

# Synthesis and optical properties of halogen-doped ZnO phosphor

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Received 22 September 2007; accepted 30 January 2008

Available online 5 February 2008

## Abstract

A simple and convenient method has been demonstrated to fabricate halogen-doped ZnO phosphors via annealing the mixture of ZnS and KX (X = Cl, Br, I) in air. The as-prepared products were characterized by X-ray diffraction (XRD), photoluminescence (PL), and photoluminescence excitation (PLE), respectively. The experimental results indicate that the green PL intensity and the excitation band at  $\sim 3.20\text{eV}$  are enhanced significantly for the samples doped with halogens, compared with those of the undoped ZnO. The incorporation of halogens into ZnO is proposed to increase the oxygen vacancies and consequently the PL intensity of the green emission band is highly enhanced.

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*Keywords:* Zinc oxide; Phosphors; Semiconductors; Photoluminescence

## 1. Introduction

As an important II–IV semiconductor, zinc oxide (ZnO) is one of the most promising materials for fabrication of optoelectronic devices in the blue and UV region, owing to a direct wide band gap ( $E_g = 3.37\text{eV}$  at room temperature) and large exciton binding energy (60mV). Currently, modification of ZnO properties by chemical doping has become a hotspot for a long time, since the incorporated elements offer an effective method to adjust its electrical, optical, and magnetic properties, which is important for its practical applications [1–4]. For example, the band gap of ZnO nanocrystals can be tuned in the range of 2.9–3.9eV via doping with Cd, Mg, Mn, and Fe ions [5]. Other metallic elements like Cu, Al, and rare earth (RE) etc. have also been investigated extensively [6–10]. Recently, doping in ZnO with anions has gained a considerable amount of attention. For instance, N and P elements have been chosen as the ideal dopant source for fabricating p-type ZnO [11–15]. Furthermore, S-doping in ZnO is expected to modify the electrical and optical properties due to the large electronegativ-

ity and size differences between S and O [16,17]. However, investigations about doping in ZnO with halogens are rarely reported.

In this work, a simple and convenient method has been presented for preparation of halogen-doped ZnO phosphors via annealing the mixture of ZnS and KX (X = Cl, Br, I) in air. The structure of as-prepared products was investigated by X-ray diffraction (XRD). Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were also studied at room temperature. The results indicate that the incorporation of halogens into ZnO lattice greatly intensifies the excitation band at  $\sim 3.20\text{eV}$ , resulting in significantly enhancing the PL intensity of green emission band centered at 2.50eV. The possible mechanisms are also discussed.

## 2. Experimental

All materials were purchased from commercial sources (analytical grade) and used without further treatment. In a typical synthesis, 1.0g of ZnS powders was mixed with 10at.% KX (X = Cl, Br, I) with an agate mortar. After the mixture was ground for 20min, the mixed powders were placed in a crucible and transferred into the furnace and annealed in air at different temperatures for 2h. After that, the heat treatment powders were

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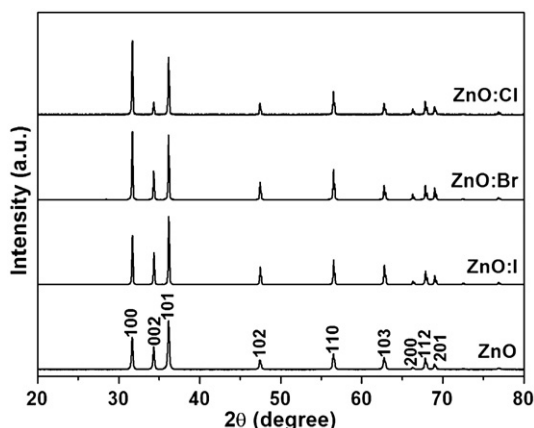


Fig. 1. XRD patterns of as-obtained samples annealed at 900 °C.

cooled to ambient temperature naturally, washed several times with distilled water and alcohol, and dried in an oven at 80°C for 3h. For comparison, ZnS powders without adding alkali halide were annealed under the same condition.

