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Spectroscopic studies of rare earth-doped halogeno-phosphate glasses

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New series of rare earth doped halogeno-phosphate glasses with compositions: (100-x-y) $NaPO_3$ – x $PbCl_2$– y $BaCl_2$: LnF_3 (Ln=Er or Ho) were prepared and characterized. These glasses exhibit a good resistance against devitrification. Spectroscopic analyses based on Judd-Ofelt theory were performed. Starting from absorption spectra, the oscillator strengths and the intensity parameters Ω_2, Ω_4 and Ω_6 have been evaluated, and various radiative properties like radiative transition probability, branching ratio and radiative lifetime were determinated. Spectroscopic quality factor (Ω_4 /Ω_6) has been evaluated to understand the lasing efficiency of these materials. These glasses could be used as lasing materials and offer prospects for photonics applications.

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1. Introduction

Rare earth doped glasses have potential applications for solid state lasers, optical fiber amplifiers and waveguide lasers. The use of rare earth elements as doping agents result of their various transitions in the visible and infrared regions and their insensitivity to the matrix in which are introduced. Host glass materials are very important for developing rare-earth doped optical devices. Glassy materials are attractive in these applications due to their ability to be cast in large pieces, their optical homogeneity and their low cost.

Among different glass host materials, halogeno-phosphate glasses offer significant advantages over other glass host materials. They are easily prepared by introducing selected metal halides (fluoride and chloride in our case) into polyphosphate glasses.

The trivalent Holmium ion is well known as an important active ion applied to upconversion luminescence, due its energy level structure, which allows and favors upconversion processes [1]. Ho^{3+} doped glasses can product laser emissions at several wavelengths in the near infra red: around 2µm from the $^5I_7 \rightarrow {}^5I_8$ transition in the eye-safe region [2,3] and around 1,2µm with the $^5I_6 \rightarrow {}^5I_8$ transition [4,5]. These wavelengths are attractive for remote sensing and medical applications. Holmium has been also used in the green region for applications including ophthalmology, medical diagnostics, holography, data storage, and pump source for the other laser systems [6,7,8].

The trivalent erbium ion is of major importance in the technology of optical amplification, and also in bulk lasers and fiber lasers. The most common transition is the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ around 1.53µm. This transition is especially important for optical communications because standard single mode optical fibers have minimal loss at this particular wavelength. A large variety of medical and other applications can be found [9-11]

In this paper, we report a spectroscopic study of trivalent erbium and holmium ions in halogeno-phosphate glasses with molar composition: (100-x-y)$NaPO_3$–x$PbCl_2$ –y$BaCl_2$: LnF_3 (Ln=Er or Ho).

2. Experimental details

2.1 Glass preparation

Series of halogeno-phosphate glasses with general formula (in mol%): (100-x-y)$NaPO_3$–x$PbCl_2$–y$BaCl_2$: LnF_3 (Ln = Er or Ho) were prepared by melt-quenching technique described in [12,13]. The doping concentration of the rare earth was set at 1 mol %. Synthesis includes a series of classical steps: mixing of starting materials, melting, fining, casting and annealing. The above batch compositions were melted in a platinum tube under room atmosphere.

2.2 Physical measurements

Characteristic temperatures (temperature of glass transition T_g and temperature of onset crystallization T_x) were determined by differential scanning calorimetry (DSC) using DSC TA Instrument. Density was measured by Archimedean method. Refractive index was measured by an Abbe refractometer. Absorption spectra were recorded at room temperature using a double beam spectrophotometer UV-Vis - Near IR CARY 5G brand operating between 200 and 3000 nm. Compositions and properties of glass samples are presented in table 1 and table 2 respectively.

3. Judd-Ofelt theory

It is well known that the different spectroscopic parameters of the trivalent rare-earth ions in various hosts are calculated by the application of the theory proposed by Judd [14] and Ofelt [15]. The detailed assumptions of the theory have been described in original articles. For clarity, a brief summary of the theory is presented, taking into account only the formulas necessary to determine the different spectroscopic parameters: oscillator strengths, Judd-Ofelt parameters, radiative transition probability, branching ration and radiative lifetime.

