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Synthesis and long-period phosphorescence of $ZnGa_2O_4$:Mn^{2+} spinel

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Abstract

Novel long-period phosphor $ZnGa_2O_4$:Mn^{2+} was prepared by a conventional solid reaction of ZnO, Ga_2O_3 and $Mn(NO_3)_2$ under conditions of > 1000°C for 24 h in flowing Ar gas. The phosphor had green intense emission peaking at 503.6 nm. The improvement of emission intensity was brought out by the higher temperature processing. This implied that long lifetime phosphorescence was closely related to the formation of vacancies at the Zn^{2+} sites of the host lattice. The carrier trap level was positioned at 0.71 eV higher than the valence band of host lattice. The possible mechanism for prolonging the emission for a long time was discussed. © 1997 Elsevier Science S.A.

Keywords: Long-period phosphorescence; Zinc gallates; Non-stoichiometric spinel; Manganese-activated phosphor; Green intense emission

1. Introduction

Long-period phosphors can light up in the dark after irradiation with sunlight or artificial light. One-hundred years have passed since this type of emission was discovered in natural phosphor. Most of the phosphors contained sulphide. For instance, ZnS:Cu^{2+} is widely used as the phosphor in luminous paint and for military and security usages. However, its brightness is not sufficient to develop many optical applications. Also, sulphide-based phosphors are occasionally unstable under humid conditions. In this context, studies on long-period phosphors gradually declined. Recently, Matsuzawa et al. [1] reported that $SrAl_2O_4$:Eu^{2+},Dy^{3+} had the characteristics of a long-period phosphor. Accordingly, much interest was aroused in oxide-based phosphors and their applications for luminous displays, fluorescent lamps, emergency signs, etc.

$ZnGa_2O_4$:Mn^{2+} has been well known as a phosphor for low-voltage cathodoluminescence and was widely used in cathode-ray tubes, image intensifiers, television screens, etc. [2]. However, there was no information available on prolonged emission. Very recently, we found that $ZnGa_2O_4$:Mn^{2+} has long-period characteristics. In this paper, the synthetic conditions of the phosphor with more intense emission were examined. Also, it was found that long-period phosphorescence was substantially governed by the energy levels of lattice defects and dopant ions. In addition, the possible mechanism of prolonged-decay luminescence was proposed.

2. Experimental

Phosphors, denoted by the formula $Zn_{1-x}Mg_xGa_2O_4$:Mn^{2+}, was prepared by the solid-state reaction of ZnO, MgO and Ga_2O_3 and $Mn(NO_3)_2$. The desired oxides were intimately mixed with ethanol by ball milling and then air-dried overnight. The mixture was moulded into the shape of a disk and calcined at the desired temperature of 1100–1300°C for 24 h in flowing argon gas.

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The products were identified by powder X-ray diffraction patterns measured with Ni-filtered CuKα radiation. The emission and excitation spectra were recorded with HITACHI 850 type fluorescence spectrophotometer at room temperature. The period of emission was immediately measured with the fluorescence spectrophotometer after irradiation with excitation light for 2 min, corresponding to the optical absorption of $ZnGa_2O_4$ host lattice.