The powder X-ray diffraction (XRD) studies were carried out on a Rigaku DMAX 2000 diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda = 0.15405\text{nm}$ ) (40kV, 40mA). The optical properties of as-prepared samples were investigated by photoluminescence (PL) and photoluminescence excitation (PLE) spectra, which were taken on a VARIAN Cary-Eclipse 500 fluorescence spectrophotometer equipped with a 60W Xenon lamp as the excitation source. The halide ions present in the samples were estimated by Volhard's chemical analysis.

### 3. Results and discussion

Fig. 1 shows the XRD patterns of undoped and halogen-doped ZnO annealed at 900°C. It can be seen that the as-prepared samples are well crystallized and the diffraction peaks are in good agreement with hexagonal wurtzite-phase ZnO (JCPDS Card, No. 36-1451). No peaks from other impurities were detected.

Photoluminescence (PL) spectra are powerful tools which are used widely to investigate the effect of chemical doping on luminescent properties of ZnO. Fig. 2 presents the PL spectra of undoped and halogen-

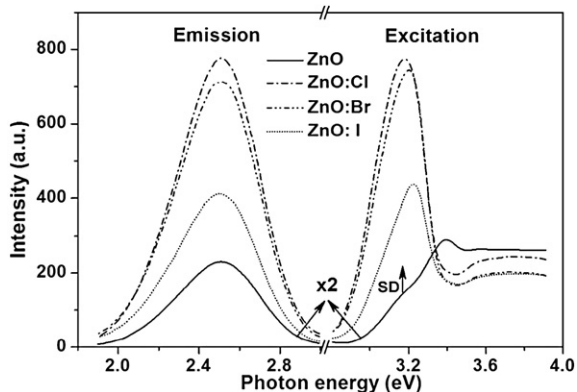


Fig. 2. PL (left) and PLE (right) spectra of as-obtained undoped and halogen-doped ZnO annealed at 900 °C.

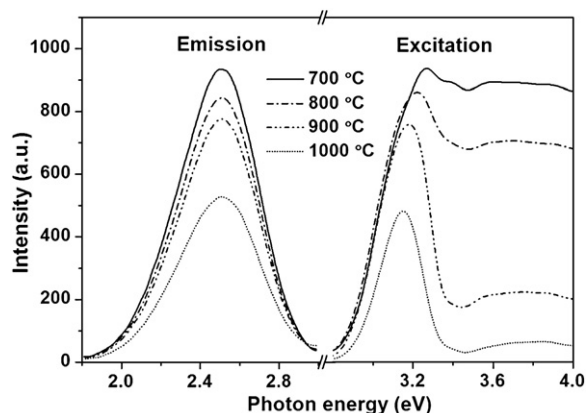


Fig. 3. PL (left) and PLE (right) spectra of as-obtained Cl-doped ZnO annealed from 700–1000 °C.

doped ZnO prepared under the annealing temperature of 900°C. A broad green emission band centered at 2.50eV is observed from all samples, which is normally attributed to the recombination of the photoexcited holes with the electrons occupying the singly ionized oxygen vacancies [18]. However, compared with that of the undoped ZnO, the PL intensity of the green emission band has been increased 3–6 times for the samples doped with diverse halogens. The photoluminescence excitation (PLE) spectra about the green emission band have also been displayed in Fig. 2. A rather wide excitation band with the main peak at 3.40eV is observed from the undoped ZnO, which corresponds to the bound exciton (BE) and is basically consistent with that of the bulk ZnO. Moreover, a side band (denoted as SD) situated at about 3.18eV is discernible. This SD band has been enhanced significantly and become the maximum excitation band for the halogen-doped ZnO. The positions of the SD bands for the samples doped with Cl, Br, and I are located at 3.18, 3.20, and 3.23eV, respectively. Further investigations will be focused on the Cl-doped ZnO powders, since the other two halogen-doped samples exhibit the similar properties.

