Preparation and Characterization of Yb$^{3+}$-Doped Metaphosphate Glasses for High Energy and High Power Laser Applications

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ABSTRACT

Ytterbium-doped metaphosphate laser glasses were prepared by the melt-quenching technique and their optical, thermo-mechanical and laser properties were characterized. Linear and non-linear refractive indices, laser-induced damage threshold, microhardness number and thermal expansion co-efficient have been evaluated for 1.0 mol% Yb$_2$O$_3$-doped glass. Low non-linear refractive index, high laser-induced damage threshold and low thermal-expansion coefficient have been noticed. Vickers hardness (4.07 GPa) for the present glass is found to be higher than that of Schott (APG-1; 3.09 GPa) glass and comparable with the Hoya (HAP-4; 4.70 GPa) glass. Higher magnitudes of absorption cross-sections (4.49–1.47 $\times$ 10$^{-20}$ cm$^2$), emission cross-sections (6.08–2.06 $\times$ 10$^{-20}$ cm$^2$) at 975 nm and at 1.0 $\mu$m (1.28–0.63 $\times$ 10$^{-20}$ cm$^2$) have been found along with an acceptable bandwidth (52–58 nm) when the Yb$_2$O$_3$ concentration varied from 0.01 to 1.0 mol%. All the studies reveal that the Yb$^{3+}$-doped metaphosphate laser glasses could be suitable as a gain media for high energy and high power laser applications at $\sim$ 1.0 $\mu$m region.

KEYWORDS: Yb$^{3+}$ Ions, Metaphosphate Glasses, NIR Emission, Optical and Laser Properties.

1. INTRODUCTION

The first observation of laser action has been reported for Nd$^{3+}$-doped silica glass by Snitzer$^1$ in 1961, and makes the 2011 as 50th anniversary of laser glass science and technology. However, the search for glass compositions with new active ions to perform an efficient laser action in the ultraviolet to near infra-red (UV-NIR) region still remains of great interest for a wide variety of applications, such as fusion energy ignition demonstration, fundamental research, material processing, fiber lasers and amplifiers, industrial, medical and sensor fields. Glass materials are very attractive as active media as well as tunable laser sources for the generation of femtosecond laser pulses. The increasing demand for high energy, high power (HEHP), high repetition rate lasers for various applications, mainly, in the inertial confinement thermonuclear fusion reactors and also in laser-plasma X-ray sources, has led to the exploration of new laser materials.

Among potential host materials, phosphate glasses are promising for the development of HEHP and petawatt (PW) lasers due to their optical and laser properties, such as low non-linear refractive index, high stimulated emission cross-section and athermal optical properties. Moreover, the thermo-mechanical properties of phosphate glasses can be further improved by chemical strengthening. In addition, phosphate laser glasses can be produced in larger dimensions and free of platinum inclusions, which drastically improves the resistance to laser damage.$^2$–$^4$ The drawbacks of phosphate glasses are that they exhibit a lower mechanical strength than silicate glasses, which do not allow one to use high average pump powers, and show low resistance to atmospheric moisture. These drawbacks are caused by weak chemical bonds between the main structural elements of phosphate glasses (PO$_4$ tetrahedrons).$^5$ However, diode pumped passively mode locked Yb$^{3+}$:phosphate$^6$ and silicate$^7$ glasses have been used for the generation of femtosecond (fs) lasers.
The most popular Nd\(^{3+}\)-doped glass is limited by a poor thermal conductivity and low wall plug efficiency. Ytterbium-based glasses have attracted increasing interest over the past few years as high field lasers, fiber lasers\(^9\) and ceramic lasers.\(^{10}\) Recently, highly efficient laser action has been perceived at 1028 nm from QX:Yb phosphate glass when pumped by a 0.975 \(\mu m\) fiber-coupled laser diode in end pump geometry at room temperature. Laser slope efficiencies as high as 88% have been obtained, leading to pump-to-laser conversion efficiencies greater than 50%.\(^{11}\) Currently, the research focused on new laser materials doped with Yb\(^{3+}\) ions led to development of diode pumped solid state lasers. Many merits can be attributed to Yb\(^{3+}\)-doped crystals and glasses, which explain why they are being explored and proclaimed as the next generation high power laser materials for Laser Induced Nuclear Fusion.\(^{12}\) Yb\(^{3+}\)-doped heavy metal oxide glasses are very attractive for designing optical fibers in the NIR spectral range due to their high transparency (up to 60%) within the 0.6–8.7 \(\mu m\) range.\(^{13}\) The wide range of transparency is due to relatively low frequency of the maximum phonon energy. The accurate knowledge of the optical, thermal and spectroscopic properties of glasses are important for the design of high-power solid-state lasers, since these properties are directly related to the heat generation.\(^{15,16}\)

