Rare Metal Materials and Engineering
Volume 47, Suppl. 1, July 2018
Cite this article as: Rare Metal Materials and Engineering, 2018, 47(S1): 078-082.

Long-lasting Blue Persistent Luminescence from *β*-Ga_2O_3 with B^{3+} Addition

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Abstract: Blue persistent luminescent *β*-Ga_2O_3:B^{3+} was synthesized by high temperature solid-state reaction. The phosphor exhibits more than 0.5 h afterglow in the wavelength range of 380~600 nm after ceasing the ultraviolet light (260 nm) irradiation. The emission and excitation spectra, persistent luminescence decay curve, and thermoluminescence curve were measured. The emission and excitation spectra indicate that the B^{3+} doping improves photoluminescent properties of *β*-Ga_2O_3. The thermoluminescence (TL) curve of *β*-Ga_2O_3: 80% B^{3+} show that B^{3+} increases the traps and improves the depth of the traps.

Key words: *β*-Ga_2O_3:B^{3+}; blue persistent luminescence; H_3BO_3; afterglow

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Gallium oxide (Ga_2O_3) can adopt five different crystalline structures, that is *α*-, *β*-, *γ*-, *δ*- and *ε*-phases[1]. Among these phases, *β*-Ga_2O_3 is an important wide band gap compound, which has long been known to have conduction and luminescence properties[2,3]. Great efforts have been made to investigate their applications as optoelectronic devices[4, 5], as well as a candidate for a high-temperature stable gas sensor[6,7], transparent conductor[8] and supported selective catalysts[9,10]. Particularly, *β*-Ga_2O_3 possesses excellent optical properties since its wide band gap provides the possibility of light emission in a broad region of the spectrum [11].

Long-persistent luminescent materials are receiving considerable attention because of their important application insecurity, solar energy utilization, and in vivo bio-imaging [12, 13]. In the design of long-persistent phosphors, the emitter and host need to be carefully selected. For blue photoluminescence, *β*-Ga_2O_3 is a favorable host. The defects in the host are favorable emitters. However, persistent blue luminescence from *β*-Ga_2O_3 was rarely reported because of poor initial intensity and short decay time. It has been found that the appropriate doping or vacancy defects in the crystal lattice can change the energy band structure of *β*-Ga_2O_3 by introducing new defect levels between the band gaps [14]. If appropriate doping in the crystal lattice can increase the traps and improve the depth of the traps, the persistent blue luminescent properties of *β*-Ga_2O_3 can be improved.

Herein, we report the persistent blue luminescence from *β*-Ga_2O_3 with B^{3+} doping synthesized by high solid-state reaction. The *β*-Ga_2O_3:B^{3+} exhibits persistent luminescence in the 380~600 nm wavelength range with an afterglow time of more than 0.5 h at room temperature. No persistent blue luminescence was reported in B^{3+}-doped Ga_2O_3 before.

1 Experiment

The samples *β*-Ga_2O_3:*x*% B^{3+} were synthesized via the high temperature solid-state reaction method. Stoichiometric amount of Ga_2O_3 (99.99%), and H_3BO_3 (99%) powders were used as raw powders. The raw powders were mixed for about 1 h in an agate mortar to form a homogeneous fine powder for sintering. The mixed powders were moved into a corundum crucible and sintered at 1200 ℃ for 5 h in an air atmosphere.

All the crystalline structures of the samples were measured by a Rigaku D/max-IIIB X-ray powder diffractometer with Cu Kα1 (λ=0.154 05 nm) radiation. The photoluminescence spectra and persistent luminescence decay curves were recorded using a HITACHI F-7000 fluorescence spectrofluorometer equipped with a 150 W Xe lamp. All the experiments were performed at room temperature. An FJ27A1 dosimeter was used to record thermoluminescence curve with the heating rate of 1 ℃/s.

2 Results and Discussion

Received date: July 25, 2017
Foundation item: Fundamental Research Funds for the Central Universities (N130423002); Basic Key Program of Applied Basic Research of Science and Technology Commission Foundation of Hebei Province in China (14961108D, 15961005D)

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The typical XRD patterns of the samples (β-Ga_2O_3:x% B^{3+}) obtained after high solid-state reaction are shown in Fig.1. All the reflections were indexed to β-Ga_2O_3 (JCPDS 41-1103). The peaks were sharp and narrow, indicating the high crystallinity of samples. No peaks related to B-containing phases were detected within the detection limit of the XRD, though the B^{3+} was doped with high concentration.

