Luminescence Properties of Impurity-Doped Zinc Oxide Phosphor for Novel Neutron Detection

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A neutron detection sheet composed of Ag-doped zinc sulfide (ZnS) as a scintillator and 6LiF as a neutron converter has been conventionally used for neutron detection, and as an imaging detector using the photon counting method, because of its high luminescence rate for neutrons. However, the weak point in a Ag-doped ZnS scintillator is the slow component of its lifetime. Thus, we began to investigate other II–VI compound phosphors without the slow component of its lifetime for neutron detectors using the photon counting method. In this study, Cu-, In-, Al-, and Ga-impurity-doped ZnO phosphors without the slow component of lifetime for neutron detectors at a high counting rate have been fabricated using a spark plasma sintering method. It was found that Ga-doped ZnO exhibited the highest intensity of luminescence at a wavelength of 383 nm. The intensity of the 383 nm luminescence due to exciton emission with a lifetime of about 4 ns was comparable to that of the Ag-doped ZnS phosphor with a lifetime of about 220 ns, indicating that the Ga-doped ZnO phosphor could be used as a promising phosphor material for a neutron image sensor. It was also found that the luminescence intensity of the Ga-doped ZnO phosphor samples did not decrease when B2O3 was added as a neutron-alpha (n, alpha) converter. It was confirmed that a Ga-doped ZnO scintillator with B2O3 converter responds to the neutron beam emitted by the Japan Research Reactor-3 (JRR-3).

1. Introduction

Recently, the next-generation pulsed neutron source using a high-intensity proton accelerator has been constructed in Japan Proton Accelerator Research Complex (J-PARC) project. It is expected that the pulsed neutron source can emit powerful neutrons which are incident to detectors within short time.(1) At the experimental sites, a novel neutron detector that can detect neutrons one by one is necessary. Currently, a neutron imaging detector using Ag-doped zinc sulfide (ZnS) phosphors covered with neutron-alpha converters is used as a neutron scintillator, because the luminescence from the Ag-doped ZnS phosphor for alpha rays is higher than that of other phosphors, and its
lifetime is about 200 ns, which is relatively short. The weak point of the Ag-doped ZnS phosphor is the slow component of its luminescence lifetime, which is about 0.1 ms.\(^{11}\) For this reason, the maximum counting rate is about 100 kcps in neutron detectors using a \(^{6}\text{LiF}/\text{Ag}-\text{doped ZnS sheet.}\) It is difficult to use the Ag-doped ZnS phosphor for the detection of a high-intensity neutron beam from a highly intense proton accelerator owing to the pile-up phenomenon, as shown in Fig. 1. We began to investigate other II–VI compound semiconductors without a slow component of lifetime; consequently, we have become interested in zinc oxide (ZnO) with an exciton luminescence with a very short lifetime.

Since ZnO is a direct-band-gap II–VI compound semiconductor with a 3.37 (eV) band gap energy that is stable over a wide range of temperatures and is mechanically robust, some compounds based on ZnO have been considered as promising materials for fast scintillators,\(^{2–6}\) ultraviolet (UV) emitters,\(^{7,8}\) transparent conducting oxides,\(^{9,10}\) and gas sensors.\(^{11–13}\) Recently, an efficient ultrafast scintillation in the UV wavelength region has been observed in Ga- and In-doped ZnO phosphors, because room-temperature exciton emission with ultrafast (about 4 ns) is observed in ZnO phosphors with large exciton bonding energies.\(^{14,15}\) In this paper, we report the optical and structural properties of a ZnO phosphor prepared using the spark plasma sintering (SPS) method. This phosphor could be useful as neutron detectors for high-power neutron beams.

