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UV to NIR Down-Shifting in Yb$^{3+}$-Doped Phosphate Glass via Divalent Tin Centers

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**ABSTRACT**  The conversion of ultraviolet (UV) to near-infrared (NIR) photons is demonstrated for the first time in Yb$^{3+}$-containing glass via Sn$^{2+}$. Glasses with barium phosphate matrix were prepared by melt-quenching adding 2 mol% Yb$_2$O$_3$ alongside SnO up to 10 mol%. The investigation encompassed X-ray diffraction (XRD), UV-Vis-NIR absorption, $^{119}$Sn Mössbauer spectroscopy, and photoluminescence (PL) spectroscopy measurements with emission dynamics assessment. XRD data showed that the amorphous nature of the glasses is maintained within the range of dopant concentrations considered, while the optical absorption, $^{119}$Sn Mössbauer, and PL data supported the occurrence of divalent tin centers. The NIR PL data showed that exciting Sn$^{2+}$ centers around 290 nm results in the NIR emission from Yb$^{3+}$ near 1000 nm which becomes more intense with the increase in SnO. The Yb$^{3+}$ decay curves revealed a rise time for the $^2$F$_{5/2}$ emitting level followed by a single exponential decay. An energy transfer process proceeding via charge transfer states involving tin (donor) and ytterbium (acceptor) was proposed to account for the enhanced UV-excited NIR emission from Yb$^{3+}$ ions.

**Keywords:** glasses; luminescence; optical properties; rare earths; solar cells
INTRODUCTION

The near-infrared (NIR) emission from Yb$^{3+}$ ions has been considered valuable for optical applications such as lasing$^1$ and for spectral converters aiming to boost the efficiency of silicon-based solar cells.$^2$ The latter application has gained increasing attention$^{2-13}$ given the growing energy demand and climate change concerns linked to the burning of fossil fuels.$^{12}$ Nevertheless, a challenge is presented in that Yb$^{3+}$ ions have a simple energy level structure and cannot absorb visible or ultraviolet (UV) light directly. Hence, various alternatives have been explored as UV/Vis sensitizers for converting high-energy photons to the NIR (950-1100 nm) in different Yb$^{3+}$-containing hosts: rare-earth ions such as Ce$^{3+},$ $^{2,4,5,10}$ Tb$^{3+},$ $^{3,6}$ Pr$^{3+},$ $^7$ Eu$^{3+},$ $^8$ other metal cations such as Bi$^{3+},$ $^{2,8}$ Cr$^{3+},$ $^8$ Te$^{4+},$ $^9$ silver in the form of aggregates,$^{11}$ and host-induced sensitization.$^{13}$ The search for suitable sensitizers for Yb$^{3+}$ thus continues to be an active area of research largely stimulated by global demands for clean energy.$^{12}$

With respect to the host containing the luminescent species, a transparent dielectric material is desired which could be installed with the solar cells aiming for a more effective light utilization.$^{12,14,15}$ Phosphate-based glasses are particularly attractive hosts since they possess high optical transparency and the ability to incorporate high concentrations of Yb$^{3+}$ ions$^1$ as well as other metals relevant to photonics and photovoltaic cells.$^{16,17}$ As an interesting $ns^2$-type center, divalent tin has been the subject of investigation in phosphate glasses given its bluish photoluminescence (PL) which has been considered attractive for light-emitting applications.$^{18-23}$ Further, a sensitizer role has been also indicated for tin species in phosphate glasses leading to the enhanced emission from various rare-earth ions such as Eu$^{3+},$ $^{24,25}$ Pr$^{3+},$ $^{26,27}$ Dy$^{3+},$ $^28$ Sm$^{3+},$ $^{29}$ Er$^{3+},$ $^{30,31}$ Gd$^{3+},$ $^{32}$ and Tb$^{3+}.$ $^{33}$ From these, the NIR emission of Pr$^{3+}$ and Er$^{3+}$ ions has been reported via the excitation of divalent tin centers in barium phosphate glasses.$^{27,30}$ However, the influence of UV-
absorbing Sn$^{2+}$ on NIR-emitting Yb$^{3+}$ ions in glasses has not been reported to the best of the authors’ knowledge. Divalent tin is valuable not only for its visible PL suitable for lighting$^{18-23}$ and its energy donor role enhancing activators’ emission,$^{24-30}$ but its ability to undergo valence state changes encourages evaluating charge transfer transitions when coupled with an electron acceptor. It is noteworthy that Yb$^{3+}$ is amongst the reducible rare-earth ions capable of undergoing charge transfer transitions.$^{4,5,10}$ In this context, the present work was conducted to evaluate the potential of tin(II) with electron donating character as sensitizer for ytterbium(III) which is susceptible to reduction. As barium-phosphate glasses are known for having desirable physical, thermal and optical properties,$^{16,34-36}$ the binary barium phosphate glass matrix used as host in prior studies involving tin and other trivalent rare-earths$^{25,27-30}$ was likewise employed in this work. The glasses were prepared by the melting technique with fixed Yb$_2$O$_3$ content at 2 mol% and increasing amounts of SnO added up to 10 mol% (relative to network former P$_2$O$_5$). Experimental evaluations were then carried out by X-ray diffraction (XRD), UV-Vis-NIR optical absorption, $^{119}$Sn Mössbauer spectroscopy, and PL spectroscopy with decay dynamics assessment. The results indicate a role of divalent tin as UV sensitizer for the NIR-emitting Yb$^{3+}$ ions in the glass matrix. A model is ultimately proposed to explain the energy transfer in terms of charge transfer transitions involving tin (donating) and ytterbium (accepting).

