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The phosphorescent properties of Er^{3+} in $\text{Gd}_2\text{O}_2\text{S}$ by two-step absorption

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Abstract

We report on a novel luminescent phenomenon in $\text{Gd}_2\text{O}_2\text{S}:\text{Er},\text{Yb}$ prepared by a solid-state reaction. After irradiation at 980 nm, the afterglow emission of Er^{3+} is observed. X-ray diffraction, photoluminescent emission, long-lasting phosphorescence emission and decay curves were used to characterize the phosphor. It is found that the afterglow is improved with the co-doping of Ti^{4+} and Mg^{2+} . Also the upconversion luminescent spectrum of Er^{3+} is changed. We ascribe this phenomenon to the change in the environment of activator ions. The phosphorescence properties of the sample are researched in detail. Due to the dependence of afterglow intensities on different irradiative powers, a possible two-step-absorption upconversion long-lasting phosphorescence mechanism is proposed. This kind of mechanism may overcome the shortcomings of the long persistent phosphors which are used for UV irradiation.

1. Introduction

A long persistent phosphor is a type of phosphor that has a very long-lasting afterglow emission after the excitation source is turned off. As a kind of energy storing material, long-lived phosphors are widely exploited for various display and design applications. Early research and developments on long persistent phosphors can be dated to about 100 years ago. At the beginning of the 20th century, $\text{ZnS}:\text{Cu}^+$ phosphor was known as a long persistent phosphor [1]. Its persistent time could be as long as 40 min. In 1971, Abbruscato *et al* [2] reported a new type of long persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$. Recently the persistence time of this phosphor was extended to longer than 16 hours after co-doping with Dy^{3+} [3,4]. It has taken over 100 years to extend the persistence time from minutes to tens of hours. We believe that the phosphorescence or afterglow is related to the capture of energy by various types of traps and the subsequent release of this energy through emission.

Rare-earth oxysulfides have been known for a long time as excellent phosphor host materials and have been used in cathode ray tubes, field emission displays, etc [5]. Also, as a kind of large band-gap semiconductor system, it was

widely investigated [6, 7]. Recently, a new long-lasting phosphorescence material $\text{Y}_2\text{O}_2\text{S}:\text{Ti},\text{Mg}$ has been reported by Kang and Liu [8]. Zhang and Liu [9] observed the persistent phosphorescence from Er^{3+} in $\text{Gd}_2\text{O}_2\text{S}:\text{Er},\text{Ti}$ after UV irradiation. But because of the large band gap in rare-earth oxides and oxysulfides, the excitation energies for the long persistent phosphors are usually high, up to UV and even to VUV, which is a shortcoming for some of the applications.

Two-step-absorption upconversion is a way to convert long-wavelength excitation radiation into shorter wavelength output radiation. It is based on the existence of at least two real, metastable emitting states. Therefore its efficiency can be much higher than second-harmonic generation (SHG) and two-photon absorption (TPA). Also, because of the weak autofluorescence background and the unique properties of infrared light, it has many fascinating applications, such as lasers, infrared quantum counters, displays and bio-labels [10]. The upconversion long-lasting phosphorescence of Tm^{3+} in $\text{Y}_2\text{O}_2\text{S}:\text{Tm},\text{Mg},\text{Ti}$ phosphor was reported by Lei and Liu [11].

In this paper, we report an unusual infrared-to-visible upconversion afterglow in $\text{Gd}_2\text{O}_2\text{S}:\text{Er},\text{Yb}$. The phosphorescence lasts for more than 15 min to the light

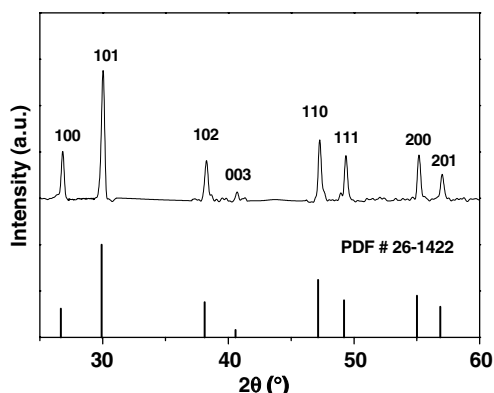


Figure 1. Powder XRD pattern of Sample 1 and the standard data of $\text{Gd}_2\text{O}_2\text{S}$.

perception of the adapted-to-dark human eye (0.32 mcd m^{-2}). To the best of our knowledge, there have been no reports of upconversion persistent phosphorescence from Er^{3+} . This unusual phosphorescence phenomenon will be useful in understanding the origin of afterglow and probably opens a new field of long-lasting phosphor research.

