Photochromism and white long-lasting persistent luminescence in Bi^{3+}-doped $ZnGa_2O_4$ ceramics

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Abstract: White long-lasting persistent luminescence covering the whole visible region in Bi^{3+}-doped $ZnGa_2O_4$ ceramics is reported. The afterglow luminescence can be observed for several tens of minutes after 360 nm or 280 nm excitation. Photochromism is also observed during ultra-violet excitation. The persistent luminescence and photochromism are considered to originate from electron trapping by defect centers in the $ZnGa_2O_4$ crystals. The Bi^{3+}-doped $ZnGa_2O_4$ ceramics are expected to be potential white-color afterglow phosphors.

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References and links

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1. Introduction

The phenomena of long-lasting persistent luminescence were documented as early as 17th century by an Italian shoemaker, V. Casciarolo [1]. Then new discovery and research progressed slowly during several hundred years. At the end of 20th century, Matsuzawa *et al.*, reported Eu^{2+}-Dy^{3+}-doped $SrAl_2O_4$ phosphors, which show sufficient brightness and duration of persistent luminescence for practical application [2]. Extensive research activity on reporting new persistent phosphors as well as discussing mechanism models was triggered [3–7]. Most of the reports focused on alkaline aluminates (e.g. MAl_2O_4, M = Ca or Sr) and alkaline earth disilicate (e.g. $M_2MgSi_2O_7$, M = Ca, Sr or Ba) activated by rare-earth ions, especially by Eu^{2+} as emitters and Dy^{3+} as sensitizers. Long duration of blue and green persistent luminescence for several hours has been achieved.

White-color (full-color) afterglow phosphors as persistent emitting light sources would be important in many dark-environment applications [8]. One of possible strategies is by combining three individual blue, green, and red persistent phosphors. However, the inconsistence of the duration of these three colors, especially due to weak and short red persistent luminescence, precludes practical application. Another idea of integrating several afterglow emissions with similar decay rate in one single material seems promising but very few studies have been reported.

The $ZnGa_2O_4$ crystal is a large band-gap semiconductor with band-gap of about 4.5 eV. The $ZnGa_2O_4$ crystallizes in normal spinel structure with Zn^{2+} ions occupying tetrahedral sites and Ga^{3+} ions occupying octahedral sites [9]. Some kinds of defect centers depending on synthesis condition exist in $ZnGa_2O_4$ crystals, which are responsible for self-activated ultra-violet (UV) and blue luminescence in non-doped $ZnGa_2O_4$ ceramics [10]. With some transition metals doping, specific optical properties, for example green emission in $ZnGa_2O_4$: Mn^{2+} and red emission in $ZnGa_2O_4$: Cr^{3+}, can be obtained [11,12]. Recently, red long-lasting persistent luminescence in $ZnGa_2O_4$: Cr^{3+} ceramics were reported by A. Bessière *et al.* [13]. The host of $ZnGa_2O_4$ crystal shows ability of trapping excited electrons of luminescent centers.

Bismuth is an interesting luminescent center with many mysteries [14]. Bi-doped silicate and germanate glass fibers are promising candidates for broadband optical amplifiers in the next generation of telecommunication system. However, the nature of the active centers is still controversial [15,16]. Several kinds of Bi^{3+} and Bi^{2+}-activated crystals have been reported for potential phosphors in white light emitting diodes (white LEDs) applications. The emission bands cover various wavelength regions from blue to red, depending on the coordination states of the active centers [17–21].

In this research, we report a new white persistent phosphor of Bi^{3+}-activated $ZnGa_2O_4$ ceramics. The persistent luminescence of Bi^{3+} covers the whole visible region after 360 nm excitation.

2. Experimental

Polycrystalline ceramics of $ZnGa_2O_4$ (ZGO) and $ZnGa_{1.98}O_4$:$Bi_{0.02}$ (ZGO-Bi) were synthesized by a solid state reaction method. Commercial powders of ZnO (99.9%), Ga_2O_3 (99.99%) and Bi_2O_3 (99.99%) were used as starting materials. The batches of starting powders were mixed in an alumina mortar by hand. The obtained powders were pressed into pellets with 13-mm-diameter and sintered at 1350 °C for 10 h under air atmosphere.

Crystal phases of the sintered samples were identified by X-ray diffraction (XRD) measurement (Shimadzu, XRD6000). 5 wt% of silicon powers (Siltronic AG, SRM 640d) was mixed with sample powers before measurement for calibration of diffraction peaks.