The majority of the intraconfigurational f-f transitions of trivalent rare earths observed in the absorption spectra are induced electric dipole transitions, although a few magnetic dipole transitions are also present. The intensities of these transitions can be described by the oscillator strengths f_{mes} of each J→J' transition. The band absorption intensity is proportional to the oscillator strength. Experimentally it is deduced from the surface under the absorption curve. The oscillator strength f_{mes} can be calculated from the value of the absorption coefficient α(λ) at a particular wavelength λ according to the relation:

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

Where m is the electron mass, c is the celerity of the light in the vacuum and e is the electron charge.

On the other side, the oscillator strength can be given in term of the electric dipole line strength S_{ed}:

$$f_{cal} = \frac{8\pi^2 mc}{3h(2J+1)\lambda} \frac{(n^2+2)}{9n} S_{ed} \tag{2}$$

$$S_{ed} = e^2 \sum_{k=2,4,6} \Omega_k \left| \langle J' \| U^{(k)} \| J \rangle \right|^2 \tag{3}$$

Where Ω_k (k = 2, 4 and 6) are phenomenological intensity coefficients, generally known under the name of Judd-Ofelt parameters that are dependent on both the chemical environment and the lanthanide ion [16]. The factor $(n^2+2)/9n$ takes into account the fact that the rare earth ion is not in a vacuum, but in a dielectric medium, n being the refractive index of this medium. $U^{(k)}$ are the components of the reduced tensorial operator that are independent of ligand field. The values of $U^{(k)}$ are usually considered to be host invariant and they are tabulated [17]. h is the Planck's constant and λ is the average wavelength of the transition.

The values of the Ω_k are empirically determined by comparing the computed values starting from the formula (2) with the values obtained from the absorption spectra at ambient temperature of the oscillator strengths (formula (1)). If q is the number of the absorption bands considered in experiments, the resolution of a system of q equation to 3 unknown factors, by a least square approximation, makes it possible to obtain the values of the parameters Ω_k. These parameters are expressed in cm^2. A measure of the accuracy of the fit is given by the root mean square deviation (RMS):

$$RMS = \sqrt{\frac{\sum (f_{cal} - f_{mes})^2}{q-3}} \tag{4}$$

The values of Judd-Ofelt parameters obtained are used to calculate the line strength of the transitions between the initial state J and the final state J' using the equation (3). The probabilities of the radiative transitions are given by the equation:

$$A_{rad}(J, J') = \frac{64\pi^4}{3h(2J+1)\lambda^3} \left[\frac{n(n^2+2)^2}{9} \right] S_{ed} \tag{5}$$

The branching ratios can be obtained from the probabilities of radiative transitions A_{rad} by the equation:

$$\beta = \frac{A_{rad}(J, J')}{\sum_{J'} A_{rad}(J, J')} \tag{6}$$

The radiative lifetime of the level J is given by:

$$\tau_{rad} = \frac{1}{\sum_{J'} A_{rad}(J, J')} \tag{7}$$

Another term, integrated emission cross-section (in m), which is particularly useful to determine the possibility of lasing in glass, is defined as:

$$\Sigma = \frac{\lambda^2}{8\pi c n^2} A_{rad}(J, J') \tag{8}$$

When the value of the integrated emission cross-section is close to or greater than $\sim 10^{-20}$ m, there is a possibility of lasing [18].