Yb\(^{3+}\)-doped phosphate glasses are ultimate materials for HEHP lasers as they exhibit broad absorption and emission cross-sections, small quantum defect (resulting low thermal load) compared to Nd\(^{3+}\) ions (resulting in a low heat generation per excited ion), simple electronic structure (preventing undesired processes, such as excited state absorption, up-conversion, and concentration quenching), broad effective bandwidth (50 nm, allowing the generation of ultra short pulses), long fluorescence lifetime (in particular advantageous for Q-switched lasers and can be utilized to store large energy and gain, etc.),\(^{17}\) high energy storage capacity at the metastable \(2F_{5}\) level and low heat generation. The intense and broad absorption lines allow excitation with high power 0.98 \(\mu m\) diode laser. The broad intensity behaviors indicate a strong influence of electron-phonon contributions.\(^{13}\) The problems relating to Yb\(^{3+}\)-doped laser materials are its quasi-three-level character and relatively small cross-section for stimulated emission compared to those of Nd\(^{3+}\)-doped materials.

Consequently, it is a great challenge to accomplish superior optical and laser properties in Yb\(^{3+}\)-doped metaphosphate laser glasses. In this direction, it is interesting to investigate Yb\(^{3+}\) ions doped metaphosphate laser glasses of base composition (P\(_2\)O\(_5\)-K\(_2\)O-BaO-Al\(_2\)O\(_3\)-Yb\(_2\)O\(_3\)) by means of absorption, luminescence and its associated lifetime. Moreover, the base composition includes ions having high field strength, which allows a laser glass with high damage threshold and eliminates the formation of metallic or semi-conductive inclusions. The non-linear refractive index, thermo-mechanical and laser damage threshold measurements have been performed for 1.0 mol% Yb\(_2\)O\(_3\)-doped glass. The discussion includes comparison among the results obtained in the Yb\(^{3+}\)-phosphate and those of other reported commercial glasses.

2. MATERIALS AND METHODS

Yb\(^{3+}\)-doped metaphosphate glasses with compositions (in mol%): (59-x/2) P\(_2\)O\(_5\)+17.0 K\(_2\)O+(15-x/2) BaO+9.0 Al\(_2\)O\(_3\)+xYb\(_2\)O\(_3\) (where x = 0.01, 0.05, 0.1 and 1.0 referred as PKBAYb001, PKBAYb005, PKBAYb01 and PKBAYb10, respectively) were prepared by conventional melt-quenching technique. High purity metaphosphates (Al(P0\(_3\)\(_2\)), KPO\(_3\) and Ba(P0\(_3\)\(_2\))\(_2\)) and Yb\(_2\)O\(_3\) were used as starting materials for preparation of glasses. About 30 g of raw materials were thoroughly crushed in an agate mortar and the homogeneous mixture was transferred into a platinum crucible and melted in an electric furnace at 1100 °C for 1 h under continuous stirring. Molten glass was air quenched by pouring it onto a preheated brass mold and annealed at 380 °C for 15 h to reduce thermal stress and strains. Then the glass samples were allowed to cool to room temperature (RT). A slab of 10 mm × 10 mm × 2 mm sample was cut from the specimens and both sides were optically polished for the measurements.

Phase modulated spectroscopic ellipsometry (UVISEL \(^{TM}\) 460) was used to measure the refractive index of the sample in the region of 350–800 nm at 65° angle of incidence. The Leica (model:VM 30T) semiautomatic microhardness tester was used to measure Vickers hardness value. TMA instrument (model:TMA-92, M/s Setaram, France) was used to measure linear coefficient of thermal expansion at heating rate of 10 °C/min under continuous flow of Ar atmosphere at 10⁻² mbar pressure. Laser induced damage threshold (LIDT) measurements were carried out with Nd:YAG laser system operating at 1064 nm with beam diameter of 10 mm, pulse energy of 1.6 J, repetition rate of 10 Hz and pulse duration of 7 ns. The laser beam was focused on the sample using plano-convex lens to a diameter of 1160 \(\mu m\). Optical absorption spectra were measured using a Perkin Elmer Lambda-950 spectrophotometer in the range of 900–1070 nm with the resolution of 0.1 nm. NIR emissions were measured by exciting glass samples with 860 nm radiation of Ti:sapphire pumped by a multilinie 10 W Ar+ laser (2060-10 Beam lock Spectra Physics) in the range of 900–1070 nm with 0.05 nm spectral resolution. The NIR emissions were focused with a convergent lens onto a 0.18 m single-grating monochromator (Jobin Yvon Triax180) and the signals detected with the NIR extended photomultiplier tube (Hamamatsu R406). The decay curves were measured by exciting the glass samples with the 950 nm radiation of optical parametric oscillator (EKSPLA/NT342/3/UV) by monitoring the 980 nm emission. The signal was acquired by a digital oscilloscope (LeCroy 200 MHz Oscilloscope) and all the measurements were performed at RT.
3. THEORY