2. Experimental Procedure

Each powder mixture (purity of 99.99%) of ZnO containing copper oxide (CuO), aluminum oxide (Al\(_2\)O\(_3\)), indium oxide (In\(_2\)O\(_3\)), and gallium oxide (Ga\(_2\)O\(_3\)) was sintered using a conventional SPS system (SPS Syntax Inc). The B\(_2\)O\(_3\) and H\(_3\)BO\(_3\) powders as neutron converter materials were supplied by the Japan Atomic Energy Association.

Powdered mixtures of ZnO, supplied by Hakusui Chemicals Co., Ltd, Furuuchi Chemicals Co., Ltd., and Kojundo Chemicals Co., Ltd., were sintered at 750 °C for 30 min using the SPS apparatus in vacuum at a pressure of 7–10 Pa. Pulsed currents of about 300 A were applied to the ZnO mixture without applying compressed pressure. In order to anneal the ZnO powder in vacuum, the sintering of the ZnO powder using the SPS apparatus was carried out in vacuum without pressure

![Fig. 1. (Color online) Schematic diagram of the pile-up phenomenon.](image)
by external mechanical force. Details of the preparation of sintered ZnO phosphors have been reported in previous papers.\textsuperscript{(16–18)}

As for the crystallinity measurement of the ZnO phosphors, their crystallographic structure was evaluated using an X-ray diffraction (XRD) apparatus (Rigaku Electric Co. Ltd., Model: RINT2000, Cu target, 40 kV/30 mA). Photoluminescence (PL) spectra caused by excitation with UV light (330 nm) were observed using a Hitachi F-3010 spectrofluorometer at room temperature. The radioluminescence was observed by excitation with alpha rays from a $^{241}$Am source. The PL and radioluminescence spectra were corrected for the diffraction efficiency of the grating and the optical response of the photomultiplier.

3. Results and Discussion

3.1 PL characteristics of undoped ZnO and impurity-doped ZnO phosphor

In order to optimize the phosphor materials composition, the luminescence properties of ZnO phosphors was evaluated using the PL spectra by excitation with 330 nm (3.76 eV) light, because of ease of measurement. It is possible to perform band-to-band excitation using 360 nm light as an excitation source for luminescence measurement, because the energy (3.76 eV) of such excitation light is larger than the band gap energy of ZnO (about 3.37 eV).

The PL spectra of undoped ZnO phosphors from three different suppliers are shown in Fig. 2. It can be seen that the PL spectrum consists of two emission bands: a broad visible emission band (at about 450 nm) and a very sharp UV emission band (at about 380 nm). It can also be seen that the luminescence intensity and spectral shape are strongly dependent on the ZnO powder supplier. The differences in the spectral shape may be understood from the crystal size and type of impurity in the phosphor; they are different from sample to sample, because previous reports\textsuperscript{(18,19)} suggest that the visible and UV emission bands are ascribed to native-defect-associated emission and exciton-type emission, respectively.

![Fig. 2. (Color online) Typical PL spectra of undoped ZnO phosphors prepared by the SPS method using the 4N ZnO powders supplied by Hakusui Chemicals Co., Ltd., Furuuchi Chemicals Co., Ltd., and Kojundo Chemicals Co., Ltd.]
Typical PL spectra of undoped ZnO phosphors that were uncrushed but then crushed in the crucible before heat treatment are shown in Fig. 3. The spectra indicate that the ratio of the visible emission band to the UV emission band depends on how crushed the ZnO powder is. The difference in the ratio between the visible and UV bands is ascribed to the difference in the homogeneity of crystal size, because the crystallinity and homogeneity of crushed ZnO powder are better than those of uncrushed ZnO powder.

The lifetimes of the visible and UV emission bands were about 240 and 4 ns, respectively, as reported previously. The lifetime (about 4 ns) of the UV emission band is fairly shorter than that (about 220 ns) of the main emission band in a commercially available Ag-doped ZnS scintillator.