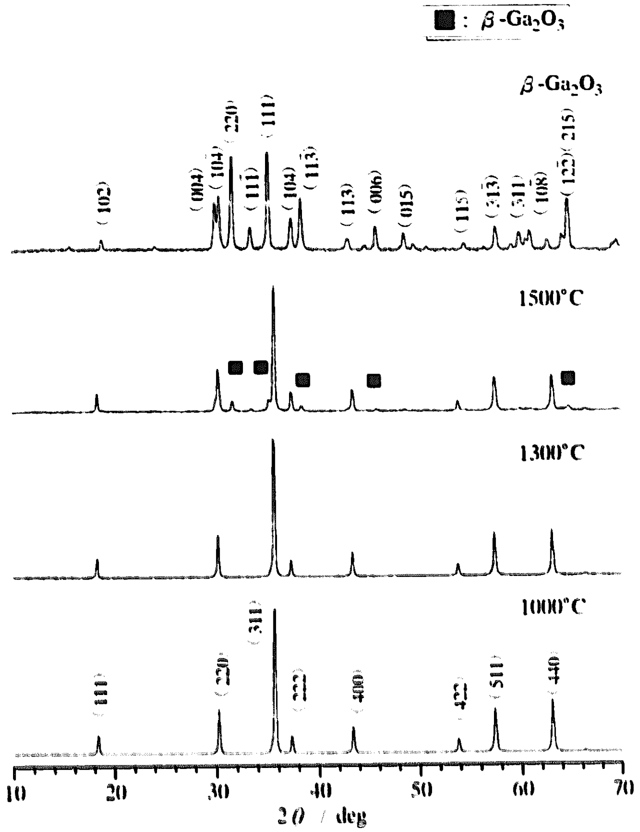

Fig. 1. XRD patterns of β-Ga_2O_3 and $ZnGa_2O_4$ calcined at various temperatures for 24 h.

The resulting phosphor was first put on a proper copper plate and fixed into the cryostat. The cryostat was evacuated with a diffusion pump and then filled with liquid nitrogen. The phosphor was irradiated by 352.6-nm light of a low-pressure mercury lamp for 30 s at 77 K and the temperature was allowed to increase successively at a constant rate.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the products calcined at various temperatures for 24 h. It was found that the spinel $ZnGa_2O_4$ was obtained above 1000°C. Above 1400°C some small peaks, identified as β-Ga_2O_3, were observed. This implied that Zn^{2+} was volatilized above 1300°C and the deficiencies of Zn^{2+} were formed in the spinel structure. At higher temperatures, the spinel lattice should collapse with increasing defects. This coincides with the observation that $ZnGa_2O_4$ was non-stoichiometric on annealing in flowing hydrogen gas. [3]

Fig. 2 shows the excitation and emission (photoluminescence) spectra of $ZnGa_2O_4$:Mn^{2+}. Upon excitation by ultraviolet light, the emission spectrum shows a broad band peaking at 504 nm, which is identified as the ${}^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+}. Two peaks were observed at 248 nm and 290 nm in the excitation spectrum. One was due to the host-lattice absorbtion band and the other was due to the charge-transfer absorption band or the $d^5 \rightarrow d^4s$ transition band.

Various emission intensities of $Zn_{1-x}Ga_2O_4$ doped

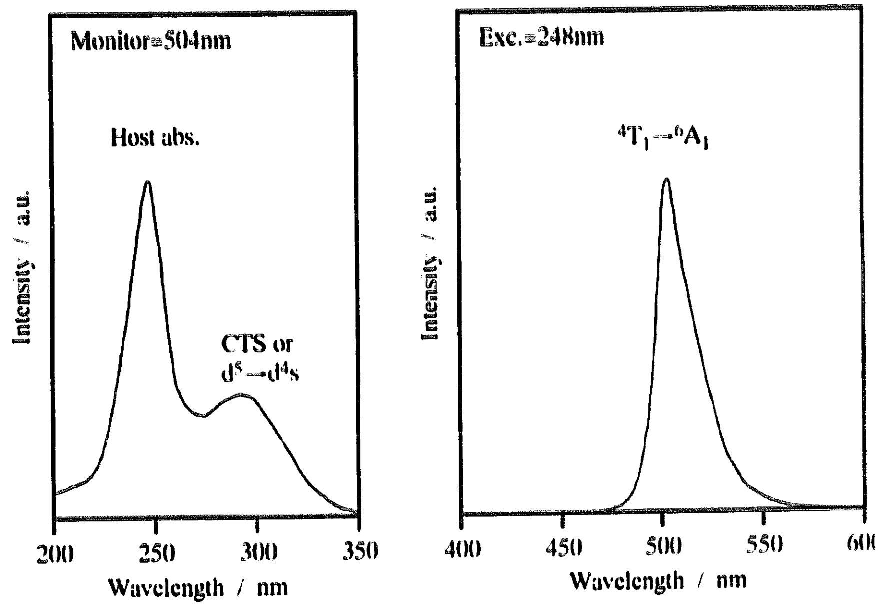

Fig. 2. Emission and excitation spectra of $ZnGa_2O_4$:$0.001Mn^{2+}$ calcined at 1300°C for 24 h in flowing Ar gas.