3.1. Optical Properties

3.1.1. Linear and Non-Linear Refractive Indices

Optical glass is generally specified by \( n_d \), the value of refractive index at the helium yellow line (587 nm) and the Abbe number (\( v_d \)). The \( v_d \) is defined as

\[
\nu_d = (n_d - 1)/(n_f - n_c)
\]

(1)

where \( n_f \), \( n_d \) and \( n_c \) are linear refractive indices measured at 486 nm, 587 nm and 656 nm, respectively. \( n_f - n_c \) defines the principal dispersion. Non-linear refractive index is an important parameter to access laser properties of glasses, which can be affected by the refractive index and polarizability of the constituents. When the beam of laser propagates in an optical medium a phase aberration can be built up by a change in the refractive index at higher intensities. This effect degrades the beam focus, nevertheless reducing the extraction efficiency of the laser and increasing the risk of laser-induced damage due to self-focusing. Generally, self-focusing is divided into two types; (i) whole beam self-focusing (producing damage in the laser material) and (ii) localized self-focusing (due to associated damage on optics along the axis of the laser beam). The former describes the natural consequence of the Gaussian shape of many small-aperture laser beams and the latter is associated with the spatial or temporal noise on the beam. The non-linear refractive index plays an important role in the laser designing. Due to higher non-linear refractive index the laser beam will get the self-focusing effect. The non-linear refractive index can be measured by Z-scan technique.\(^{18–20}\) Locally, the refractive index increases in the presence of intense laser beam as given by

\[
n(I) = n + \gamma I
\]

(2)

where ‘\( \gamma \)’ is non-linear refractive index coefficient and ‘\( I \)’ is the intensity of the laser beam. Direct measurement of \( \gamma \) is difficult, therefore, an empirical correlation has been developed. The \( n_f \) and \( \gamma \) are related with the \( n_d \) and \( \nu_d \) as

\[
\gamma = \frac{K(n_f - 1)(n_f^2 + 2)^2}{n_d \nu_d [1.52 + n_f^2 + 2(n_f + 1)\nu_d/6n_d]^{1/2}}
\]

(3)

\[
n_f = cn_d \gamma /40\pi
\]

(4)

where \( K = 2.8 \times 10^{-18} \text{ m}^2/\text{W} \) is an empirically determined constant, \( c \) is the velocity of light.

3.1.2. Linear Co-efficient of Thermal Expansion

The laser glass must have high optical homogeneity to achieve the beam quality necessary to propagate and focus the laser output beam. For laser application, the value of linear co-efficient of thermal expansion (\( \alpha_T \)) should be as low as possible.\(^{20}\) Thermal variations in the laser glass can produce optical distortions by changing the optical path length. Therefore, it is desirable to have a glass with low temperature co-efficient of the optical path length. The linear co-efficient of thermal expansion, \( \alpha_T \), is a measure of change in length of a material per unit length, due to change in temperature. Symbolically represented by \( \Delta L/L_0 \), where \( \Delta L \) is the observed change in length (\( \Delta L = L_f - L_0 \)), the \( \alpha_T \) can be defined as:

\[
\alpha_T = \frac{L_f - L_0}{L_0(T_f - T_0)} = \frac{\Delta L}{L_0 \Delta T}
\]

(5)

3.1.3. Microhardness Measurement

Microhardness measurement is used for probing the hardness of a material on a microscopic scale, using an indentation method. Vicker’s hardness method is widely used for hardness measurement where the Vicker’s hardness number (\( V_{HN} \)) is expressed as

\[
V_{HN} = \frac{1.8544F}{d^2}
\]

(6)

where ‘\( F \)’ is the force in kg and ‘\( d \)’ is the average diagonal length of the indentation mark in mm. Although hardness has been defined in several ways, it is generally accepted that the resistance offered to dislocation motion. There are different contributions of the resistance to the dislocation motion and they can be classified into two types as (i) intrinsic resistance, which depends on some structure insensitive physical parameter of the material and (ii) a disorder parameter, which depends on the concentration of the impurities.

3.1.4. Laser Induced Damage Threshold Testing

The laser induced damage threshold (LIDT) is an important parameter for any laser glass to be used for laser applications. The laser glass can be used in conjugation with high power lasers only if it has a high LIDT. On irradiating a glass with high power lasers, the presence of inclusions as well as self-focusing effect due to \( n_f \) leads to the damage of glass. To avoid LIDT, the laser glass must be precision-polished and free of defects, specifically microscopic inclusions (either metallic or ceramic) left from the melting process.\(^{20}\)

