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# Thermal stability and spectroscopic study of Ho<sup>3+</sup>/Yb<sup>3+</sup> co-doped fluorophosphates glasses

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## ABSTRACT

Holmium/Ytterbium co-doped fluorophosphate glasses with compositions (80-x-y) NaPO<sub>3</sub>-10SrF<sub>2</sub>-10ZnF<sub>2</sub>-xHoF<sub>3</sub>-yYbF<sub>3</sub> (x = 1 and y = 0.5, 1, 1.5 and 2 mol%) were prepared by melt-quenching technique. The stability criteria indicate that these glasses exhibit a good resistance against devitrification. Densities of glasses were determined and showed an almost linear variation with increase of YbF<sub>3</sub> content. Spectroscopic parameters of Ho<sup>3+</sup> such as radiative transition probability, branching ratio, spectroscopic quality factor, integrated emission cross section and radiative lifetime, were calculated on the basis of Judd-Ofelt analysis. The results showed that these glasses could be proposed as suitable lasing materials. © 2017 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Rare earth ions doped glasses have a potential application in different fields as a solid state lasers, optical fiber amplifiers and waveguide lasers. Rare earth ions are used as doping agents because of their various transitions in the visible and infrared regions and their insensitivity to the matrix in which are introduced. Up to now, a variety of glassy materials such as silicate (Bai et al., 2011), phosphate (Rivera-López et al., 2011; Hraiech et al., 2013), fluoride (Mortier et al., 2007; Reichert et al., 2015), chalcogenide (Li et al., 2016; Ari et al., 2017), tellurite (Meruva et al., 2014; Costa et al., 2015; Sajna et al., 2016), germanate (Fan et al., 2011, 2015) and halogeno-phosphates glasses (Babu and Ratnakaram, 2016; Galleani et al., 2017) have been investigated as host materials for rare earth ions in the aim to developing of optical devices. Among different glassy host materials, halogeno-phosphates glasses offer significant advantages. They are easily prepared by introducing selected metal halides (fluoride in our

case) into polyphosphate glasses. These glasses exhibit low phonon energy than that of phosphate glasses and a less complex fabrication route than that of fluoride glasses and can accept a high concentration of rare earth ions which can improve or induce new optical properties (Poulain et al., 1992; Kenyon, 2002; Dwivedi et al., 2010; Polishchuk et al., 2011; Galleani et al., 2017).

Solid state lasers operating at 2 μm wavelength has attracted so much attention in recent years owing to their potential applications in several fields such as eye safe laser radars, remote sensing, military, atmospheric pollution detection, medical surgery, etc (Tian et al., 2010; Wu et al., 2012; Ryabochkina et al., 2017). Efficient 2 μm emission required an appropriate rare earth ions and host materials. 2 μm laser emission can be achieved in some rare earth ions such as Ho<sup>3+</sup> with the transition <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> (Fan et al., 2015). However, Ho<sup>3+</sup> ions have no corresponding absorption energy levels to be pumped directly by the commercial 800 nm or 980 nm laser diode (LD). Thus, Co-doping with other rare earth ions such as Tm<sup>3+</sup> (Seshadri et al., 2014; Chen et al., 2016) and Yb<sup>3+</sup> (Žmojda et al., 2012; Pandey et al., 2016) ions can sensitize efficiently Ho<sup>3+</sup> to achieve 2 μm emission. Yb<sup>3+</sup> is frequently chosen as a sensitizer because this ion has a strong absorption band around 980 nm, and the Yb<sup>3+</sup>: <sup>2</sup>F<sub>5/2</sub> level is close to the Ho<sup>3+</sup>: <sup>5</sup>I<sub>6</sub> level which can provide an efficient energy transfer from Yb<sup>3+</sup> to Ho<sup>3+</sup> ions.