**EXPERIMENTAL**

**Materials.** The glasses were made with a 50BaO:50P$_2$O$_5$ (mol%) composition from high purity Alfa Aesar compounds P$_2$O$_5$ (≥ 98%) and BaCO$_3$ (99.8%) by the melting technique.$^{30}$ Doping of the glasses was done in an additive manner in mol% in relation to network former P$_2$O$_5$ in the matrix: Yb$_2$O$_3$ (≥ 99.9%) was kept fixed at 2 mol%, while SnO (≥ 99.9%) was added incrementally as 3, 5, 7 and 10 mol%. An Yb-doped glass (2 mol% Yb$_2$O$_3$) and also a merely Sn-
containing glass (having the highest SnO content of 10 mol%) were prepared as references. The raw materials (about 20 g batches) were weighed, thoroughly mixed and melted in porcelain crucibles at 1150 °C for 15 min under ambient atmosphere conditions, and quenched in a steel mold. To remove mechanical/thermal stress, the glasses were annealed for 3 hours at 420 °C. Finally, the glasses were cut and polished to about 1 mm thick slabs for measurements. The labels for the several glasses made along with their nominal compositions are summarized in Table 1.

Table 1. Glass codes, matrix composition and additive concentrations (mol%) of Yb₂O₃ and SnO in the phosphate glasses synthesized.

<table>
<thead>
<tr>
<th>Glass</th>
<th>BaO (mol%)</th>
<th>P₂O₅ (mol%)</th>
<th>Yb₂O₃ (mol%)</th>
<th>SnO (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb</td>
<td>50</td>
<td>50</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>50</td>
<td>—</td>
<td>10</td>
</tr>
<tr>
<td>3SnYb</td>
<td>50</td>
<td>50</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>5SnYb</td>
<td>50</td>
<td>50</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>7SnYb</td>
<td>50</td>
<td>50</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>10SnYb</td>
<td>50</td>
<td>50</td>
<td>2</td>
<td>10</td>
</tr>
</tbody>
</table>

Measurements. XRD was carried out on glass samples as powders (ground by mortar and pestle) at room temperature with a PANalytical Empyrean X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å) over the 10° ≤ 2θ ≤ 80° angular range. The acceleration voltage and current were 45 kV and 40 mA, respectively.

The UV-Vis-NIR optical absorption measurements were made on the 1 mm-thick glass slabs fixed on a sample holder for solids (5 mm diameter) in an Agilent Cary 5000 series double-beam spectrophotometer at room temperature. While most measurements were recorded with air as the
reference, the 3-10SnYb glasses were also scanned together with the Yb glass as reference with the purpose of detecting the contribution of tin$^{25}$ to UV absorption.

$^{119}$Sn Mössbauer spectroscopy was performed using an M6 Resonant Gamma-ray Spectrometer (SEE Co.) with a Kr/CO$_2$ proportional counter and a $^{119m}$Sn/CaSnO$_3$ radioisotope source (Ritverc). All measurements were performed with the sample and source at room temperature. The velocity axis was calibrated using a $^{57}$Co/Rh radioisotope source and a 25 µm thick α-Fe reference foil (Ritverc), and all isomer shifts are given relative to a natural abundance SnO$_2$ powder at 0 mm/s.

