Characterization of the rare earth doped-lead- indium phosphate glasses

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Abstract

In this work, optical absorption, fluorescence emission, frequency up-conversion and life time in rare earth doped - lead- indium phosphate glasses, have been investigated. Judd-Ofelt parameters for Er and Nd – doped PbIn(PO₄) glasses were also calculated. Lead- indium phosphate glasses exhibit a number of useful properties such as the efficient transmission of visible light, a high index of refraction, a low preparation temperature, low melt viscosity and have potential application as a storage medium for high-level nuclear wastes. Infrared to visible frequency up-conversion (530, 550 and 670 nm) and fluorescence emission (1500 nm) in Er³⁺-doped PbIn(PO₄) glasses pumped under 800 nm radiation excitation were observed. Several absorption (750, 800, 870, 1490 and 1600 nm) and fluorescence emission (890, 1060 and 1320 nm) lines in Nd-doped-PbIn(PO₄) were also observed. Finally, we measured the life times of the transitions ⁴I₁₅/₂ → ⁴I₁₃/₂ (Er-doped PbIn(PO₄) ~ 2.8 ms), ⁴F₅/₂ → ⁴I₉/₂, ⁴F₃/₂ → ⁴I₁₁/₂ and ⁴F₃/₂ → ⁴I₁₃/₂ (Nd-doped PbIn(PO₄)).

Introduction

A lot of the current knowledge concerning the structure of matter is based on spectroscopic investigations that offer notable contributions to the atomic and molecular physics, chemistry and molecular biology. Information about the molecular structure and the molecular interactions can be derived from the emission spectra and/or absorption generated when the radiation interacts with the atoms and/or matter molecules. Wavelength measures allow atomic and molecular energy levels determination. The line intensity is proportional to the transition probability that measures how strongly two levels of a molecular (or atomic) transition are coupled. As the transition probability depends on the wave functions of both energy levels, intensity measures are useful to verify the excited electrons space distribution, which can be esteemed from approximate solutions of the Schrödinger equation. The natural width of a line can be solved for special techniques, allowing us to determine average life times of excited molecular states.

The generally poor chemical durability of phosphate glasses has previously hampered large scale investigations of their potential for industrial applications. However, the addition of appropriate modifying cations into the parent P₂O₅ network former is known to produce phosphate glasses with drastically different physical and chemical properties [1-6]. The structure of vitreous P₂O₅ consists of a 3D network of corner-sharing PO₄ tetrahedra, each of which has a P=O (non-bridging O) double bond. The structural instability arises from the energetic imbalance between the delocalized π electron bonding character in the terminal P=O and the bridging P-O-P configurations which tend to break up the cross-linking network. [7] Accordingly, introducing metal oxides (MO) into P₂O₅ will generate additional non-bridging O-M-O linkages across different PO₄-chains thereby forming a more stable structure [2]. The lead-phosphate glass system is one of the more extensively studied cases. Although binary PbO-P₂O₅ glasses near the metaphosphate composition are somewhat susceptible to aqueous corrosion and crystallization at low temperatures [8], their chemical durability can be enhanced dramatically by adding a third metal-oxide component. Moreover, the resulting ternary glasses may exhibit unique properties that are desirable for novel applications. Sales and Boatner [9,10] have evaluated the durability and other properties of lead-iron phosphate glasses and indicated their potential application as a storage medium for high-level nuclear wastes. The same authors also searched for durable and optically clear lead-phosphate-based glasses and identified two candidates, namely Pb-In-P-O and Pb-Sc-P-O glass compositions [11]. These glasses have an index of refraction of 1.75 -1.83 in the visible region, an ultraviolet absorption edge at a wavelength near 300 nm and strong infrared absorption beyond 2800 nm. The preparation temperatures are relatively low (900-1000°C) and the chemical durability and resistance to both weathering and c-radiation are good. These glasses contain less than 5 mol% of In₂O₃ or Sc₂O₃, hence their mechanical properties are similar to the corresponding binary lead-phosphate glasses. In this work, we present the characterization of the rare earth
doped-lead-indium phosphate glasses \((\text{PbO})_{56.3} \text{In}_3 \text{O}_{2.42} \text{P}_2 \text{O}_5 \)\(^{39.5}\), where optical absorption, fluorescence emission, frequency up-conversion and life time have been investigated.