A several number of recent studies reporting the spectroscopic properties of Ho<sup>3+</sup> doped glasses and Ho<sup>3+</sup> doped glasses sensitized with either Tm<sup>3+</sup>, Yb<sup>3+</sup> or Er<sup>3+</sup> are available in the literature

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(Babu and Ratnakaram, 2016; Bai et al., 2011; Chen et al., 2016; Gandhi et al., 2010; Hemming et al., 2014; Rai et al., 2003; Satyanarayana et al., 2010). Furthermore, to our knowledge, there are few number of investigations on  $\text{Ho}^{3+}/\text{Yb}^{3+}$  co-doped fluorophosphate glasses (Gómez et al., 2009; Tian et al., 2010; Wang et al., 2011). In this work we report thermal and spectroscopic studies of a new composition of fluorophosphate glasses co-doped  $\text{Ho}^{3+}/\text{Yb}^{3+}$  with doping concentration of  $\text{Yb}^{3+}$  varied from 0.5 mol% up to 2 mol% while the doping concentration of  $\text{Ho}^{3+}$  is kept constant at 1 mol%.

## 2. Experimental

### 2.1. Glass preparation

Samples of fluorophosphate glasses with general formula (in mol%):  $(80-x-y) \text{NaPO}_3-10\text{SrF}_2-10\text{ZnF}_2-x\text{HoF}_3-y\text{YbF}_3$  ( $x = 1$  and  $y = 0.5, 1, 1.5$  and  $2$  mol%) were prepared using high-purity of  $\text{NaPO}_3$ ,  $\text{SrF}_2$ ,  $\text{ZnF}_2$ ,  $\text{HoF}_3$  and  $\text{YbF}_3$  powder. The doping concentration of the rare earth was set at 1 mol% for  $\text{Ho}^{3+}$  ions and varying from 0.5 to 2 mol% for  $\text{Yb}^{3+}$  ions. A stoichiometric mixture of the starting materials (about 10 g) is placed in a platinum crucible and melted at  $900^\circ\text{C}$  for 15 min. The melts were cast on preheated brass molds at a temperature  $10^\circ\text{C}$  below the glass transition temperature. Thermal annealing of the samples is performed for several hours, in order to eliminate the internal stresses of mechanical or thermal origins created during quenching, following by a slow cooling to room temperature. After annealing, the glass samples were cut and polished. The samples obtained after polishing have parallel faces allowing the optical characterization. In the other hand, some local defects, such as scratches and unevenness, are difficult to avoid.

### 2.2. Measurements

The 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 with a programmed heating rate of  $10^\circ\text{C}/\text{min}$ . The accuracy on the temperature is about  $\pm 2^\circ\text{C}$ . Density was measured by Archimedeon method with an accuracy of  $\pm 0.001$ . Refractive index was measured by an Abbe refractometer with a mean error  $\pm 0.001$ . 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 with a spectral resolution of 0.1 nm.

## 3. Results

### 3.1. Glass samples

Fig. 1 shows all the samples: non-doped, doped with  $\text{Ho}^{3+}$  only and co-doped  $\text{Ho}^{3+}/\text{Yb}^{3+}$ . Compositions of glass samples were presented in Table 1.

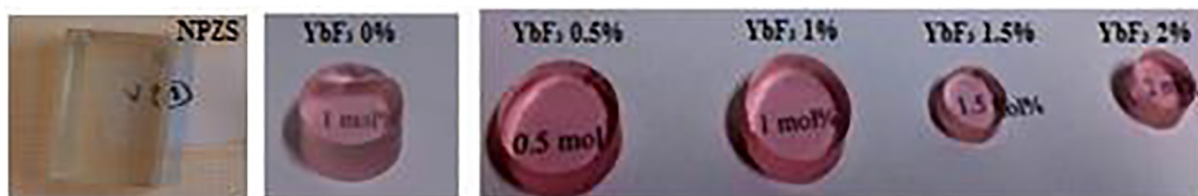


Fig. 1. Fluorophosphates glass Samples.