The PL data was acquired at room temperature with a UV-Vis-NIR Horiba-PTI QM-8075-21 spectrofluorometer equipped with continuous illumination and pulsed (~ 2 µs) Xe lamps and an N$_2$-cooled InGaAs detector. Emission and excitation spectra were obtained under steady-state conditions with the continuous illumination Xe lamp and a step size for spectral acquisitions of 1 nm. For the decay curve measurements, the frequency of the Xe flash lamp was adjusted to allow data collection from µs to ms scale as needed. The PL measurements were recorded with samples mounted in a solid sample holder with attention given to keeping sample position and experimental conditions constant during experiments.

RESULTS AND DISCUSSION

**XRD, Optical Absorption, and $^{119}$Sn Mössbauer Spectroscopy.** Powder XRD was performed on the various glasses synthesized to confirm the amorphous nature. The data is shown in Fig. S1 of the Supporting Information file. The diffractograms exhibit similarly the broad diffuse scattering at lower angles consistent with long-range structural disorder, whereas no crystallization peaks were registered. Thus, the non-crystalline form of the materials synthesized by the additive approach according to the nominal compositions in Table 1 is supported.
Figure 1 shows the UV-Vis-NIR absorption spectra recorded in the 200-1200 nm range for the different glasses synthesized. The Yb-containing glasses show similarly the $^2 \text{F}_{7/2} \rightarrow ^2 \text{F}_{5/2}$ absorption peak of Yb$^{3+}$ ions detected at about 976 nm. The absorption spectra for the glasses otherwise resemble that of the Sn reference lacking any visible absorption features and displaying the UV edge with strong absorption at $\lambda < 330$ nm. The absorption of divalent tin centers has been previously appraised in similar glasses and found to lie within the absorption of the host itself.\textsuperscript{28,33,37,38} For instance, Wang and Gan\textsuperscript{33} detected an absorption peak around 288 nm by obtaining the difference spectrum between the tin-containing glass and the lithium-zinc phosphate host, ascribed to electronic transitions from the ground singlet state $S_0$ to a first excited singlet state $S_1$ in Sn$^{2+}$. In barium phosphate glasses doped up to 10 mol\% SnO as in the present work, Sn$^{2+}$ has been similarly revealed as a peak within ~280-290 nm from difference absorption spectra obtained using the Sn-free glass as reference.\textsuperscript{25,27,28} The prevalence of Sn$^{2+}$ in the Eu$^{3+}$ and Pr$^{3+}$ containing glasses studied in Refs. 25 and 27 was further substantiated by Sn 3d$^{5/2}$ X-ray photoelectron spectroscopy (XPS) analysis. Hence, the 3-10SnYb glasses in this work were scanned together with the Yb glass as reference to detect the contribution of divalent tin to UV absorption. The corresponding difference UV absorption spectra obtained are shown in the inset of Fig. 1. Absorption peaks were detected at about 270, 275, 279 and 286 nm, for the 3SnYb, 5SnYb, 7SnYb and 10SnYb glasses, respectively. In accord with previous works,\textsuperscript{25,27,28,33,37} these may be considered as reflecting the presence of increasing contents of divalent tin centers undergoing $S_0 \rightarrow S_1$ electronic transitions. In the context of glass structure, these have been identified as twofold-coordinated tin centers, also referred to as =Sn= where = represents the bonds with two oxygen atoms and “ represents the two lone pair electrons.\textsuperscript{27,37,39,40} In phosphate glasses the =Sn= species have been indicated to have a network former role.\textsuperscript{41-43} Such tin centers generally considered herein
as Sn$^{2+}$ species then appear to be incorporated in the 3-10SnYb glasses as perceived from the considerable absorption in the UV.

![Graph showing UV-Vis-NIR absorption spectra for various phosphate glasses.](image)

**Fig. 1.** UV-Vis-NIR absorption spectra obtained for the various phosphate glasses studied; the $^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$ absorption peak of Yb$^{3+}$ ions is detected for the Yb-containing glasses at about 976 nm. The inset shows the difference UV absorption spectra between the 3-10SnYb glasses and the Yb reference glass as recorded in dual-beam configuration; the resultant absorption bands are attributed to the singlet-to-singlet transitions ($S_0 \rightarrow S_1$) in divalent tin centers.