**Experimental Setup**

In the experiment, samples of \(\text{Er}^{3+}\) and \(\text{Nd}^{3+}\)-doped lead- indium phosphate glasses with concentrations of 10000 ppm/wt, maximum phonon energy (~1070 cm\(^{-1}\)), thickness of 5.0 mm and mass density of 5.30 g/cm\(^3\), were utilized. Optical absorption spectra in the visible and near infrared (VIS–NIR) regions were measured at room temperature using white light as source (LS-1 Tungsten Hologen Lamp – Ocean Optics inc). Room temperature fluorescence spectra were performed using the 800 nm line of a Ti:Saphire laser as the excitation source. The fluorescence signal was collected by a fiber-bundle and dispersing the fluorescence light with a 64 cm single-grating monochromator with a resolution of 0.5 nm. The light was detected using a S-20 uncooled photomultiplier tube or photodetectors (silicon, germanium and PBS) and a lock-in amplifier in conjunction with a microcomputer was used for data acquisition. The investigation about the life time of the atomics levels of the samples was realized doing the laser beam to pass through a telescopic and focused in a chopper.

**Results and Discussions**

The figures from 1a and 1b shows the room temperature absorption spectra of \(\text{Er}^{3+}\) and \(\text{Nd}^{3+}\)-doped lead- indium phosphate glass sample in the visible and infrared regions, respectively. In all measurements, the absorption light was collected by a fiber bundle in a direction parallel (front of) to the pump white light. The observed absorptions correspond to transition of \(\text{Er}^{3+}\) and \(\text{Nd}^{3+}\) ions of the ground state to excited states. The Judd-Ofelt parameters were estimated using the plots of Fig. 1a and 1b for the observed absorptions.

Figure 1: Room temperature absorption spectra of \(\text{Er}^{3+}\) and \(\text{Nd}^{3+}\)-doped lead- indium phosphate glass sample in the visible (1a) and infrared regions (1b)

Figure-2 shows the room temperature upconversion spectrum of \(\text{Er}^{3+}\)-doped lead- indium phosphate glass sample. The spectrum of Fig.2 exhibits three distinct emission bands centered around 525, 550 and 660 nm. The green fluorescence emission could easily be seen by the naked eye. This observation indicates an efficient upconversion process in such glass, the pumping mechanism is accomplished via two-photon absorption. In the figure-2, the detail shows a plot of the log \(I_p\) x log \(I_f\) for the green divers emissions under 800 nm excitation. Corresponding to the 525 and 550nm, emissions were obtained with slopes 1.97 and 1.98, respectively. These results indicate that a two-photon process populates the \(^4S_{3/2}, ^2H_{11/2}\) and \(^4F_{9/2}\) levels.