To fabricate a ZnO scintillator emitting only UV light, ZnO (purity: 4N) phosphors doped with impurities such as CuO, Al$_2$O$_3$, In$_2$O$_3$, and Ga$_2$O$_3$ were prepared using the SPS method. Two types of ZnO powder, which were supplied by Furuuchi Chemicals Co., Ltd. and Hakusui Chemicals Co., Ltd., were used as the mother phosphor materials. The powder mixture of ZnO doped with CuO, Al$_2$O$_3$, In$_2$O$_3$, or Ga$_2$O$_3$ powder was crushed for 40 min before heat treatment.

Figure 4 shows typical PL spectra of the Cu-doped ZnO phosphor (Furuuchi Chemicals Co., Ltd.) compared with those of an undoped ZnO phosphor. The concentration of CuO dopant was changed from 0.01 to 0.1 mol%. It can be seen that Cu doping was not effective in reducing the intensity of the visible emission band in the PL spectrum, although it is expected that substitutional Cu atoms will act as acceptors in the ZnO phosphor.

Figure 5 shows typical PL spectra of an Al-doped ZnO phosphor in which the Al$_2$O$_3$ concentration was changed from 0.03 to 0.15 mol%. In this case, the ZnO powder from Furuuchi Chemicals Co., Ltd. was used as the mother phosphor material. It can be seen that doping was not effective in reducing the intensity of the visible emission band.

It was found that In and Ga doping among group III elements such as Al, In, and Ga as donors in ZnO is effective in reducing the intensity of the visible emission band and increasing the intensity of the UV emission band. It was confirmed that the intensity of the UV emission band in a Ga-
doped ZnO phosphor was higher than that of an In-doped ZnO phosphor. Typical PL spectra of In-doped ZnO phosphors are shown in Fig. 6, in which the concentration of In$_2$O$_3$ was changed from 1.5 to 60 mol%. Typical PL spectra of the Ga-doped ZnO phosphors are also shown in Fig. 7, in which Ga$_2$O$_3$ concentration was changed from 1 to 99 mol%. In this case, the ZnO powder supplied by Furuuchi Chemicals Co., Ltd. was also used as the mother phosphor material. The PL peak intensities of the UV emission band in the Ga-doped ZnO phosphors are plotted in Fig. 8, indicating that the ZnO phosphor doped with 30 mol% Ga$_2$O$_3$ exhibited the most intense UV emission band without a visible emission band. It was also confirmed that the UV emission band intensity of the Ga-doped ZnO phosphor prepared using ZnO powder supplied by Furuuchi Chemicals Co., Ltd. was higher than that of the Ga-doped ZnO phosphor from Hakusui Chemicals Co., Ltd.
Fig. 6. (Color online) Typical PL spectra of In-doped ZnO phosphors, in which In$_2$O$_3$ concentration was changed from 1.5 to 60 mol%.

Fig. 7. (Color online) Typical PL spectra of Ga-doped ZnO phosphors, in which Ga$_2$O$_3$ concentration was changed from 1 to 70 mol%.

Fig. 8. (Color online) PL intensity of the UV emission band as a function of Ga$_2$O$_3$ concentration (1.0–99 mol%) in Ga-doped ZnO phosphors.
The normalized PL spectra of Cu-, Al-, In-, and Ga-doped ZnO phosphors are shown in Fig. 9, in which the normalization of the spectra was done at the peak of the UV emission band. It was confirmed that the UV band intensity of Ga-doped ZnO phosphor (Furuuchi Chemicals Co., Ltd.) is comparable to those of other phosphors such as Ga-doped ZnO (Hakusui Chemicals Co., Ltd.) and In-doped ZnO and undoped ZnO (Furuuchi Chemicals Co., Ltd. and Hakusui Chemicals Co., Ltd.).