3.2. Spectroscopic Properties

The performance of a Yb\(^{3+}\)-glass laser can be accessed from effective absorption and emission cross-sections of \( 4f^1-4f^3 \) transitions and lifetimes of \( ^2F_{5/2} \) fluorescent level. These parameters can be obtained from absorption and emission spectra. The absorption cross-section for the \( ^2F_{7/2} \) \( \rightarrow ^2F_{5/2} \) transition of Yb\(^{3+}\) ion can be obtained by
using the equation mentioned in Refs. [21, 22]; the emission cross-section \( \sigma_{em}(\lambda) \) can be evaluated from the reciprocity method described by McCumber (McC)\(^2\) method using the measured absorption cross-section \( \sigma_{ab}(\lambda) \) as:

\[
\sigma_{em}(\lambda) = \sigma_{ab}(\lambda) \frac{Z_i}{Z_u} \exp \left( \frac{E_{zz} - \hbar c \lambda^{-1}}{kT} \right) \tag{7}
\]

where \( Z_i \) and \( Z_u \) are the partition functions of the lower (ground) and upper (excited) levels, respectively, \( E_{zz} \) is the zero-line energy, which is equal to the energy separation between the lowest Stark components of the upper and lower levels of the Yb\(^{3+} \) ion, \( h \) and \( k \) are the Planck’s and Boltzmann’s constants, respectively. The ratio of the partition functions \( Z_i/Z_u \) becomes the degeneracy weighing of the two states corresponding to the \( ^2F_{5/2} \rightarrow ^2F_{7/2} \) absorption transitions. Hence, the ratio does not change significantly with the change of chemical compositions and it is equal to 4/3 at RT. The radiative transition probabilities \( (A) \), effective bandwidths \( (\Delta\lambda_{eff}) \) and experimental lifetimes \( (\tau_f) \) are evaluated by using the equations mentioned in Refs. [21, 22].

### 3.3. Laser Performance Parameters

The complete assessment of the laser performance of Yb\(^{3+} \)-doped glasses involves the evaluation of the following laser parameters by using the spectroscopic properties of absorption and emission cross-sections and lifetimes. The minimum fraction of Yb\(^{3+} \) ions that must be excited to balance the gain with the ground state absorption at laser wavelength \( \lambda_0 \) is known as \( \beta_{min} \) and can be expressed as a function of the absorption and emission cross-sections. Another important parameter that characterizes the pumping dynamics is the pump saturation intensity \( (I_{sat}) \), which requires an accurate measurement of the absorption cross-section at the peak wavelength \( \lambda_0 \) and the luminescence lifetime \( (\tau_f) \) of the Yb\(^{3+} \) ion. With the above parameters, the minimum absorbed pump intensity \( (I_{min}) \) can be evaluated.\(^2\) This parameter is used to know the threshold to be reached which takes into account both the absorption and emission properties. The gain coefficient \( (G) \) is closely related to the product of the \( \sigma_{ab}(\lambda_p) \), \( \sigma_{em}(\lambda_0) \) and the \( \tau_f \), which is given by:\(^2\)

\[
G = C \times E_p \times \sigma_{ab}(\lambda_p) \times \tau_f \times \sigma_{em}(\lambda_0) \tag{8}
\]

where \( C \) and \( E_p \) are the RE\(^{3+} \) ion concentration and the pump energy, respectively. It is worth noting that the product of \( \sigma_{ab}(\lambda_p) \times \tau_f \) is proportional to the stored energy and \( \sigma_{em}(\lambda_0) \times \tau_f \) is proportional to the extraction efficiency or figure of merit. The higher stored energy and extraction efficiency is an indication for the glass as laser host material. Therefore, it has been suggested that the laser glass should have high \( G \) value for laser applications.

The wavelength dependent gain cross-section can be expressed as\(^2\)

\[
\sigma_g(\lambda) = \beta \sigma_{em}(\lambda) - (1 - \beta)\sigma_{ab}(\lambda) \tag{9}
\]

where \( \beta \) (0 to 1 with increments of 0.1) denotes the ratio of inverted ions to the total Yb\(^{3+} \) ion density.

Finally, high-intensity lasers produce ultra-intense pulses by concentrating a given amount of optical energy both temporally and spatially. The temporal limit is imposed by the time and bandwidth product as \( \tau_{min} = 1/\Delta\nu = \lambda_0^2/(c \times \Delta\lambda_{ab}) \),\(^2\) where \( \tau_{min} \) is the minimum pulse duration and \( \Delta\nu \) is the effective bandwidth.

### 4. RESULTS AND DISCUSSION

#### 4.1. Optical Properties

The refractive indices are evaluated by using the best-fit parameter of the dispersion formula in the range of 350–800 nm (visible region), shown in Figure 1, and found to be 1.549, 1.546 and 1.545 at 486 nm, 587 nm and 656 nm, respectively. As can be seen from Figure 1, the refractive index is wavelength dependent. Historically, optical systems have been designed with the eye as the visible detector. Therefore, the shape of the dispersion curve in the visible region is of critical importance. The Abbe number (which gives the variation of refractive index with wavelength) has been derived to be 136.5 from Eq. (1), which is higher than those of other reported glasses (Table I). The higher value of \( v_g \) represents low dispersion (low chromatic aberration) in the studied glass.