### 3.2. Thermal properties, density and refractive index

Fig. 2 represents the DSC curves of the samples: without any doping ions (dash-dotted line), doped with  $\text{Ho}^{3+}$  only (dotted line) and  $\text{Ho}^{3+}/\text{Yb}^{3+}$  co-doped (with 1 mol%  $\text{YbF}_3$ , solid line). Glass transition temperature  $T_g$  for NPSZ-HYy series still situated around  $250^\circ\text{C}$  and the crystallization onset  $T_x$  around  $450^\circ\text{C}$ .

The values of refractive index and the density of glass samples were presented in Table 2. The results show a small almost linear variation of refractive index and density with the variation of  $\text{YbF}_3$  content.

### 3.3. Absorption spectra and Judd-Ofelt analysis

The absorption spectra are shown in Fig. 3. We can count ten absorption bands centered at 1957, 1155, 642, 538, 486, 472, 448, 418, 386 and 360 nm corresponding to the optical transitions of the  $\text{Ho}^{3+}$  ion from its ground state  $^5\text{I}_8$  to the different excited states:  $^5\text{I}_7$ ,  $^5\text{I}_6$ ,  $^5\text{F}_5$ ,  $^5\text{F}_4$ ,  $^5\text{F}_3$ , ( $^5\text{F}_2$ ,  $^3\text{K}_8$ ),  $^5\text{G}_6$ ,  $^5\text{G}_5$ ,  $^5\text{G}_4$  and  $^3\text{H}_6$  respectively. We can also observe an absorption band at 980 nm correspond to the transition  $^2\text{F}_{7/2}$  to  $^2\text{F}_{5/2}$  of the  $\text{Yb}^{3+}$  ion in the four co-doped samples.

The different spectroscopic parameters of the trivalent rare-earth ions in various hosts can be calculated by the application of the theory proposed by Judd (Judd, 1962) and Ofelt (Ofelt, 1962). The detailed assumptions of the theory have been described in original articles. A brief summary of the theory will present below taking into account only the formulas necessary to determine the different spectroscopic parameters.

The intensities of intraconfigurational  $f-f$  transitions of trivalent rare earths observed in the absorption spectra can be described by the oscillator strengths  $f_{mes}$  of each  $J \rightarrow J'$  transition. The majority of these transitions are induced electric dipole transitions, although a few magnetic dipole transitions are also present. From the absorption spectra, we can calculate the oscillator strength  $f_{mes}$ , which is proportional to the band absorption intensity, from the value of the absorption coefficient  $\alpha(\lambda)$  at a particular wavelength  $\lambda$  according to the formula:

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

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  $S_{ed}$ :

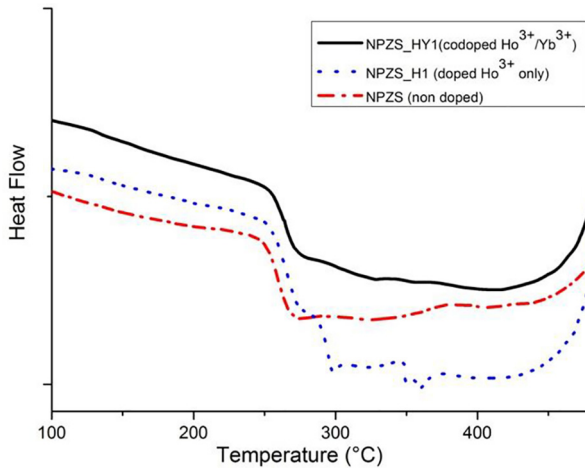
$$f_{cal} = \frac{8\pi^2 mc}{3h(2J+1)\lambda} \frac{(n^2+2)}{9n} S_{ed} \quad (2)$$

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

where  $\Omega_k$  ( $k = 2, 4$  and  $6$ ) are known as Judd-Ofelt parameters. These parameters are dependent on both the chemical environment and the lanthanide ion (de Sá et al., 2000). The factor  $(n^2+2)/9n$  takes