2. Experiment

In order to investigate in detail the luminescent properties of $\text{Gd}_2\text{O}_2\text{S}:\text{Er}^{3+}$, Yb^{3+} samples, the phosphors were synthesized by high-temperature solid reaction with the aid of sulfurizing flux. Stoichiometric amounts of Gd_2O_3 , Er_2O_3 , Yb_2O_3 , S, TiO_2 and $\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$ were mixed homogeneously blended with a flux of Na_2CO_3 , S (S and Na_2CO_3 in a ratio of 1:1 at 30 wt% of the total weight of raw material). The raw materials were sintered at 1050°C for 4 h in a sealed crucible.

The samples were examined for their chemical phase purity using x-ray powder diffraction (XRD) analysis (Cu $K\alpha$ radiation $\lambda = 1.54178$). The XRD profiles were collected in the range of $25^\circ < 2\theta < 60^\circ$. The photoluminescence (PL), afterglow emission spectra and decay curves were measured with a Hitachi F-4500 fluorescence spectrophotometer (resolution of monochromator: $\sim 1.0 \text{ nm}$; emission slit: 2.5 nm and 5 nm for PL and afterglow emission spectra, respectively; time resolution during the afterglow decay test: 1 s). In the measurements, a continuous 980 nm diode laser with a power maximum of 2 W was used for excitation, with a focused area of 0.25 mm^2 . All measurements were carried out at room temperature.

3. Results and discussion

3.1. XRD of samples

The phase structure of the samples was investigated by XRD. Figure 1 shows the XRD pattern of $\text{Gd}_{1.96}\text{O}_2\text{S} : 0.01\text{Er}, 0.03\text{Yb}$ (Sample 1) and the standard data for $\text{Gd}_2\text{O}_2\text{S}$ as well. The results of the XRD indicate that the sample is well crystallized, and the pattern is in good agreement with the structure known from the crystal (JCPDS Card 26-1422).

Co-doping of ions into hosts which serve as trapping centres is one of the most popular methods to improve the

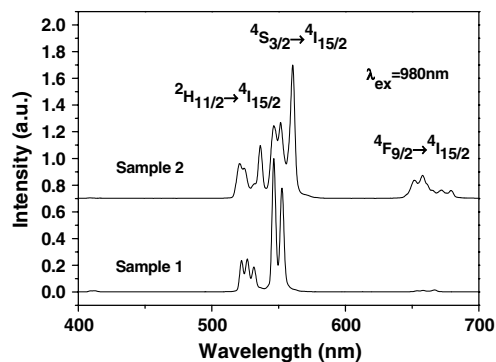


Figure 2. Upconversion emission spectra for samples.

afterglow phosphors. Ions with different ionic valence states from host cation or anion ions are co-doped into a host to produce unbalanced charges. Wang *et al* [12] have improved the long-lasting emission after UV excitation of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ by the introduction of Ti^{4+} ions. In order to prevent the presence of Ti^{4+} ions in the Ti^{3+} form, Mg^{2+} would be co-doped. Here, $\text{Gd}_{1.93}\text{O}_2\text{S} : 0.01\text{Er}, 0.03\text{Yb}, 0.02\text{Ti}, 0.01\text{Mg}$ (Sample 2) was prepared which shows the same pattern (not given) as Sample 1.

3.2. The luminescent properties of samples

Figure 2 shows the upconversion fluorescence spectra of samples (excited at 980 nm). There are several major emission bands which were assigned to $^2\text{H}_{11/2}$ (526 nm), $^4\text{S}_{3/2}$ (550 nm) and $^4\text{F}_{9/2}$ (660 nm) to $^4\text{I}_{15/2}$ transitions in Er^{3+} , respectively. The excitation process has been well established in some publications [10].