Fig.2 shows the excitation and emission spectra of the raw material β-Ga_2O_3 and β-Ga_2O_3: B^{3+} with varying concentrations of B^{3+} at room temperature. The spectra of raw material β-Ga_2O_3 and raw material β-Ga_2O_3 sintered at 1200 ℃ without B^{3+} doping (named β-Ga_2O_3:0% B^{3+}) are illustrated in Fig.2a and 2b. The emission spectrum of raw material β-Ga_2O_3 shows a broad blue emission band centered at 451 nm under a 260 nm excitation. The emission spectrum of β-Ga_2O_3:0% B^{3+} shows a blueshift from 451 nm to 410 nm. It has been suggested that the oxygen vacancy (V_O) and gallium-oxygen vacancy pairs (V_{Ga}, V_O) in the Ga_2O_3 are responsible for the blue emission [2,14]. High temperature sintering process may shorten the distance of gallium-oxygen vacancy pairs, which leads to the emission peak blue shift. The emission spectra of β-Ga_2O_3: B^{3+} with varying concentrations of B^{3+} in Fig.2c show a redshift from 410 nm to 451 nm with the increasing B^{3+} concentration. Ionic radius of B^{3+} is 0.0027 nm. It is far less than Ga^{3+} (0.062 nm). The incorporation of part B^{3+} may be positioned on interstitial lattice sites. It increases the distances of gallium-oxygen vacancy pairs (V_{Ga}, V_O), which results in the redshift of the emission peak. The emission intensity of blue band enhances with the increase of the B^{3+} concentration. It starts to decrease at B^{3+} concentration x=70%.

The 260 nm UV light can induce long-lasting persistent luminescence in β-Ga_2O_3:80% B^{3+} with a long time about 0.5 h. The afterglow spectra of raw material β-Ga_2O_3, β-Ga_2O_3: 0% B^{3+}, and β-Ga_2O_3:80% B^{3+} after turning off the UV lamp immediately are shown in Fig.3. The long-lasting luminescence peaks are at 500 nm in raw material β-Ga_2O_3, 444 nm in β-Ga_2O_3:0% B^{3+} and β-Ga_2O_3:80% B^{3+}. All the peaks show redshift. The afterglow emitting centers are different from the PL emitting center.

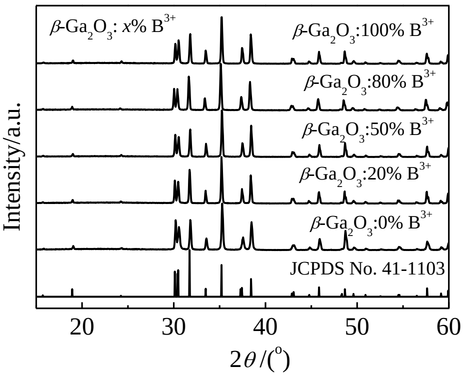

Fig.1 Typical XRD patterns of the samples (β-Ga_2O_3: x% B^{3+})

Fig.4 shows the persistent luminescence decay curves of β-Ga_2O_3:0% B^{3+} and β-Ga_2O_3:80% B^{3+} monitored at 444 nm after irradiation by 260 nm UV light for 5 min. The persistent luminescence of raw material β-Ga_2O_3 is too weak to show in the figure. The persistent luminescence of samples with B^{3+} doping enhances with the increasing B^{3+} concentration. The best one is the sample β-Ga_2O_3:80% B^{3+}, whose decay curve is shown in Fig.4. As can be seen, great improvement of persistent luminescence intensity by B^{3+} doping in β-Ga_2O_3 is proved. After removal of UV light, the initial intensities of β-Ga_2O_3:

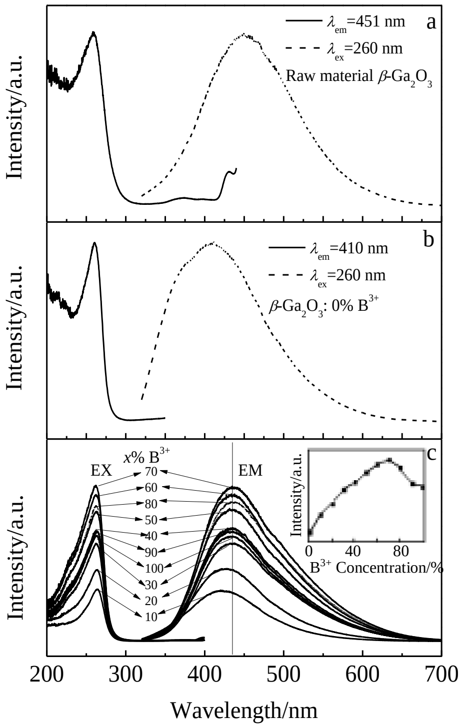

Fig.2 Excitation and emission spectra of the raw material β-Ga_2O_3 and β-Ga_2O_3: B^{3+} with varying concentrations of B^{3+} at room temperature

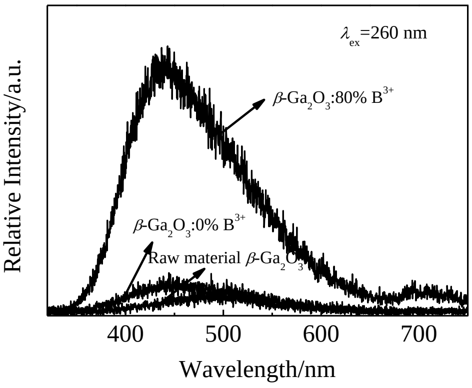

Fig.3 Afterglow spectra of raw material β-Ga_2O_3, β-Ga_2O_3:0% B^{3+}, and β-Ga_2O_3:80% B^{3+} after turning off the UV lamp immediately

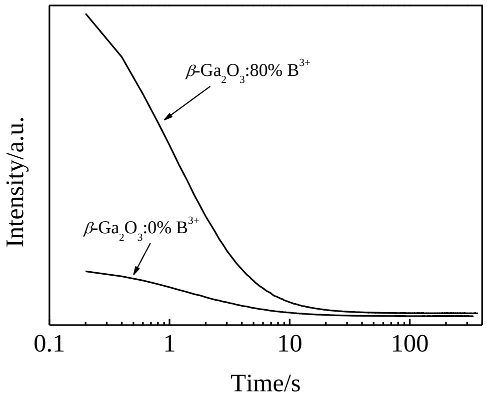

Fig.4 Persistent luminescence decay curves of β-Ga$_2$O$_3$: 0% B^{3+} and β-Ga$_2$O$_3$:80% B^{3+} monitored at 444 nm after irradiation by 260 nm UV light for 5 min

80% B^{3+} are about 7 times higher than that of β-Ga$_2$O$_3$:0% B^{3+}. And the property of persistent luminescence such as duration and brightness has been improved in every aspect. It indicates that β-Ga$_2$O$_3$ with B^{3+} doping can strongly prolong persistent luminescence duration and the initial intensity.