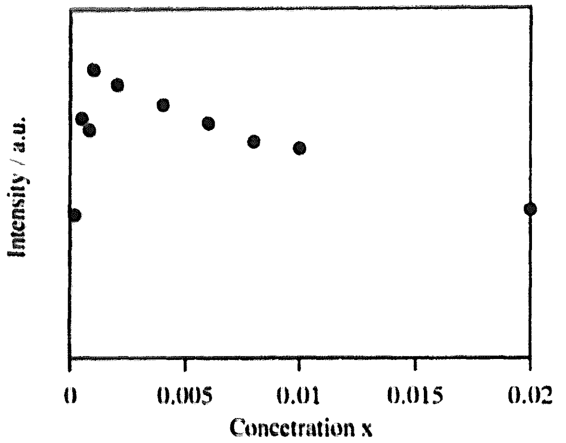

Fig. 3. Concentration dependence of emission intensity for $ZnGa_2O_4$:$x$$Mn^{2+}$ calcined at 1300°C for 24 h in flowing Ar gas (exc. = 248 nm, monitor = 504 nm).

with Mn^{2+} are shown in Fig. 3 plotted against the concentration of Mn^{2+}. This figure demonstrates that the most intense peak is observed at a concentration of $x = 0.01$. The green emission decreased gradually as the concentration of Mn^{2+} increased, due to conventional concentration quenching.

Fig. 4 shows the time dependence of luminescence intensity measured after ultraviolet-light irradiation for $ZnGa_2O_4$:Mn^{2+} calcined at various temperatures. The persistence of the phosphor tended to be prolonged by higher-temperature processing. This means that by the deficiencies of Zn^{2+}, carrier-trapping centers were created in the phosphor. The emission intensity of phosphor decreased noticeably with calcination at 1400°C. This observation was brought out by the pyrolysis of $ZnGa_2O_4$ or the formation of color center. As a result, the preferable phosphor was prepared by calcination at 1300°C. It was recognized that many carrier traps resulted in relatively prolonged emission. However, it was unclear whether or not the possible trapping sites were induced by the dropping of Mn^{2+} ion with the change of valency states e.g. Mn^{3+} or Mn^{4+}.

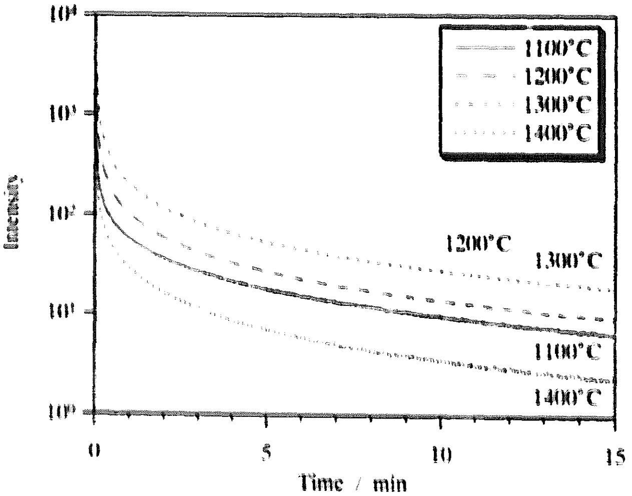

Fig. 4. Time dependence of luminsesence intensity after UV irradiation for $ZnGa_2O_4$:Mn^{2+} calcined at various temperatures (ecs. = 250 nm, monitor = 504 nm).

