Letter to the Editor

Frequency upconversion emissions in layered lead–germanate–tellurite glasses for three-color display

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Abstract

This letter is aiming to develop a full-color glass for the three-dimensional and three-color display. The Yb\(^{3+}/\)Tm\(^{3+}/\)Er\(^{3+}\) co-doped lead–germanate–tellurite bulk glass has been fabricated and the upconversion emissions have been investigated. The reduced blue and green emission intensity suggests that it is difficult to achieve three-color display in the multiple-rare-earth ions doped glass. Then a two-layer lead–germanate–tellurite glass has been fabricated and the results show that the intensities of upconverted blue and green emissions remain same as emissions in the Yb\(^{3+}/\)Tm\(^{3+}\) and Yb\(^{3+}/\)Er\(^{3+}\) co-doped glasses.

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1. Introduction

The ability to visualized real-time volumetric data in true three-dimensional (3D) form has been a goal of display development efforts for many years. The potential applications of 3D display include computer aided design (CAD), air-traffic control, medical imaging, tele robotics, television, and outdoors public art etc. A new technique for 3D volumetric displays has been developed based on two-step upconversion in rare-earth doped fluoride glasses. A pair of near infrared lasers with distinct wavelengths was used to draw the image in the region where two focused beams intersected. Blue, green, or red emission can be obtained by doping glasses with Tm\(^{3+}\), Er\(^{3+}\), and Pr\(^{3+}\), respectively [1]. Later, a one-color, one-beam pumping scheme has been used to enhance the upconverted green efficiency in an Er\(^{3+}\)-doped fluoride glasses [2]. Recently, the cooperative upconversion luminescence of Yb\(^{3+}\) in multicomponent silica glass has been investigated for 3D display and 1 \(\mu\)W blue emission has been achieved [3]. Further research for the three-color display in a bulk glass has been in progress.

On the other hand, in order to increase the upconversion efficiency, much effort has been devoted to search for glasses with low-phonon energies because the non-radiative decay of the excited electronic states of rare-earth ions in glasses is dominated by the highest-energy phonons [4]. Fluoride, chloride, bromide, and iodide glasses have been produced one after the other [5]. Although these halide glasses possess low cutoff phonon frequency, they are extremely sensitive to atmospheric moisture. Thus they are impossibly fabricated under the atmosphere and are limited to practical uses. In comparing with halide glasses oxide glasses have attractive properties such as high chemical stability and ease of fabrication. Among the oxide glasses available, tellurite glass is one of the better hosts with good optical quality.

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and low phonon energy. A variety of publications have reported upconversion luminescence emissions in the rare-earth ions doped tellurite glasses [6,7].

In this letter, we have fabricated a new type two-layer tellurite glass and investigated the upconversion properties of the glass. To our knowledge, few investigations have been conducted on the upconversion emissions in this type of glasses.

2. Experiment

2.1. Glass composition and preparation

Glasses used in this work have the following compositions in mol%: 5K2O–10ZnO–10BaO–20PbO–20GeO2–35TeO2–1.4Yb2O3–0.2Er2O3 (TE), 5K2O–10ZnO–10BaO–20PbO–20GeO2–35TeO2–1.4Yb2O3–0.1Tm2O3 (TT), and 5K2O–10ZnO–10BaO–20PbO–20GeO2–35TeO2–1.4Yb2O3–0.2Er2O3–0.1Tm2O3 (TET). They were synthesized by a conventional melting and quenching method which can be available everywhere [8]. The addition of GeO2 is to improve the thermal stability of tellurite glasses [9]. The starting materials are reagent-grade powders K2CO3, Pb3O4, BaCO3, ZnO, and high purity GeO2 (>99.999%) and TeO2 (>99.99%). The Er3+ and Tm3+ were introduced as Er2O3 and Tm2O3 with 99.99% purity, respectively. Batches of 50 g were melted in quartz crucibles in the SiC furnace at 1050 °C for half an hour. During melting, dry oxygen gas was blown into the liquid to remove bubbles. After blowing, the homogenous bubble-free melts were cast on a stainless plate and annealed in a muffle stove near the glass transition temperature for 2 h and then cooled at a rate of 5 °C/h. The samples were cut using a low-speed diamond saw and polished with 5 μm diamond paste. The two-face polished samples have a plate shape with 20 × 10 × 2 mm for optical measurements.