3.2 Dependence of PL characteristics on sintering conditions

It was found that the intensity of the UV emission band of Ga-doped ZnO phosphor is strongly dependent on the atmosphere and pressure during the phosphor sintering process, especially the pressure of vacuum. The dependence of the PL intensity of the UV band on atmospheric pressure during sintering was therefore investigated for Ga-doped ZnO (Furuuchi Chemicals Co., Ltd.) phosphors. Figure 10 shows typical PL spectra of the Ga-doped ZnO phosphors sintered at various vacuum pressures from 7.0 to 10.0 Pa, indicating that the Ga-doped ZnO phosphor sintered at 8.0 Pa exhibited the most intense UV emission without the visible emission. It was confirmed that the crystallinity of Ga-doped ZnO prepared in vacuum (in reducing atmosphere) is better than that prepared in atmospheric pressure, from the results of the XRD experiment. This result strongly suggests that Ga-doped ZnO phosphor heat-treated in reductive atmosphere has small amounts of native defects that give rise to the visible emission band. The disappearance of the visible emission band at about 500 nm is ascribed to the strongly reducing atmosphere used in the SPS technique.\(^{(19)}\)

3.3 Effects of B\(_2\)O\(_3\) doping on PL characteristics

A scintillator using a Ga-doped ZnO phosphor cannot interact directly with neutrons. To use the Ga-doped ZnO scintillator as a neutron detector, it is very effective to dope B\(_2\)O\(_3\) as a neutron converting material into the phosphor because \(^{10}\)B interacts with neutrons to emit alpha rays by...
means of the (n, alpha) reaction, and consequently the Ga-doped ZnO phosphor can be excited by alpha rays to produce luminescence. It is very important to confirm whether or not the UV emission intensity of the Ga-doped ZnO phosphor changes owing to the addition of B2O3. To confirm this, the dependence of PL characteristics on B2O3 concentration was investigated for the Ga-doped ZnO phosphor with B2O3 powder added. It was found that the Ga-doped ZnO with 30 mol% B2O3 added exhibited the most intense UV emission, as shown in Fig. 11. It was confirmed that the UV emission intensity is not reduced by doping B2O3, compared with that of the Ga-doped ZnO without B2O3, as shown in Fig. 12.

The PL intensity is not changed by adding B2O3, the concentration of which was varied from 10 to 50 mol%, though the Ga-doped ZnO with B2O3 added at concentrations above 40 mol% exhibited a low PL intensity as shown Fig. 13. From these results, we can say that the PL intensity of the Ga-doped ZnO with 10–30 mol% B2O3 added was not decreased by adding B2O3 as a neutron converter. This result strongly suggests that the Ga-doped ZnO with B2O3 as a neutron converter is useful as a phosphor for highly efficient neutron detectors, because the scintillator using the Ga-doped ZnO can be mixed uniformly with the B2O3 neutron converter.

![Fig. 11.](image1.png)  
Color online) Dependence of UV emission spectra on the concentration of B2O3 dopant from 10 to 30 mol% in Ga-doped ZnO phosphors, which were sintered at 750 °C in vacuum.

![Fig. 12.](image2.png)  
(Color online) UV emission intensity as a function of B2O3 concentration in the Ga-doped ZnO. In this case, the 30 mol% Ga-doped ZnO with 30 mol% B2O3 was sintered at 750 °C in a reducing atmosphere of 7.0 Pa.

![Fig. 13.](image3.png)  
(Color online) Dependence of PL spectra on the concentration of H3BO3 in Ga-doped ZnO phosphors. The concentration of H3BO3 was changed from 10 to 30 mol%.
3.4 XRD results of the Ga-doped ZnO phosphor

To estimate the crystallinity of the Ga-doped ZnO phosphor, the XRD pattern obtained using an XRD apparatus was observed for Ga-doped ZnO phosphors. Figure 14 shows typical XRD patterns of Ga (30 mol%)-doped ZnO phosphor with B₂O₃ (30 mol%)-doped converter powder. The crystal structure of Ga-doped ZnO phosphor estimated using Joint Committee on Powder Diffraction Standards (JCPDS) data was a mixture of crystalline ZnO and ZnGa₂O₄ without ZnO (BO₂) and B₂O₃ phases.