Nonetheless, it is known that some oxidation of Sn$^{2+}$ to Sn$^{4+}$ takes place during the melting in ambient atmosphere as shown previously by XPS.\textsuperscript{25,27,43} Thus, to verify Sn$^{2+}$ occurrence and aid in the subsequent PL characterization, tin speciation was herein carried out by $^{119}$Sn Mössbauer spectroscopy for the 10SnYb glass being key for having the highest SnO content as well as the Sn reference with same amount of SnO. The obtained spectra are shown in Fig. 2 along with the
performed Lorentzian deconvolutions employed to estimate the relative amounts of Sn$^{2+}$ in the glasses. The singlets near 0 mm/s are indicative of Sn$^{4+}$, while the quadrupolar doublets (average isomer shift $= 3.46 \pm 0.11$ mm/s, average quadrupole splitting $= 1.47 \pm 0.15$ mm/s) spanning 2-5 mm/s correspond to the Sn$^{2+}$ species. Note that the strong asymmetry of these doublets is known to arise from the Goldanskii-Karyagin effect for Sn(II) in phosphate glasses. Although Sn$^{4+}$ clearly occurs in the glasses, it is indicated that most of the tin exists as divalent tin, namely with relative amounts of Sn$^{2+}$ estimated for the Sn and 10SnYb glasses from the areas of the Lorentzian peaks at 70.0% and 88.0%, respectively. Analogous results with varying Sn$^{2+}$ values were also estimated by XPS for phosphate glasses melted with merely 10 mol% SnO, and also Eu$^{3+}$, or Pr$^{3+}$ assessed at 87.0%, 73.2% and 81.6% Sn$^{2+}$, respectively. Thus, even though the 10SnYb glass was significantly higher in Sn$^{2+}$ content than the Sn reference sample (Fig. 2), ascribing this to an influence of Yb$^{3+}$ would be premature. Nevertheless, the $^{119}$Sn Mössbauer data supports the detected UV absorption peak detected around 286 nm for the 10SnYb glass (Fig. 1, inset) as due to Sn$^{2+}$, which in fact is also consistent with the PL excitation appraisal as discussed below. It also gives confidence about the partial occurrence of divalent tin in the 3SnYb, 5SnYb and 7SnYb glasses being reflected as the absorption peaks at 270, 275 and 279 nm, respectively. As shall be seen, this correspondence is additionally supported by the NIR PL evaluation (vide infra). Meanwhile, the distinct Sn$^{2+}$ contents determined for the 10SnYb and Sn glasses become useful for the evaluation of the visible PL stemming from the Sn centers as considered next.
Fig. 2. $^{119}$Sn Mössbauer spectra (open symbols) for (a) Sn and (b) 10SnYb samples with corresponding Lorentzian deconvolutions employed for tin speciation (the solid traces are the cumulative fits); the estimated amounts of Sn$^{2+}$ in each glass are indicated.

**Visible PL Spectroscopy.** Continuing with the comparison amongst the Sn and 10SnYb glasses, shown in Fig. 3 (a) are corresponding visible emission spectra obtained for both under $S_0 \rightarrow S_1$ excitation in divalent tin centers at 290 nm. The emission spectra obtained show bands with broad maxima around 440 and 450 nm for the Sn and 10SnYb glasses, respectively. The emission can be ascribed to triplet-to-singlet ($T_1 \rightarrow S_0$) transitions as the excited triplet state is populated following intersystem crossing (ISC) in the Sn$^{2+}$ species.\textsuperscript{27,30,33,37,39,45} Apart from the small red shift, it can be noticed that the broad PL band for the 10SnYb glass is also suppressed relative to the Sn reference. This is noteworthy given the fact that the amount of Sn$^{2+}$ was estimated to be higher for the 10SnYb glass (Fig. 2). This therefore suggests a reduced $T_1$ state population for the tin centers in the presence of Yb$^{3+}$. However, unlike other rare-earth activator ions such as Pr$^{3+}$,\textsuperscript{27} and Er$^{3+}$,\textsuperscript{30} Yb$^{3+}$ has no absorption transitions resonant with Sn$^{2+}$ emission that could be involved in a resonant energy transfer leading to a decreased PL of divalent tin. Hence, it seems that rather
than quenching the phosphorescence, Yb³⁺ reduces the $S_1 \rightarrow T_1$ ISC process that ultimately leads to $T_1 \rightarrow S_0$ emission in Sn²⁺. Subsequently monitoring the emission at 450 nm for both glasses produced the excitation spectra shown in the upper inset of Fig. 3 (a). The excitation peaks were detected at about 292 and 300 nm for the Sn and 10SnYb glasses, respectively. Again, a red shift is seen in the PL excitation band for the 10SnYb relative to the Sn reference. But more conspicuously the excitation peak is significantly suppressed for the 10SnYb glass, again pointing to a decreased efficiency for populating the $T_1$ excited state following the $S_0 \rightarrow S_1$ excitation. Interestingly, the excitation peak for the 10SnYb bears resemblance with the difference absorption spectrum in Fig. 1 (inset), although somewhat bathochromically shifted. This further supports the validity of the difference UV absorption spectra for assessing the presence of Sn²⁺ species in the glasses.