The \( \gamma \) and \( n_2 \) for the present glasses have been evaluated from Eqs. (3) and (4) yield \( \gamma \) as \( 2.1 \times 10^{-26} \, m^2/W \) and \( n_2 \) as 0.775 \times 10^{-13} \, esu, respectively, compared to those of other reported commercial Kigre QX/Yb,\(^2\) New/Yb\(^{2+} \) and...
Table I. Optical and laser properties of Yb$^{3+}$-glasses.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PKBAYb10 (This work)</th>
<th>LY-12 P-Si-B$^{12}$</th>
<th>New/Yb$^{27}$</th>
<th>Kigre QX/Yb$^{27}$</th>
<th>FP:B2$^{28}$</th>
<th>IOG-2$^{28}$</th>
<th>YP1$^{31}$</th>
<th>YB1$^{31}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index ($n_2$)</td>
<td>1.546</td>
<td>1.550</td>
<td>1.530</td>
<td>1.535</td>
<td>1.510</td>
<td>1.518</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abbe number ($n_2$)</td>
<td>136.5</td>
<td>43.2</td>
<td>64</td>
<td>66</td>
<td>62.7</td>
<td>66.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration (N, $\times 10^{20}$ ions/cc)</td>
<td>3.0</td>
<td>4.2</td>
<td>3.10</td>
<td>14.5</td>
<td>16.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-linear refractive index ($n_2$, 10$^{-13}$ esu)</td>
<td>2.1</td>
<td>3.51</td>
<td>4.04</td>
<td>3.19</td>
<td></td>
<td></td>
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<tr>
<td>Vickers hardness ($V_{HN}$, GPa)</td>
<td>4.07</td>
<td>68</td>
<td>108</td>
<td>83</td>
<td>8.9</td>
<td>12.5</td>
<td>10.8</td>
<td>6.5</td>
</tr>
<tr>
<td>Thermal expansion temperature ($T_e$, °C)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Laser induced damage threshold (GW/cm$^2$)</td>
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<tr>
<td>Laser damage fluency (J/cm$^2$)</td>
<td>11.41</td>
<td>&gt; 8</td>
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<td></td>
<td></td>
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<tr>
<td>peak absorption wavelength ($\lambda_{abs}$, nm)</td>
<td>975</td>
<td>966</td>
<td>974</td>
<td>976</td>
<td>980</td>
<td>975</td>
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<tr>
<td>peak emission wavelength ($\lambda_{em}$, nm)</td>
<td>975</td>
<td>1028</td>
<td>1000</td>
<td>1053</td>
<td>1053</td>
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<tr>
<td>Extraction wavelength ($\lambda_{ex}$, nm)</td>
<td>1000</td>
<td>1028</td>
<td>55</td>
<td>66</td>
<td></td>
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<tr>
<td>Effective bandwidth ($\Delta\lambda_{ex}$, nm)</td>
<td>55</td>
<td>66</td>
<td>2.2</td>
<td>2.0</td>
<td>0.87</td>
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<td>Fluorescence lifetime ($\tau_f$, ms)</td>
<td>0.85</td>
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<tr>
<td>Radiative transition probability ($A$, s$^{-1}$)</td>
<td>521</td>
<td>883</td>
<td>1.47</td>
<td>1.06</td>
<td>1.41</td>
<td>1.65</td>
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<tr>
<td>Absorption cross-section ($\sigma_{abs}$, 10$^{-20}$ cm$^2$)</td>
<td>1.47</td>
<td></td>
<td>2.06</td>
<td>0.53</td>
<td>0.50</td>
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<tr>
<td>Emission cross-section at $\lambda_e$ ($\sigma_{em}(\lambda_e)$, 10$^{-20}$ cm$^2$)</td>
<td>2.06</td>
<td></td>
<td>0.63</td>
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<tr>
<td>Emission cross-section at $\lambda_0$ ($\sigma_{em}(\lambda_0)$, 10$^{-20}$ cm$^2$)</td>
<td>0.63</td>
<td></td>
<td>0.54</td>
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<tr>
<td>$\sigma_{em}$ at $\lambda_0$, cm$^2$ ms</td>
<td>0.54</td>
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fluorophosphates (B2:4P$_2$O$_7$–7Al$_2$O$_3$–4Nb$_2$O$_5$–10LiF–10MgF$_2$–24CaF$_2$–1Yb$_2$O$_3$) glasses. The present glass possesses low value of $n_2$, which is desirable for laser applications.

The coefficient of thermal expansion ($\alpha_T$) is controlled by atomic and molecular vibrations. As the temperature increases the amplitude of vibration increases. However, the covalently bonded structures contain spaces in which vibrations can be accommodated, reducing the thermal expansion coefficient. Moreover, the thermal expansion characteristics of the glasses are controlled by composition, structure and thermal treatment. The obtained values of $\alpha_T$ and glass transition temperature ($T_g$) are found to be 11.7 $\times$ 10$^{-6}$/°C and 522 °C, respectively. As can be seen from Table I, the value of $\alpha_T$ for Yb$^{3+}$:PKBAYb10 glass is found to be lower than those found in LY-2 (P-Si-B)$^{12}$ New/Yb$^{27}$ Kigre QX/Yb$^{27}$ IOG-2$^{28}$ and higher than commercial YP1$^{31}$ and YB1$^{31}$ glasses.

