A New Luminescent Phenomenon of ZnO Due to the Precipitate Trapping Effect of MgO

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A new luminescent phenomenon was found in the ZnO−MgO system. After $Zn_{1-x}Mg_xO$ ($x < 0.15$) pellets were sintered in an open crucible below 1600 °C or in a sealed crucible below 1300 °C, they emitted green lights upon excitation of ultraviolet (UV) lights and there was no persistent luminescence (afterglow) after the excitation light was cut off. After $Zn_{1-x}Mg_xO$ ($0.02 \leq x < 0.15$) pellets were sintered in a sealed crucible above 1300 °C, they emitted bright orange lights induced by UV excitation and showed a long orange afterglow, which persisted for about 10 min in the darkness after the removal of irradiating light. A precipitate trapping effect of MgO on ZnO luminescence was found, which resulted in the long orange afterglow. This report may shed more light on the luminescent mechanism of ZnO and supply useful information for understanding the luminescent properties of the ZnO−MgO system intensively.

1. Introduction

ZnO has been known as a luminescent material for a century. Nowadays, it is useful for various applications such as vacuum fluorescent display (VFD),[1] field emission display (FED),[2] and electroluminescent display (ELD).[3] Due to its wide gap of 3.37 eV at room temperature, ZnO is attracting considerable attention as one of the important candidates for potential applications such as UV light-emitting diodes and laser diodes.[4−6] By alloying with MgO, the band gap of the ternary alloys $Mg_xZn_{1-x}O$ could be expanded from 3.3 to 4.20 eV.[7−10] This alloy produced a brighter UV luminescence at room temperature that was found to be excitonic in nature.[7] These recent developments open up enormous interest in this materials system.

Until now, almost all of the research has been focused on finding new synthesis methods to extend the solid solution of MgO in ZnO. Actually, it is very important to study the luminescent properties of this system extensively in order to understand the luminescent mechanism and make best use of it. In this paper, we first report a precipitate trapping effect of MgO on ZnO luminescence, which results in the orange afterglow emission of ZnO.

2. Experimental Methods

In our experiment, ZnO−MgO pellets were prepared by the traditional solid-state reaction method. First, starting materials of $Mg(OH)_2 \cdot 4MgCO_3 \cdot 6H_2O$ and ZnO were mixed and milled for 4 h in water using agate grinding media in a polythene container by a planetary ball mill, dried, and then sieved through a 74-μm screen to obtain the fine powder. The powder was then pressed into pellets of 12-mm diameter and 3-mm thickness by using uniaxial pressing with a pressure of 20 MPa at room temperature, and finally the pellets were sintered in an alumina crucible in air at different temperatures for 3 h and then cooled to room temperature.

A RigakuD/MaxIIIB X-ray diffraction (XRD) meter was employed to check the crystal structure of the samples using Cu Kα radiation. Excitation, emission, and afterglow spectra at room temperature were recorded with an Hitachi F-4500 fluorescence spectrometer and the spectra were corrected using sodium salicylate. The decay curves of the afterglow at room temperature were obtained by using the ST-86LA brightness meter connected with the data collection system.

3. Results and Discussion

ZnO pellets were sintered below 1600 °C for 3 h both in an open crucible and in a sealed crucible for 3 h, and the sintering temperatures are 1000, 1200, 1300, 1400, 1500, and 1550 °C. The so-obtained ZnO pellets emitted

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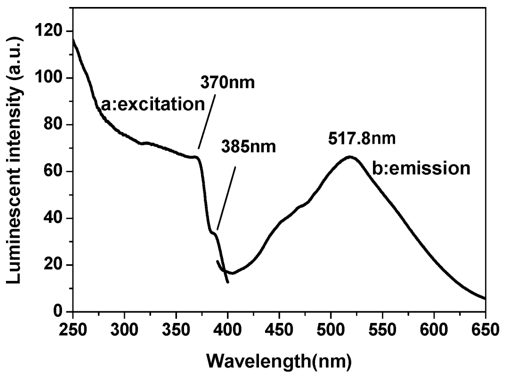

Figure 1. Excitation and emission spectra of ZnO obtained by sintering ZnO pellets in an open or sealed crucible below 1600 °C and $Zn_{1-x}Mg_xO$ ($x < 0.2$) pellets after sintering in an open crucible below 1600 °C or in a sealed crucible below 1300 °C. The sample is excited at 370 nm and the corresponding emission peak is observed at 517.8 nm. (a) Excitation. (b) Emission.