Table 1. Compositions of glass samples

Name of series	Glass compositions (mol%)				
	$NaPO_3$	$PbCl_2$	$BaCl_2$	HoF_3	ErF_3
NPE1	90	9	0	0	1
NPBE1	80	9	10	0	1
NPH1	90	9	0	1	0
NPBH1	80	9	10	1	0

Table 2.Physical and thermal properties of glass samples

Sample	Density (g/cm^3)	Refractive Index	T_g (C°)	T_x (C°)	ΔT (C°)
NPE1	2,907	1,525	273	375	102
NPBE1	3,056	1,528	270	380	110
NPH1	2,894	1,521	264	358	94
NPBH1	2,981	1,522	279	384	105

4. Results and discussions

4.1 Thermal stability

Fig. 1.shows the DSC graphs of glass samples. The values of T_g, T_x and $\Delta T=T_x-T_g$ are shown in Table 2.

Determination of T_g and T_x is interesting for many reasons; in practical terms, T_g is a measure of approximate upper use temperature for a given composition, and annealing of glass samples is carried out somewhat below T_g. T_x defines a safe upper limit for processing the melt if devitrification is to be avoided. The quantity ΔT (T_x-T_g) has frequently been used as a rough measure of the glass forming ability of a melt, i.e., of resistance to devitrification during casting. For this reason, it is frequently used as an assessment criterion to determine the stability of glass. Since fiber drawing is a reheating process and any crystallization during the process will increase the scattering loss of the fiber and then degrades the optical quality[19]. To achieve a large working range during operations such as fiber fabrication or the preparation of bulk glass articles, it is desirable to have (T_x-T_g) as large as possible. From the Table 2, we can see that all glass samples have relatively a large value of ΔT (nearby or greater than ~100°C), indicating that these glass samples are stable against devitrification.

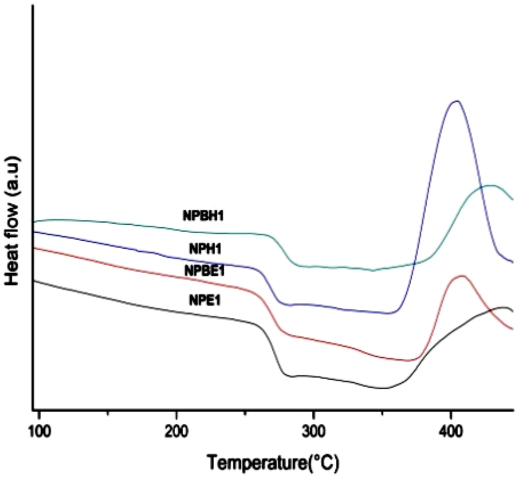

Fig. 1. Differential scanning calorimetry graphs of NPE1, NPBE1, NPH1 and NPBH1 glasses

4.2 Absorption spectra and Judd-Ofelt analysis

Absorption spectra of the Er^{3+} and Ho^{3+} doped glass samples are shown in Fig. 2 and Fig. 3 respectively.

The spectroscopic properties of our glass samples were determined with the aid of the Judd-Ofelt model. The use of this model requires that several physical properties are previously measured. This includes refractive index, density, and UV/Visible absorption spectrum. The results of these measurements as well as those obtained from the Judd-Ofelt analysis are reported in Tables 2, 3, 4, 5 and 6. A Fortran code was used to obtain the Judd-Ofelt parameters by solving the system of equations described in the previous section [20].

The f-f transitions are considered to be electric dipole in nature, because the magnetic dipole oscillator strength (f_{md}) will be relatively small [21]. For that reason in the present work, these magnetic dipole line strengths have not been considered. From the Tables 3 and 4 we can see that the low RMS values suggest the good agreement between calculated and experimental oscillator strengths of Er^{3+} and Ho^{3+} ions in our glasses samples.