Diffuse reflection spectra were measured by using a scanning-type spectrophotometer (Shimadzu, UV3600) with an $BaSO_4$-based integrating sphere. The spectrometer was equipped with photomultiplier tubes as optical detectors (ultraviolet-visible region) and halogen-D_2 lamp as light source. Probe light was obtained by monochromating the light source and the intensity was weakened by a slit to make sure the probe light did not induce obvious photochromism effect. The Photoluminescence (PL), Photoluminescence excitation (PLE) spectra, and afterglow curves were measured using a fluorescence spectrophotometer (Shimadzu, RF-5000). A set of photographs of the ZGO-Bi sample was taken by using a digital camera (Canon, 60D). The white balance was set to 5200 K of color temperature.

3. Result and discussion

Figure 1 shows XRD patterns of the ZGO and ZGO-Bi samples. Both samples show the same diffraction peaks assigned to $ZnGa_2O_4$ crystals (cubic, spinel structure) as well as peaks assigned to the reference silicon crystals. Diffraction peak shift of $ZnGa_2O_4$ phase between these two samples cannot be observed.
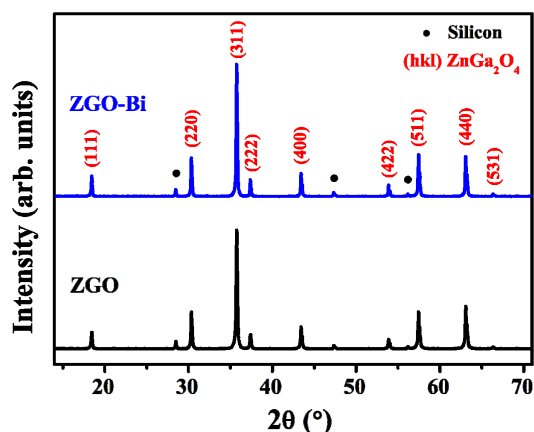

Fig. 1. XRD patterns of the ZGO and ZGO-Bi samples.

Figure 2 shows diffuse reflection spectra of the non-doped sample ZGO (black solid curve) and the Bi-doped sample ZGO-Bi (red solid curve). Before measurement, the two samples were heated up to 250 °C to release trapped electrons [22]. Other dash, dash-dot, and dot curves in Fig. 2 correspond to spectra of the ZGO-Bi samples after 2s, 5s, and 10s radiation respectively by a 360 nm LED (20 mA, 3.6 V). When the radiated ZGO-Bi sample was re-heated up to 250 °C and reflection spectra were re-measured, the same result as the ZGO-Bi-0s curve in Fig. 2 could be obtained.

The ZGO sample does not show obvious absorption in the visible region. Absorption edge of the ZGO sample starts from 300 nm and reaches maximum at 250 nm. On the other hand, three additional absorption bands at about 450, 360, and 280 nm can be identified in the ZGO-Bi sample. With increasing radiation time of the 360 nm LED, the 450 nm absorption band increases, while the 360 nm band slightly decreases.

According to S. Sampath *et al.*, the 250 nm band is due to band-gap absorption of the $ZnGa_2O_4$ host [9]. The broad 450 nm band is due to charge transfer from Bi^{3+} and to neighboring Bi^{5+} ions based on the report from H. Mizoguchi *et al.* [23]. The 360 nm and 280 nm absorption bands are assigned to the $^1S_0 \rightarrow ^3P_1$ transition of Bi^{3+} ions at two different sites in the $ZnGa_2O_4$ crystals [17,18].

After radiation by the 360 nm LED, the charger transfer band of Bi^{3+}-Bi^{5+} at 450 nm was enhanced and the intra-transition band of Bi^{3+}:$^1S_0 \rightarrow ^3P_1$ at 360 nm was slightly weakened. One can infer that more Bi^{5+} ions were temporarily converted from Bi^{3+} during the 360 nm irradiation. After irradiation, the unstable Bi^{5+} ions return to Bi^{3+} valence state spontaneously at a slow rate at room temperature. In another case, these unstable Bi^{5+} ions return to Bi^{3+} when the sample was heated up to 250 °C.
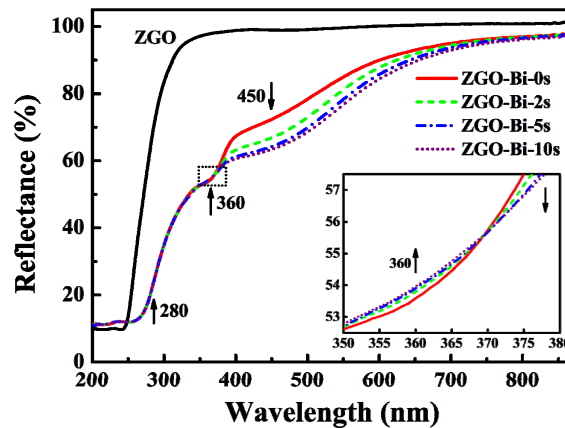

Fig. 2. Diffuse reflection spectra of non-doped sample ZGO (black solid curve) and Bi-doped sample ZGO-Bi (red solid curve). Before measurement, the two samples were heated up to 250 °C. Then the ZGO-Bi sample was radiated by a 360 nm LED (100mW) for 2s, 5s, 10s and measured again. The results were shown as dash, dash-dot, and dot curves, respectively.