**Fig. 3.** (a) Visible emission spectra obtained for the Sn and 10SnYb glasses under excitation at 290 nm exhibiting the broad emission band ascribed to triplet-to-singlet transitions ($T_1 \rightarrow S_0$) in divalent tin centers. The upper inset in (a) shows the excitation spectra recorded by monitoring emission at 450 nm, which displays the band attributed to the singlet-to-singlet excitation ($S_0 \rightarrow S_1$) in Sn²⁺. The lower inset in (a) shows semi-log plots of the decay curves obtained for the glasses.
under excitation at 290 nm with emission monitored at 450 nm. (b) The CIE 1931 chromaticity diagram with coordinates of emission color calculated from the spectra in panel (a).

Seeking to obtain additional information on the cause of the Sn$^{2+}$ PL quenching effect seen in the 10SnYb glass relative to the Sn reference, emission decay curves were obtained for the glasses under excitation at 290 nm by monitoring the emission at 450 nm. The recorded curves are shown in the lower inset of Fig. 3 (a). These were fit by a single-exponential function in accord with the typical first-order decay behavior of Sn$^{2+}$ species$^{25,37,39}$ as

$$I(t) = I_0 \exp(-t/\tau)$$

(1)

where $I(t)$ is the time-dependent luminescence intensity, $I_0$ is the initial intensity and $\tau$ is the excited state lifetime. The lifetimes extracted from the fits alongside estimated errors are 18.5 (±0.2) and 18.1 (±0.2) $\mu$s, for the Sn and 10SnYb samples, respectively. Because the small difference in the lifetimes is within the estimated error, significant non-radiative depopulation of the excited $T_1$ state by Yb$^{3+}$ is not supported. This is consistent with the absence of absorption transitions in Yb$^{3+}$ that could participate in a Sn$^{2+}$ → Yb$^{3+}$ resonant transfer. The results contrast with Wang and Gan$^{33}$ who reported a lifetime of 11.7 $\mu$s for Sn$^{2+}$ in lithium-zinc phosphate glass and subsequently decreased values in the presence of Tb$^{3+}$ due to energy transfer from Sn$^{2+}$ centers having emission overlapping Tb$^{3+}$ absorption.

Further characterizing the light emission in the glasses by the Commission Internationale de l’Eclairage (CIE) 1931 chromaticity diagram agrees with the blue-emitting character as shown in Fig. 3 (b). Calculated from the PL emission spectra in Fig. 3 (a), the (X,Y) chromaticity coordinates determined for the Sn and 10SnYb glasses were similarly obtained as (0.203, 0.228) and (0.204, 0.242), respectively. Accordingly, the quality of the emitted color has not been significantly altered
by the inclusion of Yb$^{3+}$ and the differences most likely follow the slight peak shift detected in the 10SnYb glass. The main difference appears to be the intensity drop obtained relative to the Sn reference. Henceforth, we continue with the NIR PL assessment seeking to evaluate the impact of the divalent tin centers on the emission from Yb$^{3+}$ in the glasses.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectrum.png}
\caption{Yb$^{3+}$ NIR emission spectra obtained under excitation at 290 nm for the various Yb-doped phosphate glasses. The inset shows the excitation spectra recorded by monitoring Yb$^{3+}$ emission at 977 nm which for the tin-containing glasses exhibits the band attributed to the singlet-to-singlet excitation ($S_0 \rightarrow S_1$) in Sn$^{2+}$.}
\end{figure}