**Table 1**  
Compositions of glass samples.

Name of the sample	Glass compositions (mol%)				
	NaPO <sub>3</sub>	SrF <sub>2</sub>	ZnF <sub>2</sub>	HoF <sub>3</sub>	YbF <sub>3</sub>
NPZS	80	10	10	0	0
NPZS_H1	79	10	10	1	0
NPZS_HY0.5	79.5	10	10	1	0.5
NPZS_HY1	78	10	10	1	1
NPZS_HY1.5	77.5	10	10	1	1.5
NPZS_HY2	77	10	10	1	2



**Fig. 2.** DSC Curves of the non-doped, Ho<sup>3+</sup> doped and Ho<sup>3+</sup>/Yb<sup>3+</sup> co-doped glass samples.

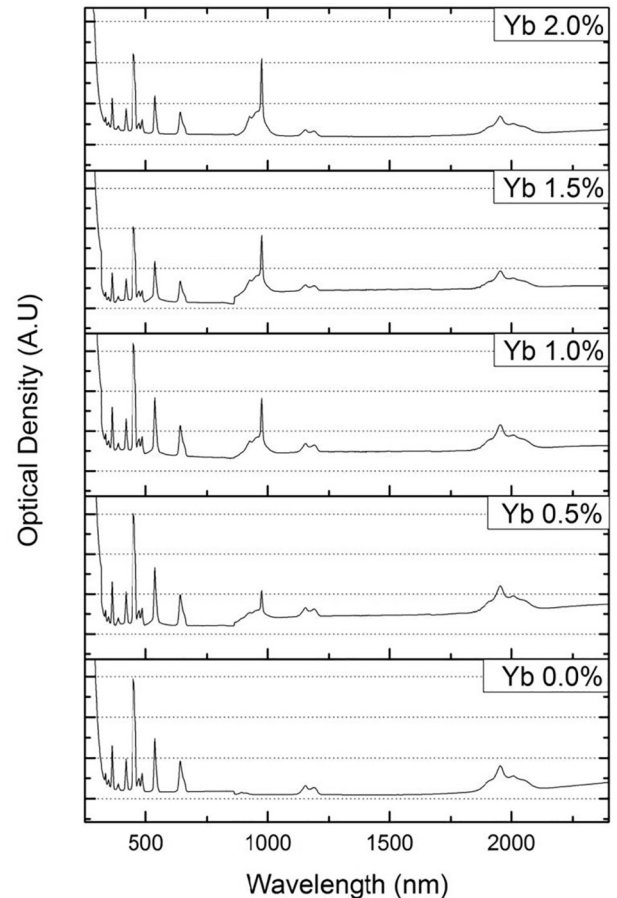
**Table 2**  
Refractive index and density of glass samples.

Samples	Refractive index ±0.001	Density (g/cm <sup>3</sup> ) ±0.001
NPZS	1.494	2.772
NPZS_H1	1.495	2.803
NPZS_HY0.5	1.493	2.820
NPZS_HY1	1.494	2.859
NPZS_HY1.5	1.495	2.883
NPZS_HY2	1.496	2.904

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 which are independent of ligand field. The values of  $U^{(k)}$  are usually considered to be host invariant and they are tabulated (Carnall et al., 1968, 1965).  $h$  is the Planck's constant and  $\lambda$  is the average wavelength of the transition.

The values of the  $\Omega_k$  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  $\Omega_k$ . These parameters are expressed in cm<sup>2</sup>. A measure of the accuracy of the fit is given by the root mean square deviation (RMS):

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



**Fig. 3.** Absorption spectra of NPZS\_HY samples.

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 Eq. (3). The probabilities of the radiative transitions are given by the equation:

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

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

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

The radiative lifetime of the level  $J$  is given by:

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

**Table 3**Measured and calculated oscillator strength for Ho<sup>3+</sup> ions in NPSZ\_HY samples.

Transition: <sup>5</sup> I <sub>8</sub> →	λ(nm)	Oscillator strength $f(\times 10^{-6})$									
		NPZS_H1		NPZS_HY0.5		NPZS_HY1		NPZS_HY1.5		NPZS_HY2	
		$f_{mes}$	$f_{cal}$	$f_{mes}$	$f_{cal}$	$f_{mes}$	$f_{cal}$	$f_{mes}$	$f_{cal}$	$f_{mes}$	$f_{cal}$
<sup>5</sup> I <sub>7</sub>	1957	1.1951	1.30792	1.2529	1.5595	1.2983	1.5987	1.3064	1.8003	1.2161	1.4308
<sup>5</sup> I <sub>6</sub>	1155	0.5946	0.96128	0.6883	1.1498	0.6651	1.1765	0.6861	1.3338	0.6485	1.051
<sup>5</sup> F <sub>5</sub>	642	2.3739	2.57079	2.6415	3.0311	2.6752	3.1015	2.6738	3.3458	2.6391	2.8484
<sup>5</sup> F <sub>4</sub>	538	3.3668	2.79476	4.5804	3.3199	4.8053	3.4026	5.6358	3.7506	3.9579	3.0808
<sup>5</sup> F <sub>3</sub>	486	0.8187	1.04389	0.3176	1.2556	0.4405	1.2903	0.3395	1.4719	0.6037	1.1409
<sup>5</sup> F <sub>2</sub> , <sup>3</sup> K <sub>8</sub>	474	0.5251	0.64620	0.6064	0.7773	0.1951	0.7987	0.3039	0.9112	0.4084	0.7063
<sup>5</sup> G <sub>6</sub>	448	12.4917	12.70179	13.331	13.625	12.587	12.869	13.473	13.743	13.006	13.292
<sup>5</sup> G <sub>5</sub>	418	2.3285	2.42021	2.5453	2.7951	2.5716	2.8468	2.5617	2.8813	2.5005	2.719
<sup>5</sup> G <sub>4</sub>	386	0.3533	0.32203	0.7069	0.3781	0.6512	0.3865	0.8467	0.4116	0.7537	0.3579
<sup>3</sup> H <sub>6</sub>	362	3.4714	2.37699	4.0711	2.5256	3.8578	2.3779	3.9563	2.5319	3.9731	2.484
RMS ( $\times 10^{-6}$ )		±0.511		±0.8946		±0.9261		±1.1160		±0.7466	

**Table 4**Judd-Ofelt parameters ( $\Omega_k \times 10^{-20} \text{cm}^2$ ) of Ho<sup>3+</sup> doped NPSZ\_HY samples and other glasses.

Sample	$\Omega_2$	$\Omega_4$	$\Omega_6$	$\Omega_4/\Omega_6$	Trend
NPZS_H1 (present work)	3.03	2.26	1.72	1.31	$\Omega_2 > \Omega_4 > \Omega_6$
NPZS_HY0.5 (present work)	3.13	2.62	2.07	1.26	$\Omega_2 > \Omega_4 > \Omega_6$
NPZS_HY1 (present work)	2.83	2.66	2.12	1.25	$\Omega_2 > \Omega_4 > \Omega_6$
NPZS_HY1.5 (present work)	3.09	2.69	2.42	1.11	$\Omega_2 > \Omega_4 > \Omega_6$
NPZS_HY2 (present work)	3.07	2.54	1.88	1.35	$\Omega_2 > \Omega_4 > \Omega_6$
Halogeno-phosphate (Bentouila et al., 2013)	2.44	1.40	1.31	1.07	$\Omega_2 > \Omega_4 > \Omega_6$
Phosphate (Reisfeld and Hormadaly, 1976)	5.20	2.72	1.87	1.45	$\Omega_2 > \Omega_4 > \Omega_6$
Germanate (Fan et al., 2015)	4.70	1.63	0.81	2.01	$\Omega_2 > \Omega_4 > \Omega_6$
Fluoride (Florez et al., 2006)	1.56	3.72	2.86	1.30	$\Omega_2 < \Omega_6 < \Omega_4$
Tellurite (Rai et al., 2003)	4.98	0.99	2.96	0.33	$\Omega_4 < \Omega_6 < \Omega_2$

**Table 5**Predicted radiative transition probability, integrated emission cross-section and radiative lifetimes for <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> transition of Ho<sup>3+</sup> ions in NPSZ\_HY samples and other glasses.