We investigated the PL spectra of the samples. There are remarkable differences in the split of the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ and the intensity of the red emission which are ascribed to changes in the environment of activators. Such kinds of differences in the split are also observed in down-conversion PL spectra which are excited at 254 nm. Based on the new phosphorescence mechanism described by Clabau, the distribution of dopant and co-dopant cations around vacancies is not random, and luminescent properties are strongly influenced by this nonrandom distribution [13]. We can explain this difference as the nonrandom distribution of some defects (the replacement of Gd^{3+} with Ti^{4+} creates electron traps) around of Er^{3+} . The traps may influence the environment of activator ions resulting in the change of the upconversion spectrum. Also, it is reported that the polarization effects of Ti^{4+} can change the luminescent properties of activators [14]. However, it is proposed that further discussions and measurements are needed for a broader study of the comparison in spectra.

In this work, in addition to the above-mentioned anti-Stokes emission of Er^{3+} , we were surprised to find that the phosphor shows long-lasting phosphorescence under 980 nm excitation.

Figure 3 shows the decay curves of phosphors after being irradiated under infrared light. It is obvious that the afterglow of phosphor co-doped with Ti^{4+} and Mg^{2+} is enhanced. And the larger initial magnitude and integrated area of curve (b) indicate

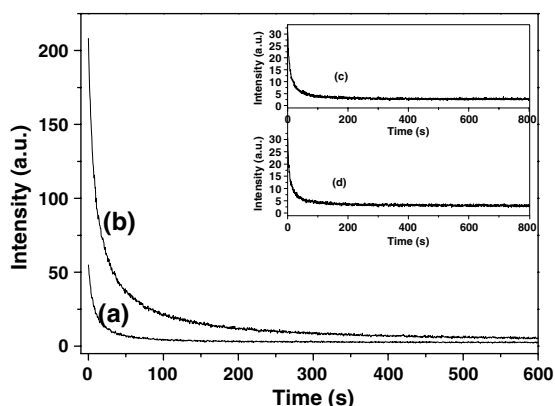


Figure 3. Decay curves of the phosphors: (a) Sample 1, (b) Sample 2, (c) excited for 3 min and (d) excited for 1 min.

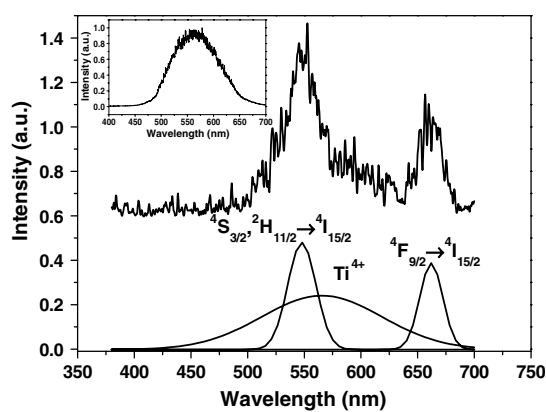


Figure 4. Afterglow emission spectrum of Sample 2 fitted with three Gaussian curves. The inset shows the photoluminescent spectrum of Gd₂O₂S:0.02Ti excited at 254 nm.

large photon storage capacity in Sample 2. Meanwhile, for Sample 2 the upconversion afterglow intensity decay curves excited for 3 min and 1 min, respectively, are shown in the inset of figure 3. It is clear that the phosphor has a very short excitation saturation time. This short saturation time is feasible for practical applications.

As shown in the phosphorescent spectrum (figure 4), it is clear that the emission spectra are different between fluorescence and afterglow. Under the IR excitation, the sample shows a strong green emission, while an orange colour (the ratio of red to green is larger) is observed when the excited source is removed. Besides ²H_{11/2}, ⁴S_{3/2} and ⁴F_{9/2} to ⁴I_{15/2} transitions of Er³⁺, it is sure that there is a broad emission band peaking at 564 nm. The site of this broad band is same as the emission band of Gd₂O₂S:Ti (inset of figure 4) which is caused by charge transfer transition [8]. In addition, because of the overlap between this broad emission band and f–f transition of Er³⁺, an energy transfer process [9] may be permitted which improves the afterglow properties of the activator and changes the ratio of red to green. The broadening of the spectrum which is attributed to ²H_{11/2}, ⁴S_{3/2} → ⁴I_{15/2} is caused by the bigger slit of the instrument during the afterglow detection.