**NIR PL Spectroscopy.** Figure 4 shows the NIR emission spectra obtained for the Yb-doped glasses under excitation of divalent tin centers at 290 nm. All glasses show the characteristic $^2F_{5/2} \rightarrow ^2F_{7/2}$ Yb$^{3+}$ emission, the intensity of which grows with tin content. It is rather weak for the Yb glass, which could be ascribed to excitation of O$^{2-}$-Yb$^{3+}$ charge transfer transitions ultimately
feeding the emitting $^2F_{5/2}$ state. However, it increases in intensity for the tin-containing glasses reaching a maximum for the 10SnYb glass, thus revealing a UV-sensitizing effect from tin. The upper inset of Fig. 4 shows the excitation spectra recorded by monitoring Yb$^{3+}$ emission at 977 nm. The Yb glass shows mainly a weak band with maximum around 298 nm with a second small feature around 232 nm which are likely associated with the O$^{2-}$-Yb$^{3+}$ charge transfer transitions. On the other hand, an excitation band develops with a peak detected at about 268, 273, 278 and 291 nm for the 3SnYb, 5SnYb, 7SnYb and 10SnYb glasses, respectively. Remarkably, the band evolution resembles the development of the UV absorption peaks characterizing the absorption by Sn$^{2+}$ species (Fig. 1, inset) detected around 270, 275, 279 and 286 nm, for the 3SnYb, 5SnYb, 7SnYb and 10SnYb glasses, respectively. Accordingly, the excitation bands point to the singlet-to-singlet excitation ($S_0 \rightarrow S_1$) in divalent tin centers ultimately leading to the enhanced NIR emission from Yb$^{3+}$ ions. Further, the apparent similarity between the UV absorption peaks and the PL excitation bands support the optical absorption approach for identifying Sn$^{2+}$ species in the glasses. Analogous UV excitation bands indicative of energy transfer processes originating at tin centers and resulting in enhanced emission properties have been reported for other rare-earths in the barium phosphate glass matrix such as Eu$^{3+}$, Pr$^{3+}$, Dy$^{3+}$, Sm$^{3+}$ and Er$^{3+}$. However, the present case differs in that the Yb$^{3+}$ ions as energy acceptors do not have energy levels resonant with the Sn$^{2+}$ centers emitting in the visible. Therefore, to gain more insights into the energy transfer process, decay curve measurements were carried out by monitoring Yb$^{3+}$ emission under UV excitation as considered next.
**Fig. 5.** Semi-log plots of the emission decay curves obtained for the Yb-doped glasses under excitation at 290 nm by monitoring Yb$^{3+}$ emission at 977 nm.

**Table 2.** Rise times ($\tau_R$) and decay times ($\tau_D$) estimated for Yb$^{3+}$ ions in the Yb-doped glasses from the decay curves obtained under 290 nm excitation by monitoring emission at 977 nm (Fig. 5).

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\tau_R$ (µs)</th>
<th>$\tau_D$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb</td>
<td>83 (±1)</td>
<td>877 (±5)</td>
</tr>
<tr>
<td>3SnYb</td>
<td>71 (±1)</td>
<td>858 (±6)</td>
</tr>
<tr>
<td>5SnYb</td>
<td>72 (±1)</td>
<td>998 (±4)</td>
</tr>
<tr>
<td>7SnYb</td>
<td>76 (±1)</td>
<td>967 (±4)</td>
</tr>
<tr>
<td>10SnYb</td>
<td>82 (±1)</td>
<td>1069 (±4)</td>
</tr>
</tbody>
</table>
Figure 5 shows the semi-log plots of the emission decay curves recorded for the Yb-doped glasses under excitation at 290 nm by monitoring Yb$^{3+}$ emission at 977 nm. The profiles all show a signal build-up rising for about 0.2 ms, and following a plateau, the signals decay after ~0.4 ms. Different authors$^{4,10}$ have reported similar Yb$^{3+}$ emission dynamics for the visible to NIR conversion in Ce$^{3+}$ and Yb$^{3+}$ co-doped materials. Ueda and Tanabe$^4$ fitted the data showing the rise time followed by the decay with a double exponential function as

$$I(t) = I_0 \left[ \exp\left( -t/\tau_R \right) - \exp\left( -t/\tau_D \right) \right]$$  \hspace{1cm} (2)$$

where $\tau_R$ corresponds to the rise time and $\tau_D$ is the decay time. The authors observed similar rise times of about 0.2 ms for various samples having different amounts of Yb$^{3+}$ ions, however with a decrease in the decay time for the highest Yb$^{3+}$ content ascribed to concentration quenching.$^4$