The geometry of Vicker’s microhardness indenter is shown in Figure 2. The hardness value measured from the observed size of the impression remaining after a loaded indenter has penetrated and removed from the surface. All the measurements were taken at the load of 50 g and dwell time of 5 s at RT. The values specified are the average values of 10 independent indentations made on the sample under identical loading conditions. Vicker’s hardness ($V_{HN}$) value of 415 kg/mm$^2$ or 4.07 GPa is obtained for the Yb$^{3+}$:PKBAYb10 glass which is better than the Schott glasses.
glass (APG-1; 315 kg/mm² or 3.09 GPa) and comparable with fluorophosphate (FP; 4.16 GPa) B28 and lower than Hoya (HPG-4; 479 kg/mm² or 4.70 GPa)32 glass.

Damage testing was performed in the single pulse damage ("1-on-1") regime. The sample was moved after each shot to provide a fresh position of the sample in each laser irradiation. The pulse energy increased slowly in subsequent pulses till damage occurs. Figure 3 shows a schematic diagram of the damage testing system. A Q-switched Nd:YAG single-mode laser with five harmonics and 7 ns pulse width have been used to irradiate Yb³⁺:PKBAYb₁₀ glass. The laser beam focused with a 75-mm focal length lens had a hat-top shape with a diameter of 350 micron. The peak fluence in the laser glass of today’s high power lasers can approach 5–20 J/cm² with peak irradiance up to 5.0 GW/cm².32 The laser damage fluence is found to be 11.41 J/cm², which is superior to the value found in LY-12(P-Si-B).12 In addition, the peak power value of laser induced damage threshold is found to be 1.63 GW/cm² for Yb³⁺:PKBAYb₁₀ glass. Nevertheless, the LIDT depends on the absorption coefficient (α) and varied from 0.18 to 4.09 cm⁻¹ with increase in Yb²O₃ concentration. Therefore, the laser damage threshold decreases with increase of α value.33 The obtained results indicate that the Yb³⁺:PKBAYb glasses could be opted as a gain media for HEHP laser and photonic applications.

4.2. Spectroscopic Properties

Figure 4 shows the absorption spectra and the inset shows the linear increase of integrated absorption coefficient with increase in Yb₂O₃ concentration. It is observed that the line shapes of the absorption spectra are similar for all the studied glasses. It is interesting to note that the well resolved Stark levels have been observed at higher Yb³⁺ concentration along with slight changes in the intensities with increases in the Yb³⁺ concentration. The observed broad absorption line shape is due to the inhomogeneous broadening that characterizes a glassy host. The emission spectra of Yb³⁺:PKBAYb glasses are shown in Figure 5 and inset shows the variation of integrated emission intensity for different Yb₂O₃ concentrations. It is observed a linear increase in intensity of ²F₅/₂ → ²F₇/₂ transition with increase in concentration.

The absorption and emission cross-section spectra of Yb³⁺:PKBAYb₁₀ is shown in Figure 6 in the range of 860–1070 nm. Emission cross-sections of Yb³⁺ ions can be obtained from the McC method.23 It is necessary to have higher emission cross-sections for greater gain and higher absorption cross-sections at the pump wavelength for an efficient diode laser pumping from the point of view of laser operation. The absorption and emission cross-sections decrease with increase in Yb³⁺ ion concentration at \(\lambda_p (975 \text{ nm})\) and \(\lambda_l (1.0 \mu m)\). Meanwhile, higher concentrations of Yb³⁺ ion, which occupy different sites in the glass host, can change the local field and reabsorption may also take place. Therefore, a decrease in \(\sigma_{\text{em}}/\lambda\) with increase in Yb³⁺ ion concentration has been noticed.

Fig. 3. The schematic layout of laser induced damage threshold measurement.

Fig. 4. Absorption spectrum of Yb³⁺:PKBAYb₁₀ glass and inset shows the variation of absorption coefficient with concentration.

Fig. 5. Emission spectra of Yb³⁺:PKBAYb glasses and the inset shows the linear increase of integrated intensity with concentration.