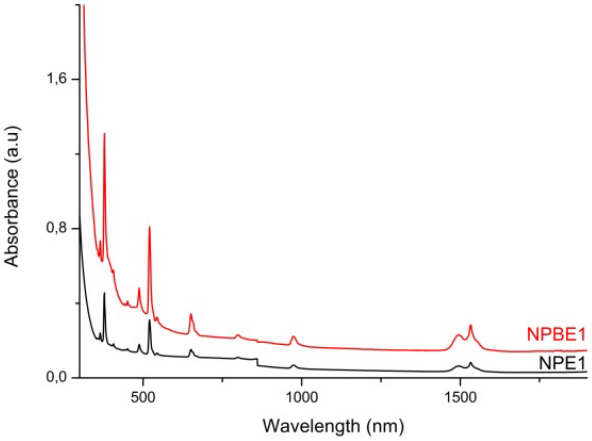

Fig. 2. Absorption Spectra of Er^{3+} doped NPE1 and NPBE1 glasses

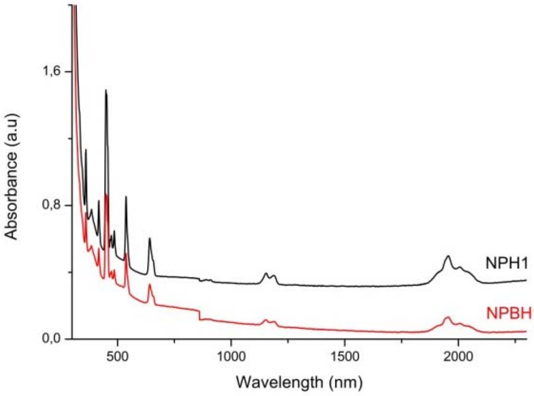

Fig. 3. Absorption Spectra of Ho^{3+} doped NPH1 and NPBH1 glasses.

The Judd-Ofelt parameters Ω_k (k =2, 4, 6) mainly depend on the host glass composition and they can provide versatile information regarding the rare earth containing glass structure. Some empirical correlations of the Judd-Ofelt parameters and the local structure of the rare earth ions have been reported in literature [22-25]. Generally, Ω_2 is an indicator of the covalency of the rare earth-ligand bonds. In our present study, no clear conclusions can be extracted from Ω_2 parameter of Ho^{3+} doped glasses, because the observed Ω_2 values are located between the higher side to the values reported for ionic glasses (for fluoride glasses, Ω_2~2x10^{-20}cm² [26]) and those of the covalent glasses (for phosphates Ω_2~5x10^{-20}cm² [27]). While the observed Ω_2 values of Er^{3+} doped glasses are found close to those of ionic glasses (for fluoride glasses, Ω_2~2x10^{-20}cm² [28]).

Table 3. Measured and calculated oscillator strength for Ho^{3+} ions in NPH1 and NPBH1 glasses

$^5I_8$→	λ (nm)	Oscillator strength f (x10^{-6})			
		NPH1		NPBH1	
		f_{mes}	f_{cal}	f_{mes}	f_{cal}
$^5I_7$	1957	1,454	1,386	1,040	0,999
$^5I_6$	1155	0,765	1,012	0,593	0,739
$^5F_5$	642	2,364	2,864	1,571	1,818
$^5F_4$	538	3,371	3,030	2,366	2,050
$^5F_3$	486	1,203	1,080	0,716	0,812
$^5F_2$,$^3K_8$	472	0,681	0,668	0,323	0,503
$^5G_6$	448	16,752	17,137	9,611	9,700
$^5G_5$	418	2,937	2,895	1,525	1,537
$^5G_4$	386	1,586	0,364	0,589	0,223
$^3H_6$	360	5,234	3,246	2,281	1,822
RMS (x10^{-6})		0,928		0,287	

On the other hand, Ω_4 and Ω_6 relate to the rigidity of the host matrices. They depend on bulk properties such as viscosity and dielectric constant of the media. They are also affected by the vibronic transitions of the rare earth ions bound to the ligand atoms. According to the theory of Jacobs and Weber [22], the rare earth emission intensity can be characterized uniquely by Ω_4 and Ω_6 parameters. Thus, we used the so-called spectroscopic quality factor (Ω_4/Ω_6). This factor is important in predicting the behavior of various lasing transitions in a given matrix. The values of (Ω_4 /Ω_6) for the glasses studied are given in the table 5. Based on this factor, it is found that the NPE1glass (doped with Er^{3+}) and the NPH1 (doped with Ho^{3+}) appear to be better optical glasses.