Rather than a cooperative energy transfer (CET) as invoked by others to explain downconversion processes involving Yb$^{3+}$,$^6$-$^9$ the interaction has been interpreted in terms of an energy transfer proceeding via Ce$^{4+}$-Yb$^{2+}$ charge transfer states (CTS).$^4,10$ The rise time has been considered indicative of a slow nonradiative relaxation from the CTS feeding the $^2F_{5/2}$ emitting state in Yb$^{3+}$.$^4$

The time-dependent emission profiles in Fig. 5 were then fit by Eq. (2) and the extracted rise and decay times are presented in Table 2. The rise time first decreases for the 3SnYb glass relative to the Yb reference; yet, a tendency to increase is thereafter observed up to the 10SnYb glass. On the other hand, while the decay time for the 3SnYb glass shows a slight decrease relative to the Yb sample, fluctuating values are produced afterwards for the 5-10SnYb. Still, the decay time for the 10SnYb glass can be considered significantly longer than the one estimated for the Yb reference glass, thus pointing to a most favorable outcome with the highest tin content. The time evolution observed for the Yb glass which has no SnO can be interpreted as the feeding of the $^2F_{5/2}$ emitting state through the $O^{2-}$-Yb$^{3+}$ charge transfer transitions. Conversely, in the presence of divalent tin
in the 3-10SnYb glasses, the participation of Sn$^{2+}$ in the CTS mechanism is suggested which ultimately populates the $^2F_{5/2}$ state in Yb$^{3+}$ nonradiatively. Such a mechanism is likely to operate when an energy donor with a tendency to become oxidized (e.g., Tb$^{3+}$, Ce$^{3+}$, Ce$^{4+}$) is coupled with an acceptor susceptible for reduction (e.g., Eu$^{3+}$, Yb$^{3+}$). In the case of two trivalent rare-earth ions (RE$^{3+}$) this is then represented as a RE$^{4+}$-RE$^{2+}$ CTS as is the case of the well-known Ce$^{4+}$-Yb$^{2+}$ CTS. Another example would be the Tb$^{4+}$-Yb$^{2+}$ CTS which as explained by Yuan et al. would involve both the light-induced ionization of Tb$^{3+}$ (Tb$^{3+}$ $\rightarrow$ O$^{2-}$) and the electron trapping by Yb$^{3+}$ (O$^{2-}$ $\rightarrow$ Yb$^{3+}$). Concerning the present case under study, Sn$^{2+}$ is also known to have an electron-donating ability as SnO is commonly used as reducing agent. Accordingly, coupled to Yb$^{3+}$ as acceptor it could lead to the CTS being responsible for the Sn$^{2+}$ $\rightarrow$ Yb$^{3+}$ energy transfer producing the NIR emission. A typical valence state of tin following oxidation is Sn$^{4+}$ as evidenced from the $^{119}$Sn Mössbauer spectra for the Sn and 10SnYb glasses in Fig. 2. If that was the case, then a two-electron transfer would require two Yb$^{3+}$ ions, that is, a Sn$^{4+}$-2Yb$^{2+}$ CTS would operate. Otherwise, a more realistic one-electron transfer could be envisioned implying then the transient Sn$^{2+}$-Yb$^{2+}$ CTS being responsible for the enhanced Yb$^{3+}$ NIR emission.