Fig. 6. Absorption and emission cross-section spectra of Yb³⁺:PKBAYb₁₀ glass.
The spectroscopic properties such as $\sigma_{ab}(\lambda)$, $\sigma_{em}(\lambda)$, $\Delta\lambda_{eff}$, $A$ and $\tau_f$ for the Yb$^{3+}$:PKBAYb glasses are listed in Table II. A systematic decrease in absorption and emission cross-sections and in radiative transition probabilities with increases in the Yb$_2$O$_3$ concentration are systematically observed. It is noticed from Table II that the absorption cross-section at $\lambda_p$ (975 nm) and $\lambda_0$ (1.0 $\mu$m) decreases from 4.49 to 1.49 $\times$ 10$^{-20}$ cm$^2$ (0.28 to 0.14 $\times$ 10$^{-20}$ cm$^2$) when Yb$_2$O$_3$ concentration increases from 0.01 to 1.0 mol%. It is also observed from Table II that the emission cross-section at $\lambda_p$ (975 nm) decreases from 6.08 to 2.06 $\times$ 10$^{-20}$ cm$^2$ while at $\lambda_0$ (1.0 $\mu$m) it decreases from 1.28 to 0.63 $\times$ 10$^{-20}$ cm$^2$ for Yb$^{3+}$:PKBAYb glasses when Yb$_2$O$_3$ concentration increases from 0.01 to 1.0 mol%.

The $\Delta\lambda_{eff}$ increases with increases in Yb$_2$O$_3$ concentration and is comparable with that of commercial YB1$^{31}$ and YP1$^{31}$ laser glasses. It is found that Yb$^{3+}$:PKBAYb10 glass has higher absorption (emission) cross-sections of 1.47 $\times$ 10$^{-20}$ (2.06 $\times$ 10$^{-20}$ cm$^2$) than that of the commercial Kigre QX/Yb: 1.06 $\times$ 10$^{-20}$ (0.9 $\times$ 10$^{-20}$ cm$^2$)$^{27}$ and IOG 1.41 $\times$ 10$^{-20}$ 30 glasses.

Figure 7 shows the measured luminescence decay curves for the $^5$F$^*_2$ $\rightarrow$ $^5$F$^*_1$ transition of Yb$^{3+}$:PKBAYb glasses, which are found to be single exponential for all the concentrations of Yb$^{3+}$ ions. It is observed that the $\tau_f$ increases up to 0.1 mol% and then decrease with increase in Yb$_2$O$_3$ concentration. Therefore, the quenching of lifetime may be either due to multiphonon relaxation or energy transfer between Yb$^{3+}$ ions (diffusion limited)$^{34}$ and/or directly coupled with OH$^-$ groups in Yb$^{3+}$:PKBAYb glasses. The magnitudes of $\tau_f$ for Yb$^{3+}$ doped systems are compared in Table I. It is observed that the $\tau_f$ values of Yb$^{3+}$:PKBAYb10 glass is comparable with that of YB1$^{31}$ laser glasses.

### 4.3. Laser Performance Parameters

In order to assess the potential of Yb$^{3+}$-doped PKBAYb glasses for laser devices, the laser performance parameters like $\beta_{min}$, $I_{sat}$ and $I_{min}$ have been evaluated using the spectroscopic parameters of absorption and emission cross-sections and lifetimes and listed in Table II. As can be seen from Table II, $\beta_{min}$, $I_{sat}$ and $I_{min}$ values are in the range of 0.16–0.19, 4.09–16.0 kW/cm$^2$ and 0.60–2.93 kW/cm$^2$, respectively. These values should be as low as possible to minimize the pump losses. Incidentally, the $\beta_{min}$ does not change much with increases in the Yb$_2$O$_3$ concentration. The parameter $I_{min}$ should be as low as possible (4.5 kW/cm$^2$) for diode pumping$^{25}$ and lower values observed in Yb$^{3+}$:PKBAYb glasses. The values of $I_{sat}$ and $I_{min}$ increase with increase in Yb$^{3+}$ ions concentration.

For good laser glasses, the product $\sigma_{ab}(\lambda_p) \times \tau_f$ is desirable to be as large as possible to provide high gain. The product is found to decrease from 4.67 to 1.25 $\times$ 10$^{-20}$ cm$^2$ ms when the Yb$_2$O$_3$ concentration is increased from 0.01 to 1.0 mol%. It is noticed that the product is higher for the Yb$^{3+}$:PKBAYb001 glass on the order of 4.67 $\times$ 10$^{-20}$ cm$^2$ ms which is twice as that of commercial Yb$^{3+}$-doped laser glasses of Kigre