2.2. Property measurements

The refractive index of glasses measured is \(n_d = 1.9192\) and its short wavelength cut-off edge locates at 358 nm. The visible spectra of Yb3+/Er3+ and Yb3+/Tm3+ co-doped lead–germanate–tellurite glasses are presented in Figs. 1(a) and (b). Three emission bands at 525, 547, and 657 nm in the TE glass correspondingly to the transitions \(2H_{11/2} \rightarrow 4I_{15/2}, 4S_{3/2} \rightarrow 4I_{15/2}, \text{ and } 4F_{9/2} \rightarrow 4I_{15/2}\), were observed. The upconverted green luminescence is very bright and can be observed with naked eyes when pumping as low as 20 mW. The dependence of the upconverted luminescence in the TE glass on pump power is quadratic, thereby indicating a two-photon process. For the TT glass, blue emission at 477 nm is observed and attributed to the transitions from the \(^1G_4\) state to the \(^3H_6\) ground state. It is important to point out that the blue emission was intense enough to be seen with naked eyes with daylight illumination in the lab. Red and near infrared emission centered at 652 and 792 nm, respectively, were also observed upon the 980

![Fig. 1](image-url)
nm excitation and they are attributed to the $^1G_4 \rightarrow ^3F_4$ and $^3H_4 \rightarrow ^3H_6$ transitions. The dependence of the upconversion emission intensities upon the excitation power was investigated and a cubic power law behavior for the blue emission and a quadratic power law behavior for the 792 nm emission were observed. From Figs. 1(a) and (b) it is also noticed that the intensity of upconverted green is larger than that of upconverted blue emission under the same excitation conditions. It is mainly due to the cubic dependence of the blue emission upon excitation intensity, whereas the green emission is the quadratic dependence.

The measurements of the upconverted luminescence in TET glass were performed upon 980 nm laser excitation under the same conditions as the measurements did on the TE and TT glasses. The upconversion spectrum of TET glass is shown in Fig. 2. The intensities of blue and green emissions are much smaller than those in TT and TE glasses. This upconversion luminescence quenching effect has been also reported in literatures [10,11]. Therefore it is difficult to achieve three-color emission simultaneously in a multiple rare-earth ions doped bulk glass.

A layered composite structure in a bulk glass may be a better way to achieve three-color display. In this configuration the bulk glass comprises many layers, each of which is incorporated different rare-earth ions. In this letter, lead–germanate–tellurite glass with two layers has been fabricated. The preparation process is firstly to cast the TE glass liquid on the preheated steel plate, secondly to press the glass liquid to 2-mm thick plane and subsequently to cast the TT glass liquid on the pre-cast TE thin plane and finally to press the glass to 4 mm thickness totally. The schematic of upconversion luminescence measurements on the two-layer glass is illustrated in Fig. 3 and the results are presented in Figs. 4(a) and (b). The excited state lifetime of Er$^{3+}$ and Tm$^{3+}$ are listed in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Er$^{3+}$ ($\mu$s)</th>
<th>Tm$^{3+}$ ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE</td>
<td>$^{2}H_{11/2}$, $^{4}S_{3/2}$</td>
<td>$^{4}F_{9/2}$, $^{4}G_{5/2}$</td>
</tr>
<tr>
<td>TT</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LG</td>
<td>$^{1}G_{4}$</td>
<td>$^{3}H_{4}$</td>
</tr>
</tbody>
</table>