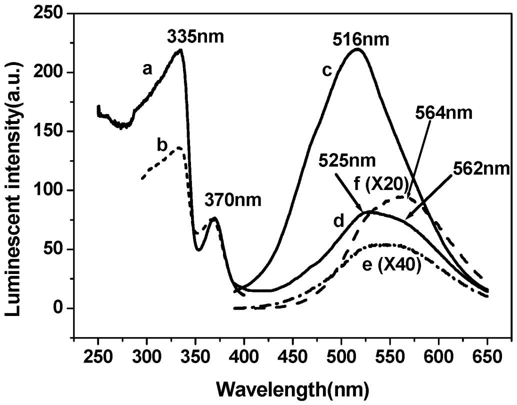

Figure 2. Excitation, emission, and afterglow spectra of $Zn_{0.9}Mg_{0.1}O$ pellets after sintering in a sealed crucible at 1500 °C. The excitation spectra indicated in (a) and (b) are obtained by monitoring emission at 516 and 562 nm, respectively. If the sample is excited at 335 nm, the corresponding emission peak is observed at 516 nm (c). If the sample is excited at 370 nm, the emission is a broad band with humps at 525 and 562 nm, respectively (d). Afterglow can be obtained if the 335-nm excitation is removed (e, ×40) or the 370-nm excitation is removed (f, ×20).

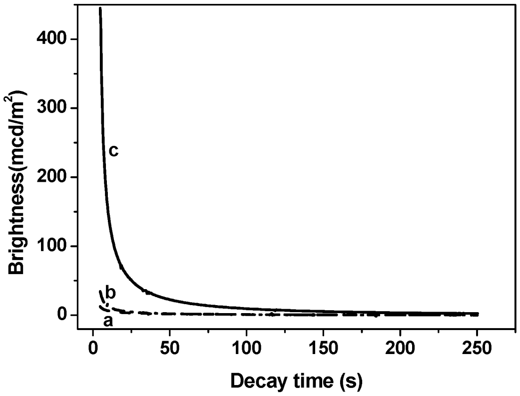

Figure 3. Decay curves of $Zn_{1-x}Mg_xO$ pellets after sintering at 1500 °C in a sealed crucible. (a) $x = 0$. (b) $x = 0.05$. (c) $x = 0.1$.

green lights under excitation of UV lights[11] and no long afterglow was observed after the excitation lights were removed. The same phenomenon was observed for the $Zn_{1-x}Mg_xO$ ($x < 0.15$) pellets when the sintering temperatures in an open crucible are in the range between 1000 and 1600 °C or when the sintering temperatures in a sealed crucible are between 1000 and 1300 °C. Figure 1 gives the excitation and emission spectra. The excitation spectrum consists of a broad band with weak peaks at 370 and 385 nm. The former results from electron transfer from valence band (VB) to conduction band (CB), and the latter is assigned to transition between electronic defects, which are presented in the forbidden band.[12,13] Some authors attribute the green emission at about 517.8 nm in Figure 1 to $Zn_i^+ \rightarrow V_{Zn}^-$ transition[12,14] and others to CB → $V_O^{\bullet\bullet}$ [15,16] transition, but neither of the two opinions has been verified directly yet.

After $Zn_{1-x}Mg_xO$ ($0.02 \leq x < 0.15$) pellets were sintered in a sealed crucible at temperatures above 1300 °C, a different phenomenon was observed. The excitation spectrum consists of two bands at 335 and 370 nm (shown in Figure 2), respectively, both showing blue shift in comparison with those in Figure 1. The emission band induced by 370 nm is a broad band with humps at 525 and 562 nm, respectively. The most interesting is that when the excitation is cut off, the latter emission can persist for about 10 min and the afterglow can be observed by the naked eye clearly in the darkness. The foreparts of the decay curves are shown in Figure 3. The initial brightness and afterglow brightness substantially increase as a function of the sintering temperature. When the pellets are excited by 335-nm UV, the emission band consists of only one peak, but they also show a long orange afterglow when excitation is cut off as indicated in Figure 2e. The afterglow intensity is only about 25% of that induced by 370-nm UV as shown in Figure 2f.