In general, the persistent luminescence of the phosphors is generated by the detrapped carriers (holes or electrons) which recombine with the decay emission. Thus the traps induced by the lattice defects and appropriate trap structures model in the phosphors play an important role in the generation of the persistent luminescence. In most cases, the maximum temperature of the thermoluminescence peak is related to the depth of the charge carrier trap, and the intensity of the thermoluminescence curve provides information on the amount of trapped charge carriers. The deep traps have contribution for the duration of the persistent luminescence, and the shallow traps make contribution to the initial intensity. In order to study the relationship between the trap energy level and persistent luminescence, the thermoluminescence curves of samples with different B^{3+} doping are recorded and shown in Fig.5. As can be seen in Fig.5, all the TL curves can be divided into two peaks. The first one is shown as red line and the second is shown as green line. The first one located at 71 ℃ in raw material β-Ga$_2$O$_3$, 83 ℃ in β-Ga$_2$O$_3$:0% B^{3+}, 105 ℃ in β-Ga$_2$O$_3$: 30% B^{3+}, 102 ℃ in β-Ga$_2$O$_3$:50% B^{3+}, 101 ℃ in β-Ga$_2$O$_3$:80% B^{3+}. The second one located at 113 ℃ in raw material β-Ga$_2$O$_3$, 115 ℃ in β-Ga$_2$O$_3$:0% B^{3+}, 208 ℃ in β-Ga$_2$O$_3$:30% B^{3+}, 207 ℃ in β-Ga$_2$O$_3$:50% B^{3+}, 202 ℃ in β-Ga$_2$O$_3$:80% B^{3+}. It is indicated that all the samples have two traps, the shallow one and the deep one. In fact, the thermal activation energy E(eV) can be reckoned by the formula of $E = T_{\mathrm{m}}(\mathrm{K})/500$ [15,16], where T_{m} is the temperature of the glow and the unit of the constant is K/eV. Thus, we can estimate the trap depths of all the samples. They are 0.73 and 0.81 eV in raw material β-Ga$_2$O$_3$, 0.75 and 0.82 eV in β-Ga$_2$O$_3$:0% B^{3+}, 0.80 and 0.82 eV in β-Ga$_2$O$_3$: 30% B^{3+}, 0.79 and 1 eV in β-Ga$_2$O$_3$:50% B^{3+}, 0.79 and 0.99 eV in β-Ga$_2$O$_3$:80% B^{3+}. The first trap is the shallow trap, and the second one is the deep. For the sake of exhibiting long persistent luminescence at room temperature, it is necessary to have a suitable trap density and trap level. Defects with a suitable structure can capture the holes or electrons more effectively and deliver them slowly to the emission centers which lead to persistent luminescence. On the one hand, if the depth of the trap level is too shallow, the electrons in the trap easily return to the energy level of the excited state. Then the phosphor would show rapid decay. On the other hand, if the depth of the trap level is too deep, it will be more difficult for the trapped electrons to be released at room temperature [17, 18]. Thus it also results in poor persistent luminescence property. According to the previous reports[15,16,19], a suitable depth of trap (0.65~0.81 eV) and the energy of the trap whose TL peak is located at 50~110 ℃ is essential for phosphors to show optimal persistent luminescence at room temperature. From Fig.5, we consider that all the samples have an opportune trap depth for exhibiting long persistent luminescence at room temperature. The trap depths of samples with B^{3+} doping are deeper than those of

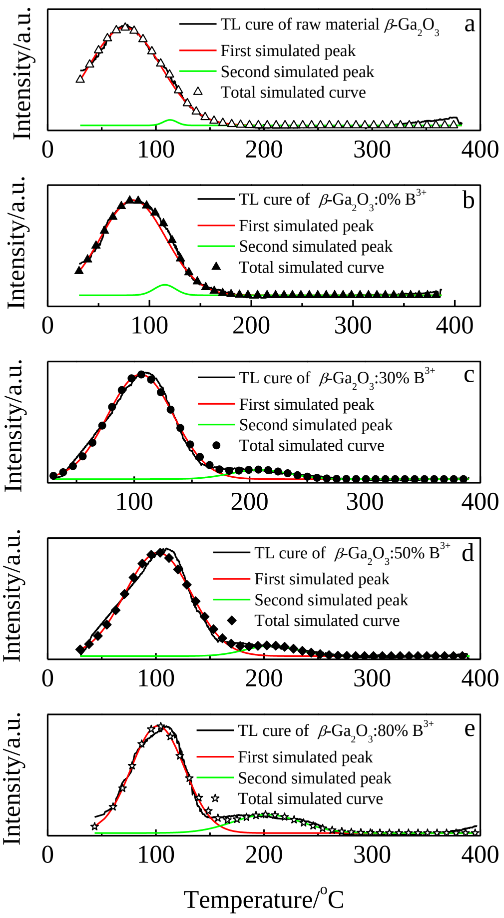

Fig. 5 Thermoluminescence curves of raw material β-Ga$_2$O$_3$ and β-Ga$_2$O$_3$:x% B^{3+} (x=0, 30, 50, 80)

the samples without B^{3+}. As already known, what influence persistent luminescence properties of the phosphor directly are the intensity of TL peak and the trap depth. The integration area of TL curve can reflect the intensity of TL peak. Moreover, we also discover that the integration areas of samples with B^{3+} doping should be higher than those of samples without B^{3+}. Meanwhile, the integration areas of samples with B^{3+} doping enhance with the increasing B^{3+} concentration. It is in good agreement with experimental results. It means the depth and the number of the traps in samples with B^{3+} addition increases. Thus, all the samples with B^{3+} addition show higher initial intensity and longer decay time than the sample without B^{3+}.