Sample	$A_{rad}(s)$	$\beta(\%)$	$\Sigma (\times 10^{-20} \text{ m})$	$\tau_{rad} (\text{ms})$
NPZS_H1 (present work)	57.357	1000	1519	17.435
NPZS_HY0.5 (present work)	68.47	100	1.56	14.60
NPZS_HY1 (present work)	70.21	100	1.60	14.24
NPZS_HY1.5 (present work)	79.25	100	1.80	12.61
NPZS_HY2 (present work)	63.00	100	1.43	15.87
Fluorophosphate (Tian et al., 2010)	73.55	100	–	13.60
Germanate (Fan et al., 2011)	97.84	100	–	10.22
Fluoride (Florez et al., 2006)	109.93	100	–	9.09

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

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

When the value of the integrated emission cross-section is close to or greater than  $\sim 10^{-20} \text{ m}$ , there is a possibility of lasing (Watekar et al., 2008).

The results obtained from the Judd-Ofelt analysis are reported in Tables 3–5.

## 4. Discussions

### 4.1. Thermal stability

Determination of glass transition temperature ( $T_g$ ) and onset crystallization ( $T_x$ ) 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  $T_g$ . In addition,  $T_g$  is an important factor for laser glass. It is reported that a glass with high  $T_g$  has a good thermal stability to resist thermal damage at high pumping power (Xu et al., 2011a,b).  $T_x$  defines a safe upper limit for processing the melt if crystallization is to be avoided. From the DSC curves, one can observe that there is no crystallization peak till  $T = 450 \pm 2^\circ \text{C}$  for all samples,  $T_g$  is about  $247 \pm 2^\circ \text{C}$  and  $T_x$  is about  $460 \pm 2^\circ \text{C}$  for the glass sample without any doping ions and for glasses containing HoF<sub>3</sub> and YbF<sub>3</sub>, the vitreous transition still situated around  $250^\circ \text{C}$  and crystallization onset around  $450^\circ \text{C}$ . One can notice that the glass transition temperature is shifted upwards high temperatures and the onset crystallization is shifted downwards low temperatures by addition of HoF<sub>3</sub> and YbF<sub>3</sub>, results in agreement with previous works (Imanieh et al., 2014). As the changes of  $T_g$  and  $T_x$  is largely depending on the major mixing elements, because the temperature is closely related to the bonding force among the constituent elements, one can explain the shifting of  $T_g$  and  $T_x$  by structure arrangement of glass due to participation of Yb<sup>3+</sup> and Ho<sup>3+</sup> ions and enhanced glassy network structure



(Chen et al., 2014). However, it has been observed that with high concentration of rare-earth, the glass became impossible to pour due to its high instability and during the pouring it could be crystallize to become opaque (Dantelle et al., 2005). Thus, an optimization of rare earth content is necessary to obtain a transparent glass.

The quantity  $\Delta T = T_x - T_g$ , known as the supercooled liquid region, defined as the temperature gap between  $T_g$  and  $T_x$ . It has been used as a rough measure of the glass forming ability of a melt, i.e., of resistance against crystallization during casting (Wang, 2008). Large  $\Delta T$  means strong inhibition to processes of nucleation and crystallization (Park et al., 2010; Xu et al., 2011a,b). For this reason, it is frequently used as an assessment criterion to determine the stability of glass. To achieve a large working range during operations such as fiber fabrication or the preparation of bulk glass articles, it is desirable to have  $\Delta T$  as large as possible. We find that all glass samples have relatively a large value of  $\Delta T$  ( $\sim 200$  °C) close to the value obtained for fluorophosphate glasses (Tian et al., 2010; Chen et al., 2014), which is significantly higher than that of other kinds of rare earth doped fluorophosphate glasses such as  $\text{Tm}^{3+}$  (Liao et al., 2007). This result means that all our glass samples are stable against crystallization.