Figures 3(a) and 3(b) show PLE and PL spectra of the ZGO and ZGO-Bi samples, respectively. The non-doped $ZnGa_2O_4$ shows a single excitation band at 254 nm. Under 254 nm excitation, two luminescence bands at 370 nm and 450 nm were observed. On the other hand, the Bi-doped sample shows three excitation bands in the UV region. Under 254 nm excitation, the similar bands as those in the non-doped sample were detected. Under 280 nm excitation, a broad luminescence band at 480 nm was shown; while under 360 nm excitation, two bands at 410 nm and 540 nm were observed.

The two luminescence bands in non-doped $ZnGa_2O_4$ crystals have been reported by J. Kim *et al.* [10]. The 370 nm and 450 bands are attributed to host emissions related to two different defects, which are formed in synthesis processes under reduction and oxidation atmosphere, respectively. In our research, the ZGO and ZGO-Bi samples were synthesized in ambient air. The two luminescence bands at 370nm and 450 nm were detected simultaneously in each sample.

The 280 nm and 360 nm excitation bands as well as corresponding luminescence bands were considered to originate from Bi^{3+} centers at different sites. Under the 360 nm excitation, two luminescence bands with Stokes shift of 3,300 cm^{-1} and 10,000 cm^{-1} were observed; while under the 280 nm excitation, single emission band with stokes shift of 14,000 cm^{-1} was detected. G. Blasse *et al.* discussed the optical properties of Bi^{3+} in various phosphors [24–

26]. The emission with small Stokes shift was attributed $^3P_{0,1} \rightarrow {}^1S_0$ electronic transitions of Bi^{3+}. The emission with large Stokes shift (usually > 10,000 cm^{-1}) was considered as a photoionization process. In the photoionization process, the excited electron non-radiatively relaxes to an exciton-like state ($Bi^{4+} + e^-$ state), which is located below the excited states $^3P_{0,1}$ of Bi^{3+} with larger offset, then the transition from the exciton-like state to the ground state of Bi^{3+} emits a photon with longer wavelength (r.f. configurational coordinate model in [25]).

It is noted that under excitation of 450 nm (charge transfer band from Bi^{3+} to Bi^{5+}), no emission (PL as well as persistent luminescence in visible and near-infrared region) can be observed. The photochromism phenomenon (increase of 450 nm absorption) may be interesting for some applications such as optical recording, however, the 450 nm absorption band is undesired from the view point of luminescent materials.
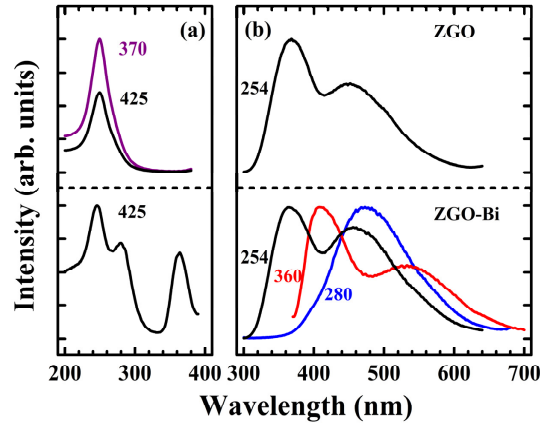

Fig. 3. PLE (a) and PL (b) spectra of the ZGO and ZGO-Bi samples at room temperature. Monitoring wavelength and excitation wavelength was noted in (a) and (b), respectively. The PL spectra of the ZGO-Bi sample were normalized.