Figure 15 shows the UV emission intensity as a function of the full-width at half-maximum (FWHM) of the main diffraction peak at 35.4 deg, indicating that the UV emission intensity increased with decreasing FWHM of the diffraction peak. This means that the UV emission intensity increased as the crystallinity of the Ga-doped ZnO phosphor with a B₂O₃-added neutron converter increased, because the smaller the FWHM of the XRD peak is, the better the crystallinity of phosphor is.

3.5 Response of Ga-doped ZnO scintillator with B₂O₃ converter for neutron beam

Figure 16 shows a picture of a prototype of a Ga-doped ZnO scintillator with a B₂O₃ converter. A schematic diagram of an ultrahigh-counting-rate neutron beam monitor using Ga-doped ZnO with B₂O₃ phosphor is shown in Fig. 17. The neutrons coming to the monitor react with the B₂O₃...
converter in the scintillator to produce alpha rays due to the \((n, \alpha)\) reaction, and the Ga-doped ZnO scintillator is excited by alpha rays to emit 380 nm light (UV emission band due to exciton emission).

To check the radioluminescence spectrum of the Ga-doped ZnO phosphor by excitation with alpha rays, the radioluminescence from the Ga-doped ZnO with \(\text{H}_3\text{BO}_3\) neutron converter powder was observed using alpha rays from a \(^{241}\text{Am}\) source, because \(\text{H}_3\text{BO}_3\) (\(\text{B}\) amount is larger than 92.4\%) is commonly used as a neutron converter.\(^{22}\) It was found that an intense UV emission can be observed in the radioluminescence of the Ga-doped ZnO with \(\text{H}_3\text{BO}_3\) powder, as shown in Fig. 18. It was confirmed that the decay time of the UV emission band was about 20 ns, which is slightly long compared with that (4 ns) reported previously. The difference in decay time is ascribed to the difference in excitation source, because phosphor is excited over the band gap to generate carriers in the case of radioluminescence. This result strongly suggests that the Ga-doped ZnO powder phosphor with \(\text{H}_3\text{BO}_3\) neutron converter powder is useful as a phosphor material for neutron scintillators with a very short lifetime.

Figure 19 shows responses of the neutron beam monitor using the Ga-doped ZnO scintillator with a \(\text{B}_2\text{O}_3\) converter as a function of reactor power from the Japan Research Reactor-3 (JRR-3) compared with those of the Ag-doped ZnS scintillator with a \(\text{B}_2\text{O}_3\) converter and a vanadium\(^{21}\) scatter plate for X-rays on the Ag-doped ZnO scintillator with a \(\text{B}_2\text{O}_3\) converter. The response of the Ga-doped ZnO scintillator mixed with \(\text{B}_2\text{O}_3\) converter powder for neutron beams was fairly good compared with that of the Ag-doped ZnS scintillator.
4. Conclusions

The ZnO family of phosphors for neutron detectors was prepared using the SPS method. The optical properties of the ZnO phosphors were investigated. The following results were obtained.

1. Two dominant PL emission peaks at 383 and 495 nm were observed.
2. The lifetime of the PL emission peak at 383 nm (UV emission band) is about 20 ns, which is suitable for neutron detection.
3. The Ga (30 mol%)-doped ZnO phosphor exhibited intense UV emission without visible emission.
4. The Ga-doped ZnO phosphor can be prepared under an atmospheric pressure of about 8 Pa using the SPS method.
5. The PL intensity of the UV emission band was increased by improving the crystallinity of the ZnO phosphor.
6. The PL intensity of Ga-doped ZnO with 10–30 mol% B₂O₃ added was not reduced by adding B₂O₃ as the neutron converter.
7. The response of the Ga-doped ZnO scintillator mixed with B₂O₃ converter powder to the neutron beam from the JRR-3 facility was fairly good compared with that of the Ag-doped ZnS scintillator.

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