<table>
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<th>Glasses</th>
<th>$\sigma_{ab}(\lambda_p)$ ($10^{-20}$ cm$^2$)</th>
<th>$\sigma_{ab}(\lambda_0)$ ($10^{-20}$ cm$^2$)</th>
<th>$\sigma_{em}(\lambda_p)$ ($10^{-20}$ cm$^2$)</th>
<th>$\sigma_{em}(\lambda_0)$ ($10^{-20}$ cm$^2$)</th>
<th>$\Delta\lambda_{eff}$ (nm)</th>
<th>$A$ (s$^{-1}$)</th>
<th>$\tau_f$ (ms)</th>
<th>$\beta_{min}$</th>
<th>$I_{sat}$ (kW/cm$^2$)</th>
<th>$I_{min}$ (kW/cm$^2$)</th>
<th>$\sigma_{ab}(\lambda_p)$ ($10^{-20}$ cm$^2$ ms)</th>
<th>$\sigma_{ab}(\lambda_0)$ ($10^{-20}$ cm$^2$ ms)</th>
<th>$\tau_{min}$ (fs)</th>
<th>$G$ (cm$^2$ ms)</th>
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<td>6.08</td>
<td>1.28</td>
<td>52</td>
<td>1195</td>
<td>1.04</td>
<td>0.16</td>
<td>4.09</td>
<td>0.60</td>
<td>1.33 (10)</td>
<td>1.17 (10)</td>
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<td>0.16</td>
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<tr>
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<td>1.74</td>
<td>0.15</td>
<td>2.35</td>
<td>0.68</td>
<td>54</td>
<td>585</td>
<td>1.09</td>
<td>0.18</td>
<td>9.70</td>
<td>1.05</td>
<td>1.89 (74)</td>
<td>1.97 (74)</td>
<td>111</td>
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<td>PKBAYb01</td>
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<td>54</td>
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<td>1.15</td>
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<td>1.89</td>
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<td>0.72 (72)</td>
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<tr>
<td>PKBAYb10</td>
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<td>0.14</td>
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<td>0.63</td>
<td>58</td>
<td>521</td>
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<td>2.93</td>
<td>1.25 (54)</td>
<td>0.54 (54)</td>
<td>134</td>
<td>2.35</td>
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QX/Yb: 2.12 × 10^{-20} \text{ cm}^2 \text{ ms}^{37} \text{ and IOG-2: } 2.11 \times 10^{-20} \text{ cm}^2 \text{ ms}.^{30} \text{ This indicates that this glass possesses better energy storage and extraction capability. The product } \sigma_{\text{em}}(\lambda_0) \times \tau_f \text{ is higher for the studied glasses than IOG-2.}^{30} \text{ The minimum pulse duration } (\tau_{\text{min}}) \text{ and gain coefficient } (G) \text{ are the key parameters for the development of ultrashort and high power lasers. The } G \text{ is entirely used to evaluate the laser performance in terms of stored energy } (\sigma_{\text{em}}(\lambda_p) \times \tau_f) \text{ and extraction efficiency } (\sigma_{\text{em}}(\lambda_0) \times \tau_f). \text{ It is apparent that the exponential decrease of } G \text{ results from the decrease of } \sigma_{\text{ab}}(\lambda) \text{, } \sigma_{\text{em}}(\lambda) \text{ and } \tau_f \text{ with increase in } \text{Yb}_2\text{O}_3 \text{ concentration. From Table II, the values of } \tau_{\text{min}} \text{ and } G \text{ are found to be in the range of } 110–134 \text{ fs and } 0.16–2.35 \text{ cm}^2 \text{ ms, respectively for Yb}^{3+}:\text{PKBAYb glasses. Gain cross-section } (\sigma_i(\lambda)) \text{ spectra of Yb}^{3+}:\text{PKBAYb10 glass is shown in Figure 8. The } \sigma_i(\lambda) \text{ has been calculated from the } \sigma_{\text{ab}} \text{ and } \sigma_{\text{em}} \text{ by MCC method and are given for the values of } \beta = 0 \text{ and } \beta = 1, \text{ respectively. As can be seen from the gain spectra, a wide tunable range from 980 to 1040 nm is expected whenever the value of } \beta \text{ is greater than 0.4. The obtained results indicate that the present glass could be opted as a laser gain media. As to the near future we are planning to carry out laser performance experiments on the title glass as carried out in the case of Nd}^{3+}-\text{doped K-Ba-Al phosphate glasses.}^{35}

5. CONCLUSIONS

Yb^{3+}-doped metaphosphate laser glasses have been developed and their optical, thermo-mechanical and laser properties have been characterized. A systematic investigation of physical properties, such as linear refractive index, Abbe number, non-linear refractive index, microhardness, laser induced damage threshold and thermal expansion co-efficient has been performed for 1.0 mol% Yb_2O_3 doped glass. The non-linear refractive index, laser induced damage threshold and thermal expansion co-efficient are 0.775 × 10^{-13} \text{ esu, } 1.63 \text{ GW/cm}^2 \text{ and } 11.7 \times 10^{-6}/\text{C}, \text{ respectively, which are advanced over those of previously reported materials. The Vicker’s hardness for the present glass has been found to be higher than that of Schott glass and comparable with the Hoya glass. Higher magnitudes in the absorption and emission cross-sections and bandwidths have been noticed. The best possibility of laser performance } (I_{\text{min}}) \text{ at } 0.60 \text{ kW/cm}^2 \text{ has been estimated for } 0.01 \text{ mol% Yb}_2\text{O}_3 \text{ doped glass with high energy storage capacity } (\sigma_{\text{em}}(\lambda_p) \times \tau_f) \text{ of } 4.67 \text{ cm}^2 \text{ ms}. \text{ Due to their superior physical, spectroscopic and laser performance parameters, metaphosphate glasses could be considered as laser active medium for the development of high energy and high power lasers.}

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References and Notes