The above results lead to a possible mechanism of persistent luminescence of β-Ga_2O_3 with or without B^{3+} addition. Under UV light irradiation, a number of holes and electrons are created (progress ①). Then the energy will be transferred to the luminescence centers oxygen vacancy (V_O, donor) and gallium-oxygen vacancy pairs (V_{Ga},V_O, acceptor) by the excited carriers (electrons or holes) (progress ②), then recombine due to donor-acceptor pair (progress ③). The oxygen vacancy (V_O) acts as an electron donor, whose energy level is far from the bottom of CB. Meanwhile, part of the electrons is trapped by the oxygen vacancy (electron trap) whose energy level is near to the bottom of CB (progress ④). The shallow trap is called trap 1 and the deep trap is called trap 2. After turning off the irradiation, with the thermal disturbance at temperature, these electrons trapped by oxygen vacancies will be released from the traps and transferred to the luminescence center near to the traps and then emit followed by the emissions as persistent luminescence (progress ⑤). As shown in Fig.2 and Fig.3, the afterglow emitting centers are different from the PL emitting center. The possible reason is that the energy level difference of donor and acceptor far from electron trap is larger than that of donor and acceptor near to electron trap. The PL is mainly from the recombination of donor and acceptor far from electron trap. The afterglow is mainly from the recombination of donor and acceptor near to electron trap. Compared to the PL peak, the afterglow spectrum has redshift. From Fig.4, it is observed that the initial intensity and decay time increase in samples with B^{3+} addition. It may be due to the depth of trap near to B^{3+} becomes deep. With the increasing B^{3+} concentration, the number of deep traps becomes large. Thus, the samples with B^{3+} doping have high initial intensities and long decay time.

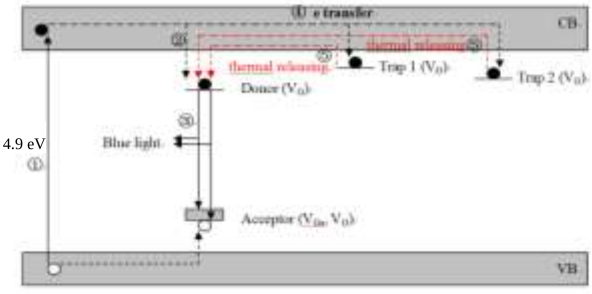

Fig.6 Schematic diagram of the persistent luminescence mechanism

3 Conclusions

β-Ga_2O_3: B^{3+} has been synthesized by high solid-state reaction. The incorporation of part B^{3+} may be positioned on interstitial lattice sites because of small ionic radius. The addition of B^{3+} enhances the photoluminescence and the persistent luminescence. The emission intensity of blue band enhances with the increase of the B^{3+} concentration. It reaches the maximum when B^{3+} concentration is 70%. The afterglow emitting centers are different from the PL emitting center. The possible reason is that the energy gap of donor and acceptor far from electron trap is larger than that of donor and acceptor near to electron trap. The samples with B^{3+} doping have high initial intensities and long decay time because the depth and the number of traps enhances with B^{3+} addition.

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β-Ga_2O_3:B^{3+}蓝色长余辉性能的研究

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摘　要：利用高温固相法制备了蓝色长余辉材料 β-Ga_2O_3:B^{3+}。β-Ga_2O_3:B^{3+}在 260 nm 紫外光辐照 5 min 后，撤去紫外光，在 380~600 nm 光谱范围内呈现宽带的蓝色余辉，余辉时间超过 0.5 h。通过激发光谱，发射光谱，余辉衰减曲线，热释光谱等实验手段对样品进行表征。结果表明，B^{3+}的掺入能够提高 β-Ga_2O_3 的发光性质。β-Ga_2O_3:80% B^{3+}的热释光谱表明 B^{3+}的掺入能够增加陷阱数目及陷阱深度。

关键词：β-Ga_2O_3；蓝色长余辉；H_3BO_3；余辉

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