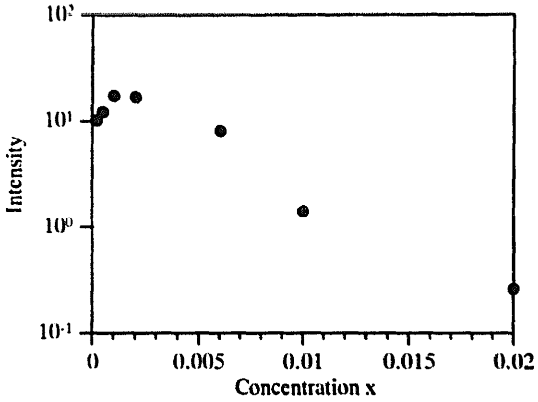

Fig. 5. Concentration dependence of luminsecence intensity 15 min after UV irradiation for $Zn_{1-x}Ga_2O_4$:$x$$Mn^{2+}$ calcined at 1300°C for 24 h in flowing Ar gas (exc. = 250 nm, monitor = 504 nm).

Fig. 5 shows the concentration dependence of luminescence intensity 15 min after the excitation irradiation. Assuming that Mn^{2+} functions as the trap, the emission intensity may increase with Mn^{2+} concentration. However, the optimum concentration of the phosphors is evaluated to be near $x = 0.001$ which is equivalent to the concentration of Mn^{2+} shown in Fig. 5. In addition, no Mn^{4+} emission is observed in the range from 620 nm to 700 nm. Consequently, it was found that some defects in the host lattice, rather than Mn^{2+} ions, played the role of the carrier-trapping center.

Fig. 6 shows the various cubic lattice constants, a, as a function of the Mg^{2+} concentration. The lattice constant, a, decreased uniformly with Mg^{2+} concentration. This indicated that Zn^{2+} ions were readily replaced by Mg^{2+} ions in order to form the substantial solid solutions $(Zn_{1-x}Mg_x)Ga_2O_4$.

The excitation and emission spectra of $MgGa_2O_4$:Mn^{2+} is shown in Fig. 7. The broad emission has a

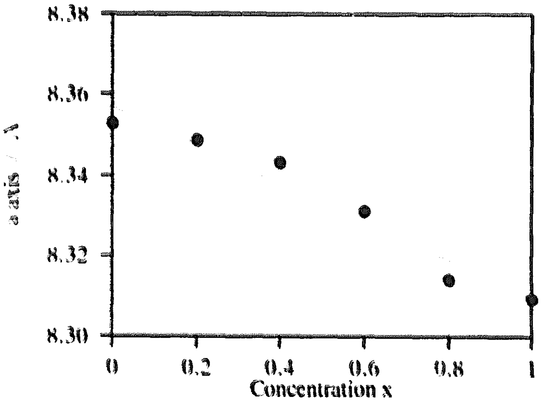

Fig. 6. Lattice constants of $Zn_{1-x}Mg_xGa_2O_4$ calcined at 1300°C for 24 h.