From the analysis of DSC curve, we can conclude that thermal properties of our glass samples are good for fiber drawing.

#### 4.2. Absorption spectra and Judd-Ofelt analysis

Absorption spectra of the  $\text{Ho}^{3+}$  and  $\text{Ho}^{3+}/\text{Yb}^{3+}$  co-doped glass samples are shown in Fig. 3. The spectroscopic properties of our glass samples were determined using the Judd-Ofelt model. The  $f$ - $f$  transitions are considered to be electric dipole in nature, because the magnetic dipole oscillator strength ( $f_{md}$ ) will be relatively small (Sooraj Hussain et al., 2006). For that reason in the present work, these magnetic dipole line strengths have not been considered. Measured and calculated oscillator strength for  $\text{Ho}^{3+}$  ions in NPSZ\_HY samples were presented in Table 3. The low RMS values suggest the good agreement between calculated and experimental oscillator strengths of  $\text{Ho}^{3+}$  ions in our glasses samples which indicates the validity of the Judd-Ofelt model for predicting the spectroscopic properties of  $\text{Ho}^{3+}$ .

The Judd-Ofelt parameters  $\Omega_k$  ( $k = 2, 4, 6$ ) are mainly depend on the host glass composition. These parameters can provide versatile information regarding the rare earth in glass structure. Some empirical correlations of the Judd-Ofelt parameters and the local structure of the rare earth ions have been reported in literature (Jacobs and Weber, 1976; Ebendorff-Heidepriem et al., 1998; Malta and Carlos, 2003). Generally,  $\Omega_2$  is an indicator of the covalency of the rare earth-ligand bonds (short-range effect), and it is hypersensitive to the compositional changes in the host materials.  $\Omega_2$  is also related with the symmetry of ligand field in the glass host. According to previous studies (Ebendorff-Heidepriem and Ehrt, 1999),  $\Omega_2$  increase with the increasing of covalency and asymmetry at the rare earth sites. The values for  $\Omega_4$  and  $\Omega_6$  provide some information of the rigidity of the host materials (Wang, 2008). They depend on bulk properties such as viscosity and dielectric constant of the media (long-range effects). They are also affected by the vibronic transitions of the rare earth ions bound to the ligand atoms. In the present work, the Judd-Ofelt parameters  $\Omega_k$  are calculated and compared with those of various  $\text{Ho}^{3+}$  doped glasses, the results were presented in Table 4. One can observe, from the values of  $\Omega_2$  of our samples, that the covalent environment for  $\text{Ho}^{3+}$  is slightly decreased with increasing of  $\text{Yb}^{3+}$  amount in glasses. The observed  $\Omega_2$  values of our samples are located between the higher side to the values reported for ionic glasses (for fluoride glasses,  $\Omega_2 \sim 2 \times 10^{-20} \text{ cm}^2$ ) and those of the covalent glasses (for phosphates  $\Omega_2 \sim 5 \times 10^{-20} \text{ cm}^2$ ). Theoretically, the polarizability of oxide ions is higher than that of fluorine ions, resulting in the

increasing covalence of the bonds between rare earth ions and surrounding ligand from fluoride to phosphate glasses due to substitution of fluorine ions by oxygen ions. As fluorophosphate glasses has both  $\text{O}^{2-}$  and  $\text{F}^-$  ions, the value of  $\Omega_2$  is larger than that of fluoride glass and smaller than that of phosphate glass (Tian et al., 2010). However, the observed lower values of  $\Omega_2$  parameter for  $\text{Ho}^{3+}/\text{Yb}^{3+}$  co-doped NPSZ\_HY glasses compared by those of phosphate glasses indicates that the ligand asymmetry around the rare earth ions in  $\text{Ho}^{3+}/\text{Yb}^{3+}$  co-doped NPSZ\_HY glasses is weaker than those in phosphate glasses. Additionally, a larger modifier ion in phosphate glass gives rise to a larger average between P-O-P chains causing the increasing average Ho-O distance to increase. Such increase in the bond lengths produces weaker local field near rare earth ions and lead to lower value of  $\Omega_2$  (Rao et al., 2012).