Figure 2: Up-conversion spectrum of \(\text{Er}^{3+}\)-doped lead- indium phosphate glass sample
In this work we propose the mechanisms ESA and ET to explain the frequency upconversion phenomenon. The $\text{Er}^{3+}$ ion is excited initially from the $^{4}\text{I}_{15/2}$ to the $^{4}\text{I}_{9/2}$ state through ground state absorption (GSA) process, under 800 nm pumping, and then decays to the $^{4}\text{I}_{11/2}$ state due to multiphonon relaxation process. The same ion absorbs further a second photon and is promoted to the $^{4}\text{F}_{9/2}$ and $^{4}\text{F}_{5/2}$ states. The ion decays to the $^{5}\text{H}_{11/2}$ state, and the $^{5}\text{H}_{11/2} \rightarrow ^{4}\text{I}_{15/2}$ transition gives 525 nm emission. Due to multiphonon relaxation process, $\text{Er}^{3+}$ ion at $^{5}\text{H}_{11/2}$ state can also decay to the $^{4}\text{S}_{3/2}$ state and the $^{4}\text{S}_{3/2} \rightarrow ^{4}\text{I}_{15/2}$ transition gives 550 nm emission. Multiphonon relaxation rate is very large and the 525 nm emission intensity is reduced ($\Delta E = 800\text{cm}^{-1}$ between the $^{5}\text{H}_{11/2}$ state and the next lower state $^{4}\text{S}_{3/2}$) and multiphonon relaxation rate from the $^{4}\text{S}_{3/2}$ level is very slow. The accumulation of population at this state gives rise to very strong 550 nm emission, due the energy gap between the $^{5}\text{S}_{3/2}$ level and the next lower state $^{5}\text{F}_{9/2}$ is ~3200cm$^{-1}$. This explains the two bands in the green. The emission in 660 nm arises from the ET process and depends on the $\text{Er}^{3+}$ ion concentration in the glass. $\text{Er}^{3+}$ ion is firstly excited from the $^{4}\text{I}_{15/2}$ to the $^{4}\text{I}_{9/2}$. The ion then decays to the $^{4}\text{I}_{11/2}$ and $^{4}\text{I}_{13/2}$ states due to multiphonon relaxation processes (despite the $\Delta E_{21}$ is larger compared to the phonon energy. This is possible because the $^{4}\text{I}_{13/2}$ level (level number-1) is a laser level (with a very large lifetime), and is promoted to the $^{4}\text{F}_{9/2}$ state of another excited ion. Finally, the $^{4}\text{F}_{9/2} \rightarrow ^{4}\text{I}_{15/2}$ transition gives 660 nm emission, as shown in Fig.2. As $\Delta E_{21}$ is very large and the $^{4}\text{I}_{13/2}$ level is a laser level, the ESA of the $^{4}\text{I}_{11/2}$ level is dominant and, thus, the 660 nm emission is reduced.

The infrared fluorescence spectra of $\text{Er}^{3+}$ and $\text{Nd}^{3+}$-doped lead- indium phosphate glass sample are shown in figures 3a and 3b. Only one signal was observed for the $\text{Er}^{3+}$-doped sample. The $\text{Er}^{3+}$ ion is excited initially from the $^{4}\text{I}_{15/2}$ to the $^{4}\text{I}_{9/2}$ state through ground state absorption (GSA) process, under 800 nm pumping, and then decays to the $^{4}\text{I}_{13/2}$ state due to multiphonon relaxation process. The $^{4}\text{I}_{13/2}$ level is a laser level with very large lifetime. Therefore, the emission occurs from the $^{4}\text{I}_{13/2}$ to the $^{4}\text{I}_{15/2}$ state emitting in approximately 1540 nm. The spectrum for $\text{Nd}^{3+}$-doped sample exhibits three distinct emission bands centered around 890, 1060 and 1330 nm. The transitions at 1060 and 1300 nm are of more importance. Because of its importance in high power and high energy laser applications, the $^{4}\text{F}_{9/2} \rightarrow ^{4}\text{I}_{13/2}$ emission is probably the most thoroughly characterized transition for both glass and crystalline hosts. This band provides four-level operation at room temperature.

![Figure 3](image1.png)

**Figure 3:** Infrared fluorescence spectra of $\text{Er}^{3+}$ (3a) and $\text{Nd}^{3+}$-doped lead- indium phosphate glass sample (3b).

The luminescence decay times of the 1537 nm signal (Er-doped PbIn(PO$_4$) sample) and the 1060 nm signal (Nd-doped PbIn(PO$_4$) sample) were investigated and the results produced time constants of 2.8 ms and 600 $\mu$s, respectively, as illustrated in Figure 4.
Conclusions

Characterization of the rare earth doped-lead- indium phosphate glasses was performed. Optical absorption, fluorescence emission, frequency up-conversion and life time were observed. Infrared to visible frequency up-conversion (530, 550 and 670 nm) and fluorescence emission (1500 nm) in Er$^{3+}$-doped PbIn(PO$_4$) glasses pumped under 800 nm radiation excitation, were observed. Several absorption (750, 800, 870, 1490 and 1600 nm) and fluorescence emission (890, 1060 and 1320 nm) lines in Nd-doped-PbIn(PO$_4$) were also observed. We measured the life times of the transitions $^4I_{15/2} \rightarrow ^4I_{13/2}$ (Er-doped PbIn(PO$_4$) - 2.8 ms), $^4F_{5/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$ and $^4F_{3/2} \rightarrow ^4I_{13/2}$ (Nd-doped PbIn(PO$_4$) - ~ 600 µs).

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