Figure 4 shows photographs of the ZGO-Bi sample. Under excitation of a UV lamp (peak wavelength at 352 nm), the sample shows white-color luminescence (b). After stopping the UV excitation, white persistent luminescence (c) was observed. The afterglow can be observed by naked eyes for several tens of minutes.
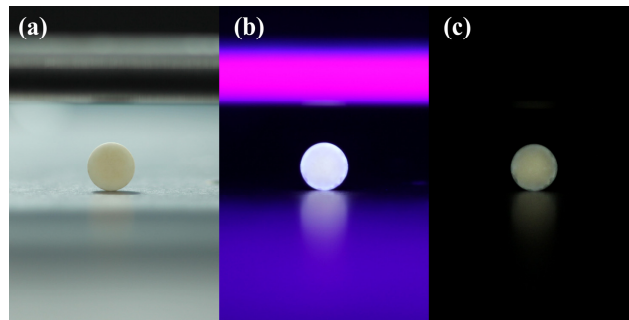

Fig. 4. Photograph images of the ZGO-Bi sample in nature light (a), under (b) and after stopping (c) excitation of an UV lamp in a dark room.

Afterglow curves of 410 nm and 550 nm in the ZGO-Bi sample after 360 nm excitation are shown in Fig. 5. The intensity of the afterglow luminescence is normalized by that of the saturated fluorescence. Persistent time $\tau_{1/10000}$ is defined as the time when the intensity of persistent luminescence becomes 1/10000 of the saturated fluorescence intensity under excitation [27]. The persistent time $\tau_{1/10000}$ was calculated as 25 and 40 min for 410 nm and 550 nm emissions, respectively. The fluorescence spectra under 360 nm excitation and

phosphorescence spectra after stopping excitation are presented in inset of Fig. 5. These two spectra show similar curves, which cover the whole visible region. These results indicate that the Bi-doped $ZnGa_2O_4$ ceramics can be used as white afterglow phosphors with long persistent time.

Meanwhile, the ZGO-Bi sample shows blue-white persistent luminescence after several minutes of 280 nm excitation. The phosphorescence spectra are similar to the fluorescence spectra under 280 nm excitation (the blue curve in Fig. 3).
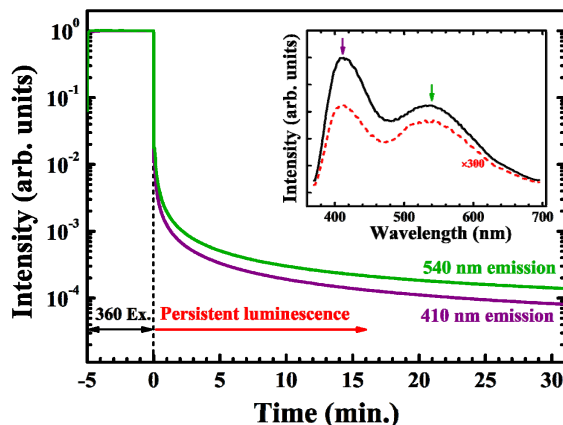

Fig. 5. Afterglow curves of 410 nm and 550 nm emissions in the ZGO-Bi sample after 360 nm excitation for 5 min. Inset shows fluorescence spectra during 360 nm excitation (solid curve) and phosphorescence spectra measured at 30 s after stopping the excitation (dash curve).

We consider that the phenomena of photochromism and long-lasting persistent luminescence are related to electron trapping processes by some defects in the Bi-doped $ZnGa_2O_4$ ceramics. When Bi^{3+} ions are excited by UV photons, the excited electrons are directly trapped by neighboring defect centers or through conduction band trapped by other defect centers [21]. Some Bi ions with higher valance state are created temporarily during UV radiation, and result in stronger absorption at 450 nm. The trapped electrons return to luminescent centers gradually at room temperature and give persistent luminescence. When a radiated ZGO-Bi sample is heated to higher temperature, the detrapping process is fast enough that intense thermoluminescence as well as obvious bleaching of the ceramics can be observed.

However, the exact defect centers for the photochromism and persistent luminescence in the Bi-doped $ZnGa_2O_4$ ceramics are not clear now. A following research on the effect of ceramic composition and synthesis atmosphere on the defect equilibrium and optical properties is in progress.

4. Conclusion

Polycrystalline ceramics with the composition of $ZnGa_{1.98}O_4$: $Bi_{0.02}$ shows two absorption bands due to $^1S_0{\rightarrow}^3P_1$ transition of Bi^{3+} ions in different sites as well as an absorption band due to Bi^{3+}-Bi^{5+} charge transfer. Photochromism is observed when the Bi^{3+}-doped ceramics are radiated by UV light. After UV excitation at 360 nm or 280 nm, the Bi^{3+}-doped ceramics show white persistent luminescence covering the whole visible region. The persistent luminescence can be observed for several tens of minutes. The photochromism and persistent luminescence are considered to originate from electron trapping by defect centers in the $ZnGa_2O_4$ crystals.

Acknowledgments