For ZnO and $Zn_{1-x}Mg_xO$ ($x \leq 0.15$) with green emission under UV excitation, the XRD patterns originate from single ZnO phase as indicated in Figure 4. After $Zn_{1-x}Mg_xO$ ($0.02 \leq x \leq 0.15$) pellets were sintered in a sealed crucible above 1300 °C, the emission light of the pellets surface induced by 370-nm excitation is orange. Indeed, an interesting phenomenon is found when the pellets are cut transversely. The center of the pellets is single ZnO phase with green emission without long afterglow. When it comes from the inside to the outside toward the surface, the emission changes from green to orange under 370-nm UV excitation, and correspondingly, the XRD patterns turn from single ZnO phase to a mixture of ZnO and MgO phases; the stronger the orange afterglow, the more MgO phase. This suggests that the precipitating second MgO phase from ZnO lattice at high temperature results in the orange emission with long afterglow.

When a mixture of ZnO and MgO was sintered, a series of reactions occurred. First, solution of MgO and

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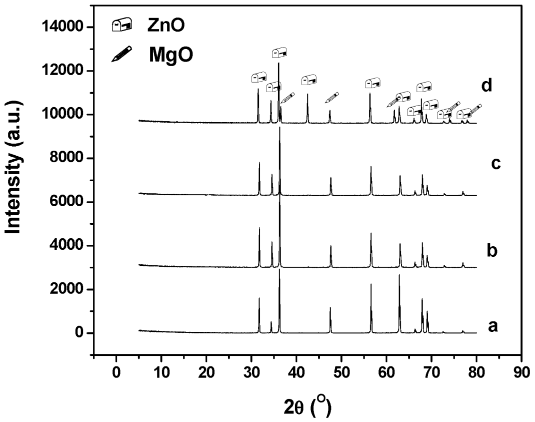

Figure 4. XRD patterns: (a) ZnO after sintering in an open or sealed crucible at 1500 °C. (b) Surface of $Zn_{0.9}Mg_{0.1}O$ pellets after sintering in an open crucible at 1500 °C. (c) Surface of $Zn_{0.9}Mg_{0.1}O$ pellets after sintering in a sealed crucible at 1200 °C. (d) Surface of $Zn_{0.9}Mg_{0.1}O$ pellets after sintering in a sealed crucible at 1500 °C.

ZnO can be obtained at low temperature. When temperature increases, ZnO and MgO evaporation takes place, and maybe MgO is easier to evaporate than ZnO.[17−21] If the crucible is sealed, the evaporation cannot escape and thus precipitates on the surface again during the cooling process. And hence, MgO is excessive on the surface.

As for $Zn_{1-x}Mg_xO$ ($x > 0.15$), the XRD shows a mixture of ZnO and MgO after sintering the pellets at all temperatures whether in an open or sealed crucible because of the low solubility of MgO in ZnO lattices. When the pellets were sintered in a sealed crucible above 1300 °C, the orange emission is very weak for those in the range of $0.15 < x < 0.2$, and there is no emission at all under UV excitation when $x > 0.2$. So it can be concluded that for $Zn_{1-x}Mg_xO$ ($0.02 \leq x \leq 0.15$), the orange emission and the corresponding long afterglow obtained after sintering the pellets above 1300 °C in a sealed crucible is due to MgO that precipitates from the previous ZnO−MgO solid-state solution.

Electrons and holes are created as UV excites the ZnO phase. Some of the electrons and holes can be trapped by some defects associated with MgO precipitates on the surface; after some time, some of those electrons and holes can return to ZnO phase. When they recombine with the emission center again, emission tales place. Since it takes some time for the electrons and holes to return to ZnO phase, the emission is a delayed one; that is, afterglow forms. Formation of a new energy level on the interface of ZnO and MgO may result in the new orange emission band.

4. Conclusions

We have studied for the first time the luminescent properties of the $Zn_{1-x}Mg_xO$ system in abnormal conditions. When the samples were sintered in an open crucible below 1600 °C or in a sealed crucible below 1300 °C, the luminescent properties are similar to those of ZnO. By sintering $Zn_{1-x}Mg_xO$ ($0.02 \leq x \leq 0.15$) in a sealed crucible above 1300 °C, MgO phase precipitates on the surface of the sample, which results in the long orange afterglow phenomenon.

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