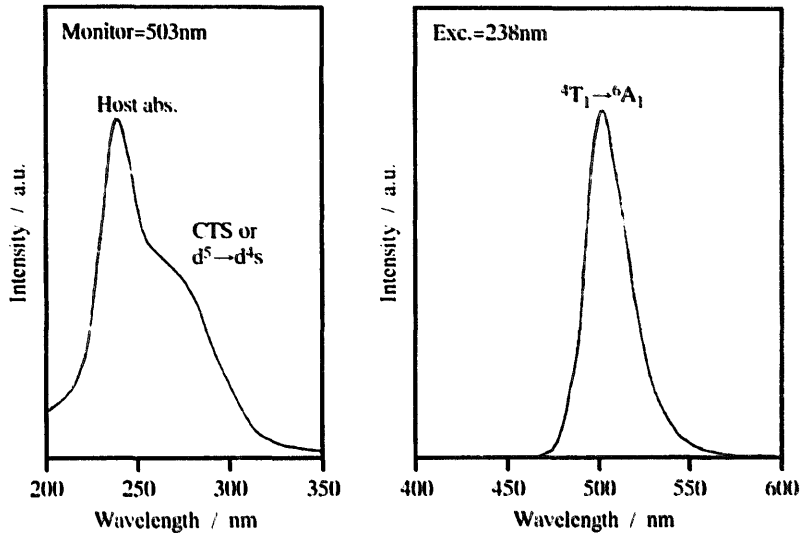

Fig. 7. Emission and excitation spectra of $MgGa_2O_4$:$0.001Mn^{2+}$ calcined at 1300°C for 24 h in flowing Ar gas.

maximum peak around 503 nm. The profiles of emission and excitation spectra were similar to those of $ZnGa_2O_4$:Mn^{2+}.

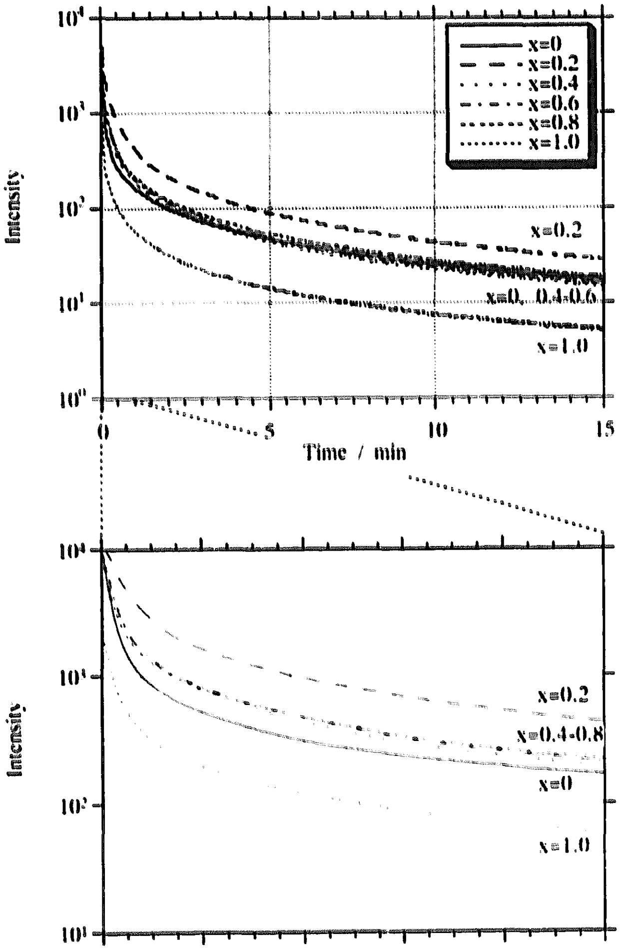

Fig. 8. Time dependence of luminescence intensity after UV irradiation for $Zn_{1-x}Mg_xGa_2O_4$:$0.001Mn^{2+}$ calcined at 1300°C for 24 h in flowing Ar gas (exc. = 250 nm, monitor = 503–508 nm).

Fig. 8 shows the time dependence of luminescence intensity of $Zn_{1-x}MgGa_2O_4$:Mn^{2+} after ultraviolet-light irradiation. When Mg^{2+} was substituted for Zn^{2+}, the intensity of afterglow was enhanced for 10 s after ultraviolet-light irradiation. However, the intensity decreased as usual with time. After 15 min the intensity was equivalent to that of $ZnGa_2O_4$:Mn^{2+} except in the case of $Zn_{1-x}MgGa_2O_4$:Mn^{2+} ($x = 0.2$). This results suggested that $Zn_{1-x}MgGa_2O_4$:Mn^{2+} could make some shallower traps. Prolonged phosphorescence was only observed in the phosphor of $x = 1.0$ because $MgZnGa_2O_4$:Mn^{2+} could not create the carrier traps such as Zn^{2+} vacancies.

