mol% Nd^{3+} doped phosphate glass under investigation is found to be lower than the τ_{rad} obtained from Judd-Ofelt analysis, which indicates the existence of non-radiative de-excitation channels from $^4F_{3/2}$ level. The non-radiative channel may be multiphonon relaxation, cross-relaxation between a pair

of Nd^{3+} ions or energy transfer to impurities. Experimental work on non-radiative transitions in complex organic molecules and the lanthanide ions doped crystals or glass have provided some useful generalizations concerning the multiphonon transition rates. In given system, the rate has an exponential dependence on the energy gap bridged by non-radiative transitions [8, 11, 19]

$$W_{MPR} = W_0(n_i + 1)^p \quad \text{and} \quad n_t = \left[\exp\left(\frac{h\omega}{kT}\right) - 1\right]^{-1}, \tag{8}$$

where W_0 is the spontaneous emission rate and n_i is the average occupation number of i-th vibrational mode. Taking into account Equations (8), the expected temperature dependence of luminescence lifetime of $^4F_{3/2}$ level may be written as

$$\tau_{\text{calc}} = \left[W_r(4F3/2) + W_0\left(\frac{\exp\frac{h\omega}{kT}}{\exp\frac{h\omega}{kT} - 1}\right)^p \right]^{-1}. \tag{9}$$

The measured fluorescence lifetimes of the $^4F_{3/2}$ state of Nd^{3+} in phosphate glass varied from $334 \pm 6\mu s$ to $284 \pm 5\mu s$, respectively, at LHeT and RT (see Figure 5). The solid line in Figure 5 is given by Equation (9) by using the calculated value $W_r = 2824 s^{-1}$, and assuming that relaxation involves the emission of four phonons of energy $1300 cm^{-1}$. According to Efimov [4], this energy corresponds to highest energy P-O vibrations. It can be seen that the theoretical approach is consistent with the calculation in the framework of the Judd-Ofelt theory and that it accounts well for the experimental data in the temperature region investigated.

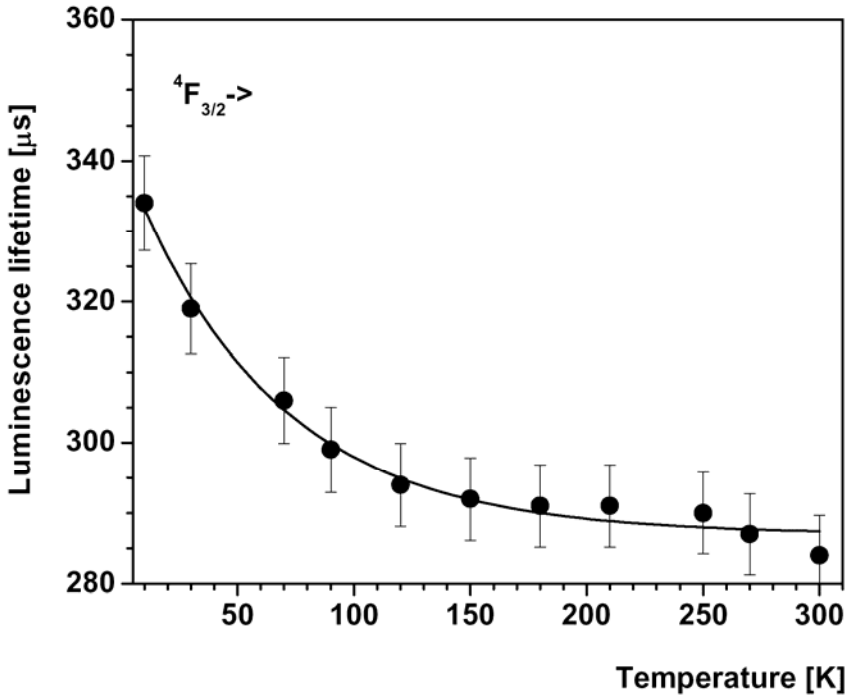

Figure 5. Influence of temperature on the decay time of $^4F_{3/2}$ level for c = 1.0Mol% Nd^{3+} ions in phosphate glass, black circle. (See text for explanation of theoretical line.)

4. Conclusion

In summary, the optical properties of the Nd^{3+} ion in transparent P_2O_5-CaO-SrO-BaO phosphate glasses have established the following points:

(i) Absorption, luminescence spectra, and fluorescence lifetimes of neodymium doped phosphate glasses were measured and analyzed. The quantum efficiency of the $^4F_{3/2}$ level is determined to be 0.80 favouring lasing action at 1055nm.

(ii) The measured fluorescent lifetimes of the $^4F_{3/2}$ of the Nd^{3+} ions in phosphate glass are 334μs at 10K and 284μs at room temperature. Multiphonon relaxation rate from the $^4F_{3/2}$ level is found to be $697s^{-1}$, making a low-order multiphonon decay possible, which could be revealed in the temperature exponential dependence of the luminescence lifetime.

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