According to the theory of Jacobs and Weber (Jacobs and Weber, 1976), the rare earth emission intensity can be characterized uniquely by  $\Omega_4$  and  $\Omega_6$  parameters. Thus, we used the so-called spectroscopic quality factor ( $\Omega_4/\Omega_6$ ). This factor is important in predicting the behavior of various lasing transitions in a given matrix. Based on this factor, it is found that the NPZS\_HY glasses appear to be better optical glasses. Moreover, it is noticed that the values of Judd-Ofelt parameters of our sample glasses follows the trend  $\Omega_2 > \Omega_4 > \Omega_6$  in consistent with that one observed for halogeno-phosphate, phosphate and germanate glasses; nevertheless, it differs from those of fluoride and tellurite glasses.

Table 5 presents the predicted radiative transition probability  $A_r$ , branching ratios  $\beta$ , integrated emission cross-section and radiative lifetimes  $\tau_{rad}$  for  $^5I_7 \rightarrow ^5I_8$  transition of  $\text{Ho}^{3+}$  ions in NPSZ\_HY samples. The results show that the values  $A_{rad}$  of the  $^5I_7$  level of  $\text{Ho}^{3+}$  were 68.4, 70.2, 79.2 and 63.0  $\text{s}^{-1}$ , which are similar to the value found for fluorophosphates glass and smaller than that of germanate and fluoride glasses. It is reasonable to obtain such result because the radiative transition probability is proportional to  $n(n^2 + 2)^2/9$  (Eq. (5) in Section 3.3) and the refractive index of fluorophosphates glasses is usually less than germanate and fluoride glasses. It is evident to find also that the radiative lifetimes of the  $^5I_7$  level of  $\text{Ho}^{3+}$  for NPZS\_HY glasses are greater than those of germanate and fluoride glasses. Further, the radiative lifetimes values for  $\text{Ho}^{3+}/\text{Yb}^{3+}$  co-doped NPZS\_HY glasses are found to be smaller than that for individually  $\text{Ho}^{3+}$  doped NPZS\_H1 glass. This result, which may be explained by the crucial contribution of phonon subsystem, is in agreement with those found by Gandhi et al. (2010) for the measured lifetime of blue, green and red transitions.

The values of the integrated emission cross-sections obtained are greater than  $\sim 10^{-20} \text{ m}$ , which indicates a possibility of lasing with these glasses. But it must be mentioned that lasing can be specifically determined only if emission cross-section and fluorescence lifetime are taken into account.

#### 5. Conclusions

A series of  $\text{Ho}^{3+}/\text{Yb}^{3+}$  co-doped new fluorophosphate glasses have been investigated and characterized. All the prepared samples exhibit a high thermal stability against crystallization compared with other kinds of rare earth doped fluorophosphate glasses. From the absorption spectra, Judd-Ofelt parameters are obtained and discussed. The spectroscopic properties of  $\text{Ho}^{3+}$  in these glasses, such as radiative transition probabilities, integrated emission cross-sections and radiative lifetimes, were calculated and compared with other glasses. Spectroscopic quality factor ( $\Omega_4/\Omega_6$ ) and the integrated emission cross-section were found greater than 1 and about  $10^{-20} \text{ m}$  respectively, which indicates better properties of these glasses as lasing materials.  $\text{Ho}^{3+}/\text{Yb}^{3+}$  co-doped fluorophosphate glasses have predicted radiative lifetimes smaller than that for individually  $\text{Ho}^{3+}$  doped

fluorophosphate glass which may be explained by the crucial contribution of phonon subsystem. Consequently, these results indicate these glasses appear as a potential lasing materials and offer prospects for photonics applications.

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