3.3. Mechanism of afterglow

There are some reports about the afterglow mechanism of oxysulfide under UV irradiation. Generally, we ascribe the

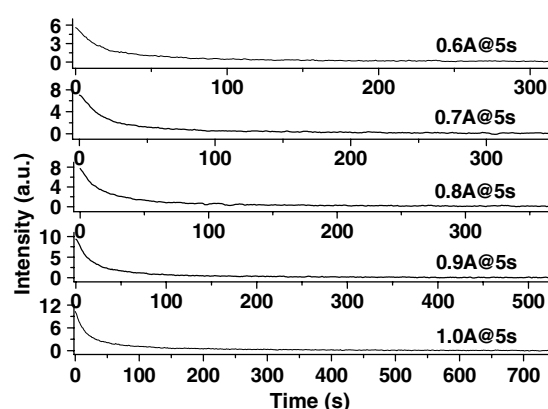


Figure 5. Afterglow decay curves after irradiation with different powers.

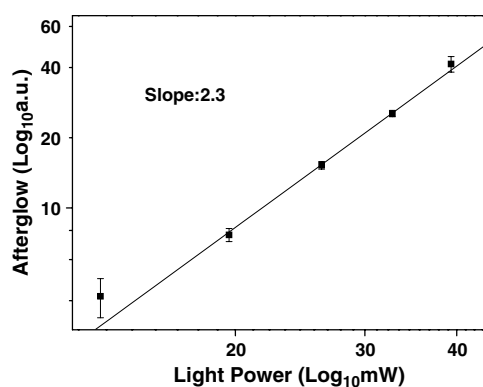


Figure 6. Dependence of afterglow intensity on irradiative power.

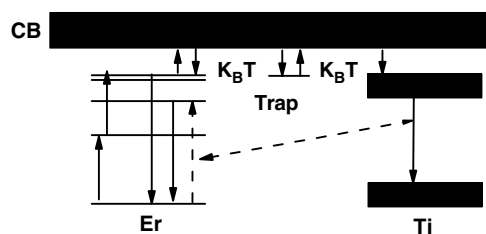


Figure 7. Tentative model of mechanism for LLP of the sample.

afterglow of rare earth in oxysulfide co-doped with Ti⁴⁺ and Mg²⁺ to the energy transfer from recombination of the trapped electrons which are introduced by Ti⁴⁺ ions [9, 15, 16]. But in the upconversion process, it is difficult for the excitation of Ti⁴⁺ related traps. So a new mechanism for the upconversion afterglow must be formulated.

In order to investigate the trapping process of electrons, further experiments were made. The sample was irradiated under 980 nm for just 5 s, which can prevent the saturation of traps. The decay curves of afterglow were recorded at different irradiative powers as shown in figure 5. The integral intensity corresponding to the irradiative power is fitted linearly with a slope of 2.3 on the log scale (figure 6). So we can infer that the trapping process is a two-step process. Under IR excitation, Er³⁺ luminescent centres are excited by the upconversion process as shown in figure 7. The electrons promoted by two-step absorption can be trapped in the vicinity of a vacancy

level introduced by Ti^{4+} . As a result of the strongly localized nature of the 4f orbitals, a direct recombination is not easy even when a vacancy is close to Er^{3+} ions. The thermal energy at ambient temperature induces the detrapping of the trapped electrons, which leads to the phosphorescence of erbium. Meanwhile, one part of the trapped electrons can cause the afterglow emission of Ti^{4+} ions, which may permit the energy transfer to Er^{3+} , thus resulting in the difference between phosphorescence and fluorescence of the sample.

Besides, we found that the afterglow is too weak to be detected without the existence of Yb^{3+} ions. It is well known that due to the strong sensitization of Yb^{3+} , infrared excitation is very efficient. So maybe high upconversion efficiency is needed for the achievement of afterglow. Hence, further work should be performed to increase the phosphorescence property by improving the excitation efficiency.

4. Conclusion

$Gd_2O_2S : Er, Yb$ phosphors were prepared by high-temperature solid reaction. And an upconversion afterglow of Er^{3+} was observed for the first time. In addition, with the co-doping of Ti^{4+} and Mg^{2+} , the unusual phosphorescence was improved. We ascribed it to the increase in traps and the change in distribution of traps. Because of the different excitation process compared with UV excitation, the possible afterglow

mechanism was discussed. We believe that this kind of interesting anti-Stokes long-lasting phosphorescence may help in the study of long-lasting phosphors with a large band gap and open a new field of long persistent phosphor research.

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