The glow curves of $ZnGa_2O_4$:$0.001Mn^{2+}$ and $Zn_{0.6}Mg_{0.4}Ga_2O_4$:$0.001Mn^{2+}$ are shown in Fig. 9. Both glow peaks were observed around 320 K. However, the glow peak of $Zn_{0.6}Mg_{0.4}Ga_2O_4$:$0.001Mn^{2+}$ tailed off towards lower temperatures. Consequently, a partial replacement of Zn^{2+} by Mg^{2+} could con-

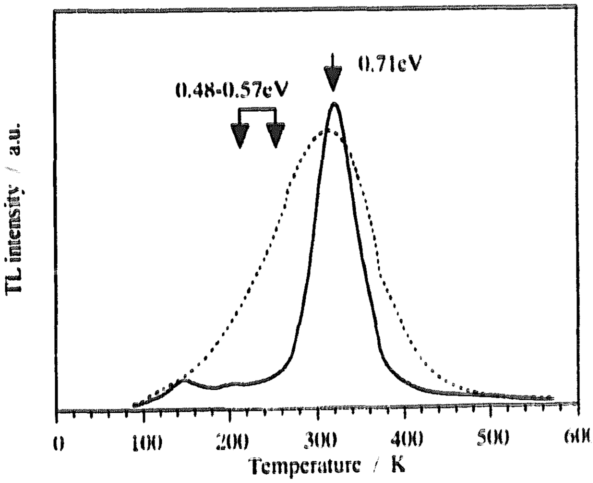

Fig. 9. Glow curves of $ZnGa_2O_4$:$0.001Mn^{2+}$ (—) and $Zn_{0.6}Mg_{0.4}Ga_2O_4$:$0.001Mn^{2+}$ (...) calcined at 1300°C for 24 h in flowing Ar gas.

tribute to the increase in the density of shallower traps. The trap depths were estimated according to the following equation

$$E(\mathrm{eV}) = [T* - T_0(\beta/s)]/K(\beta/s)$$

where T^* is the glow-peak temperature, β is the warming rate, s is a frequency factor and T_0 and K are parameters which are function of β/s. The values of T_0 and K given by Curie are 7 K and 441 K/eV, respectively. Since the value of s was unknown, we calculated the trap depth in the typical case of $s = 10^9$ s^{-1} [4]. The trap depth around 320 K was estimated to be 0.71 eV, while the shallower trap depths in the range of 220–260 K were equivalent to the values of 0.48–0.57 eV.

The possible mechanism for prolonged-decay luminescence for $ZnGa_2O_4$:Mn^{2+} is illustrated schematically in Fig. 10. According to the emission and excitation spectra, the energy levels of Mn^{2+} may be positioned between the conduction and valence bands of host lattice $ZnGa_2O_4$. Also, several carrier-trap levels are newly formed by the vacancies of Zn^{2+} sites in the depth of 0.48–0.71 eV above the valence band. Accordingly, it was elucidated that the role of vacancies as carriers has the most significant role in prolonging the emission.

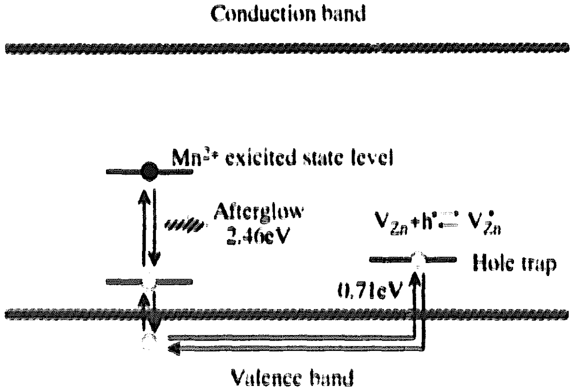

Fig. 10. The afterglow mechanism of $ZnGa_2O_4$:Mn^{2+}.

Acknowledgements

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