#### 4. Discussions

According to the energy matching conditions and the dependence of emission intensity on excitation power, the possible excitation mechanism is analyzed on the basis of the simplified energy level diagram of Er$^{3+}$, Tm$^{3+}$, and Yb$^{3+}$ as illustrated in Fig. 5. Although the Yb$^{3+}$ emission ($^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$) does not overlap with the absorption of Tm$^{3+}$, energy transfer (ET) can also occur [12,13]. For the blue emission, three stepwise ET
processes from Yb\(^{3+}\) to Tm\(^{3+}\) are involved. Firstly a 980-nm photon is absorbed by one Yb\(^{3+}\) ion, which promotes the \(2\)\(^{F}_{7/2} \rightarrow 2\)\(^{F}_{5/2}\) transition. Then the excited Yb\(^{3+}\) transfers energy to a nearby Tm\(^{3+}\) ion, exciting it to the \(3\)\(^{H}_{5}\) level. Due to the small energy gap between the \(3\)\(^{H}_{5}\) and \(3\)\(^{F}_{4}\) levels the excited \(3\)\(^{H}_{5}\)Tm\(^{3+}\) ion nonradiatively relaxed to the \(3\)\(^{F}_{4}\) level through the lattice vibration. The excited \(3\)\(^{F}_{4}\)Tm\(^{3+}\) ion obtains energy again from an excited Yb\(^{3+}\) ion and reaches the \(3\)\(^{F}_{2}\) level.

The excited \(3\)\(^{F}_{4}\)Tm\(^{3+}\) ion obtained energy again from an excited Yb\(^{3+}\) ion and reaches the \(3\)\(^{F}_{2}\) level and then decays to the \(3\)\(^{H}_{4}\) level through multiphonon relaxations. At last it is promoted to the \(1\)\(^{G}_{4}\) level from the \(3\)\(^{H}_{4}\) level with the assistance of Yb\(^{3+}\) ions. These ET processes can be briefly described as: Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Tm\(^{3+}\)(\(3\)\(^{H}_{5}\)) \rightarrow Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Tm\(^{3+}\)(\(3\)\(^{F}_{4}\)); Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Tm\(^{3+}\)(\(3\)\(^{F}_{4}\)) \rightarrow Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Tm\(^{3+}\)(\(3\)\(^{F}_{2}\)) and Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Tm\(^{3+}\)(\(3\)\(^{H}_{4}\)) \rightarrow Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Tm\(^{3+}\)(\(3\)\(^{G}_{4}\)). Below the \(1\)\(^{G}_{4}\) level the energy gap is larger, over 6000 cm\(^{-1}\) and thus an intense blue fluorescence is emitted through the \(1\)\(^{G}_{4}\) \rightarrow \(3\)\(^{H}_{6}\) transition.

For the green emission, two-photon absorption is the main upconversion mechanism. A 980-nm photon is first absorbed by an Er\(^{3+}\) ion through the \(4\)\(^{I}_{15/2}\) \rightarrow \(4\)\(^{I}_{11/2}\) transition. Then the excited Er\(^{3+}\) transfers energy to an Er\(^{3+}\) ion, exciting it to the \(4\)\(^{I}_{11/2}\) level. Due to the small energy gap between \(4\)\(^{I}_{11/2}\) and \(4\)\(^{F}_{7/2}\) levels the excited \(4\)\(^{I}_{11/2}\)Er\(^{3+}\) ion nonradiatively relaxed to the \(4\)\(^{F}_{7/2}\) level because of the small energy gap, for example, about 1700 cm\(^{-1}\) in our experiment. Between the \(4\)\(^{F}_{7/2}\) and \(4\)\(^{S}_{3/2}\) levels a fast thermal equilibrium is established. Besides, two-step successive ET from Yb\(^{3+}\) to Er\(^{3+}\) is also a main path to excite Er\(^{3+}\) ions from the ground state to the \(4\)\(^{F}_{7/2}\) level. This can be described as: Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Er\(^{3+}\)(\(4\)\(^{I}_{15/2}\)) \rightarrow Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Er\(^{3+}\)(\(4\)\(^{I}_{11/2}\)) and Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Er\(^{3+}\)(\(4\)\(^{I}_{11/2}\)) \rightarrow Yb\(^{3+}\)(\(2\)\(^{F}_{7/2}\)) + Er\(^{3+}\)(\(4\)\(^{I}_{15/2}\)). The larger energy gap below \(4\)\(^{S}_{3/2}\) level, over 3100 cm\(^{-1}\), results in a small multiphonon decay rate from the \(4\)\(^{S}_{3/2}\) level to next low-lying state. Therefore, the bright green fluorescence was emitted through the \(4\)\(^{S}_{3/2}\) \rightarrow \(4\)\(^{I}_{15/2}\) transition. For the relatively weak red emission centered at 657 nm the main upconversion mechanism is the ET process from the excited Yb\(^{3+}\) to the \(4\)\(^{I}_{13/2}\)Er\(^{3+}\) and nonradiative decay from the \(4\)\(^{S}_{3/2}\) level of Er\(^{3+}\).