Predicted radiative transition probability, Branching ratio, integrated emission cross-section and radiative lifetime for $^5I_7$→$^5I_8$ transition of Ho^{3+} in glasses are presented in Table 5. The value of Σ is greater than ~10^{-20} m, which indicates a possibility of lasing with this glasses. But it must be mentioned that lasing can be specifically determined only if emission cross-section and fluorescence lifetime are taken into account.

Radiative life times are found to be 15.72ms and 10.55ms for NPH1 and NPBH1glasses respectively. For comparison, these values are close to the values reported for alumino–germano-silica glass (15.51ms) [18] and greater than those of heavy-metal gallate glasses (5.42ms) [4] and lead–germano–tellurite glass (3.7ms) [1].

Table 4. Measured and calculated oscillator strength for Er^{3+} ions in NPE1 and NPBE1 glasses

$^4I_{15/2}$→	λ (nm)	Oscillator strength f (x10^{-6})			
		NPE1		NPBE1	
		f_{mes}	f_{cal}	f_{mes}	f_{cal}
$^4I_{13/2}$	1533	1,607	1,031	1,989	1,098
$^4I_{11/2}$	974	0,401	0,507	0,400	0,541
$^4I_{9/2}$	800	0,159	0,237	0,167	0,205
$^4F_{9/2}$	651	1,583	1,538	1,563	1,472
$^4S_{3/2}$	544	0,246	0,392	0,164	0,426
$^3H_{11/2}$	520	6,473	6,486	6,654	6,352
$^4F_{7/2}$	488	1,385	1,552	1,195	1,615
$^4F_{5/2}$	451	0,233	0,477	0,272	0,518
$^2H_{9/2}$	406	0,353	0,585	0,496	0,624
$^4G_{11/2}$	378	11,486	11,480	11,072	11,245
RMS (x10^{-6})		0,240		0,425	

Table 5. Judd-Ofelt parameters of Er^{3+} and Ho^{3+} in glass samples

Sample	Ω_2 (x10^{-20} cm^2)	Ω_4 (x10^{-20} cm^2)	Ω_6 (x10^{-20} cm^2)	Ω_4/Ω_6
NPE1	2,031	0,527	0,489	1,087
NPBE1	2,017	0,449	0,531	0,846
NPH1	4,280	2,654	1,746	1,520
NPBH1	2,442	1,407	1,312	1,072

Table 6. Predicted radiative transition probability, Branching ratio, integrated emission cross-section and radiative lifetimes for $^5I_7$→$^5I_8$ transition of Ho^{3+} in NPH1 and NPBH1 glass samples

Sample	A(s)	β(%)	Σ (x 10^{-20} m)	τ (ms)
NPH1	63,6	1	1,39	15,72
NPBH1	94,7	1	2,07	10,55

5. Conclusion

New series of rare earth doped halogeno- phosphate glasses: (100-x-y) $NaPO_3$ – x $PbCl_2$– y $BaCl_2$: LnF_3 (Ln=Er or Ho) have been investigated and characterized. Both series exhibit a good thermal stability against devitrification. Spectroscopic properties of Er^{3+} and Ho^{3+} in these glasses were investigated. The Judd–Ofelt intensity parameters Ω_k (k = 2, 4 and 6), spontaneous emission probability, integrated emission cross-section and radiative lifetimes were calculated. Spectroscopic quality factor (Ω_4/Ω_6) was determined to be 1.087 and 0.846 for the Er^{3+} doped NPE1 and NPBE1 glasses respectively, and to be 1.520 and 1.072 for the Ho^{3+} doped NPH1 and NPBH1 glasses respectively. On the basis of these results, these glasses appear as potential lasing materials and offer prospects for photonics applications.

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