As summarized in Fig. 6 for the 10SnYb glass as most distinct case, singlet-to-singlet excitation ($S_0$ $\rightarrow$ $S_1$) in Sn$^{2+}$ produces considerably the triplet-to-singlet visible emission ($T_1$ $\rightarrow$ $S_0$) from Sn$^{2+}$. However, this was seen to a lesser degree than in the Sn reference, suggesting a hindering effect by Yb$^{3+}$ on the ISC that feeds the $T_1$ state in the divalent tin centers. Finally, the NIR Yb$^{3+}$ emission was also obtained upon Sn$^{2+}$ excitation at 290 nm. It was seen most significantly for the highest tin content and exhibited a time evolution with signal buildup followed by decay. All being considered then, the light emission and energy conversion processes from Sn$^{2+}$ species to Yb$^{3+}$ may be proposed to proceed via CTS represented with the configurational
coordinate model shown in Fig. 7 (diagrams of Sn$^{2+}$ and Yb$^{3+}$ depicted separately for clarity). The diagram for Sn$^{2+}$ includes the excitation and visible photon emission in divalent tin centers following the singlet-to-triplet ISC (seemingly hindered by Yb$^{3+}$), while that for Yb$^{3+}$ also incorporates a parabola for the O$^{2-}$-Yb$^{3+}$ charge transfer transitions (indicated to occur in the Yb reference). Following the $S_0 \rightarrow S_1$ excitation in Sn$^{2+}$, the energy transfer is then considered to occur through the CTS (dashed parabola), possibly a transitory Sn$^{3+}$-Yb$^{2+}$ CTS, ultimately feeding the $^2F_{5/2}$ emitting state in Yb$^{3+}$ nonradiatively, which finally undergoes radiative relaxation to the $^2F_{7/2}$ ground state. Otherwise, exciting the O$^{2-}$-Yb$^{3+}$ charge transfer transitions directly may lead to NIR emission from Yb$^{3+}$ but with significantly less efficiency.

Fig. 6. 10SnYb glass overlay of excitation spectrum (PLE, $\lambda_{em} = 977$ nm) indicative of singlet-to-singlet absorption by divalent tin centers alongside the tin-related triplet-to-singlet visible PL and Yb$^{3+}$ NIR PL spectra obtained under excitation at 290 nm.
Fig. 7. Configurational coordinate model of emission and energy transfer (ET) from divalent tin to Yb$^{3+}$ proceeding via a charge transfer state (CTS). The singlet-to-triplet intersystem crossing (ISC) in Sn$^{2+}$ leading to visible PL is also illustrated. The dashed parabolas depict charge transfer states potentially involved, e.g. transitory Sn$^{3+}$–Yb$^{2+}$ CTS (the configurational coordinate diagrams of Sn$^{2+}$ and Yb$^{3+}$ are depicted separately for clarity).

CONCLUSIONS

To recapitulate, barium phosphate glasses were doped with 2 mol% Yb$_2$O$_3$ and up to 10 mol% SnO to evaluate the potential of tin(II) as UV sensitizer of NIR-emitting ytterbium(III). The glasses were prepared by melting and analyses were carried out by XRD, UV-Vis-NIR absorption, $^{119}$Sn Mössbauer spectroscopy, and PL spectroscopy with decay kinetics assessment. The XRD data supported the amorphous nature of the glasses within the range of dopants concentrations covered. The absorption spectroscopy data exhibited $^{2}\text{F}_{7/2} \rightarrow ^{2}\text{F}_{5/2}$ Yb$^{3+}$ absorption peaks around 976 nm in
the Yb-containing glasses. The assessment of glass properties by the optical absorption, $^{119}$Sn Mössbauer, and PL measurements supported the presence of the divalent tin centers capable of emitting bluish light as characterized by the CIE 1931 chromaticity coordinates. Further, an enhanced UV-excited NIR emission was obtained for Yb$^{3+}$ ions as a consequence of the Sn$^{2+}$ co-doping. The time evolution of the Yb$^{3+}$ emission intensity revealed a rise time indicating a slow feeding of the $^2F_{5/2}$ emitting state, followed by an exponential decay. The PL analysis overall suggested that $S_0 \rightarrow S_1$ excitation of the Sn$^{2+}$ species is at the origin of the process and leads to an energy transfer via charge transfer states involving tin and ytterbium that populates the $^2F_{5/2}$ state in Yb$^{3+}$ ions emitting within 950-1100 nm. The current results may be useful for the development of Yb-doped laser materials or spectral converters by utilizing the UV portion of the spectrum relevant to excitation of divalent tin centers.

**Conflict of Interest Statement**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**ASSOCIATED CONTENT**

The Supporting Information is available online free of charge. X-ray diffraction data obtained for the different glasses is presented in Fig. S1 of the Supporting Information file.

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TOC Graphic

Energy Transfer Model for UV-to-NIR Down-shifting

Normalized intensity (a.u.)

Wavelength (nm)

200 300 400 500 600 700 800 900 1000 1100

UV Visible NIR