In the TET glass, the upconverted blue and green emissions were suppressed due to the energy transfer between Er\(^{3+}\) and Tm\(^{3+}\) ions [11]. The dominant energy transfers are described as follows:

\[
\text{Er}^{3+}\left(4\text{I}_{13/2}\right) + \text{Tm}^{3+}\left(3\text{F}_{2}\right) \rightarrow \text{Er}^{3+}\left(4\text{I}_{11/2}\right) + \text{Tm}^{3+}\left(3\text{F}_{2}\right) \\
\text{Er}^{3+}\left(4\text{I}_{15/2}\right) + \text{Tm}^{3+}\left(3\text{F}_{2}\right) \rightarrow \text{Er}^{3+}\left(4\text{I}_{11/2}\right) + \text{Tm}^{3+}\left(3\text{F}_{2}\right)
\]

Process (1) depopulates the \(4\)\(^{I}_{13/2}\) level of Er\(^{3+}\), which leads to a decrease in the intensities of the 525- and 547-nm upconversion luminescence, and process (2) depopulate the Tm\(^{3+}\)\(^{1}\)G\(^{4}\) level.

In the two-layer composite lead–germanate–tellurite glass the intensities of upconverted blue and green emissions remain similar to those in TT and TE glasses. The lifetimes of the excited states of Er\(^{3+}\) and Tm\(^{3+}\) in the composite glass are almost same as those in TT and TE glasses. The phenomena demonstrate that no energy transfer between Er\(^{3+}\) and Tm\(^{3+}\) occurs in this bulk glass. Additionally, it is noticed that when pumping on TE glass side and detecting on TT glass side, the upconverted blue emission is missing, whereas a weak green upconversion emission is recorded when pumping on TT glass side. These are due to the large concentration of Yb\(^{3+}\) in the layered glass and large absorption coefficient of Yb\(^{3+}\) ions at 980 nm, which result in a dramatic absorption for the pumping laser. When pumping on the TE glass side the pumping beam passes through 2-mm thick TE glass and its intensity decreases rapidly. The lowered pump intensity cannot populate the Tm\(^{3+}\) ions from ground state to the \(1\)\(^{G}_{4}\) level because of the cubic dependence of blue emission on pump power. In order to achieve three-color display in a bulk glass it is necessary to decrease the thickness of each layer. Further investigations have been in progress in our institute.

5. Conclusions

In order to achieve full-color display in a bulk glass, the upconversion emission properties have been investigated in Yb\(^{3+}\)/Er\(^{3+}\)/Tm\(^{3+}\) co-doped lead–germanate–tellurite glass. The reduced intensities of the upconverted blue and green emissions have been observed due to the energy transfer between Tm\(^{3+}\) and Er\(^{3+}\). A layered structure is proposed and a two-layer lead–germanate–tellurite glass has been fabricated. The excitation experiments show that the intensities of upconverted blue and green emissions in the composite glass remain same as in Yb\(^{3+}\)/Tm\(^{3+}\) co-doped glass and Yb\(^{3+}\)/Er\(^{3+}\) co-doped glass.
glass, avoiding the luminescence suppressing or quenching in multiple-rare-earth ions doped glasses.

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References