Fig. 3 shows the PL and PLE spectra of Cl-doped ZnO products annealed at various temperatures. From the PL spectra, a broad green emission band peaking at 2.50eV can be observed for all samples. The PL intensity of the green emission band is found to decrease by elevating the annealing temperatures. The right part in Fig. 3 displays the corresponding PLE spectra of these samples. It is noted that both the powders annealed at 700 and 800°C possess a wide excitation region

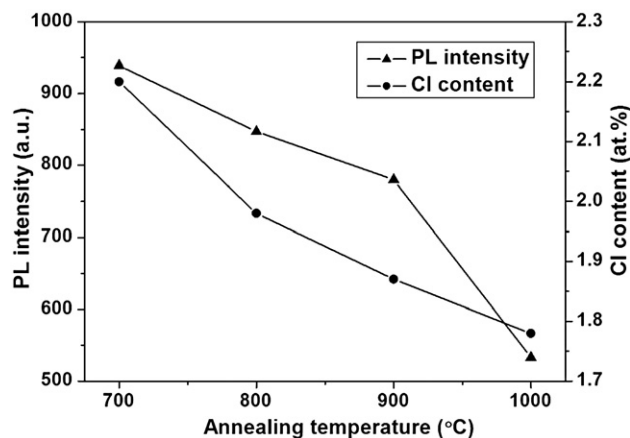


Fig. 4. Effect of annealing temperatures on green PL intensities and Cl<sup>-</sup> contents of as-obtained samples.

from 3.1 to 4.0 eV. As the annealing temperature enhances, the wide excitation region for the products annealed at 900 and 1000°C has been gradually evolved into a comparative broad peak. In addition, the maximum excitation peak shifts from 3.26 eV to 3.22 eV, 3.18 eV, and 3.15 eV at last, as the annealing temperature increases from 700 to 1000°C. The effect of annealing temperatures on the green PL intensities and Cl<sup>-</sup> contents of as-prepared samples is shown in Fig. 4. It can be observed that the two curves present the same changing trend, namely the green PL intensities and the Cl<sup>-</sup> contents decrease with enhancing of the annealing temperatures. This indicates that the PL intensities of green emission band depend on the doping concentration of Cl<sup>-</sup> closely.

Since the ionic radii of Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> are very close to that of S<sup>2-</sup>, the three halide ions can substitute S<sup>2-</sup> ions readily, while the S<sup>2-</sup> ions are easy to be removed by annealing in air. In addition, the charge compensation from K<sup>+</sup> ions also will promote the doping levels of halogens. According to our experimental results, the incorporation of halogens into ZnO influences its energy structure. This will give rise to new defects such as oxygen vacancies, which results in the considerable enhancement of the green emission band. The distinctions in the PL and PLE intensities for the samples doped with various halogen elements may be due to the differences in their ionic radii and electronegativities. The detailed mechanism will be further clarified and subsequently addressed elsewhere.

#### 4. Conclusions

Halogen-doped ZnO phosphors have been synthesized successfully by annealing the mixture of ZnS and KX (X = Cl, Br, I) in air. Both undoped and halogen-doped samples show a broad green emission band centered at 2.50 eV. However, compared with that of undoped ZnO, the green PL intensity of halogen-doped ZnO is enhanced greatly and the excitation band located at ~3.20 eV is intensified remarkably. The incorporation of halogens into ZnO is proposed to increase the oxygen vacancies, which results in the significant enhancement of the green emission band.

#### Acknowledgements

The authors would like to thank Science and Technology Development Fund (Shanghai, No. 0752 nm008) and Shanghai Leading Academic Discipline Project (JY601) for supporting the research.

#### References

- [1] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, *Science* 287 (2000) 1019.
- [2] X. Duan, Y. Huang, Y. Cui, C.M. Lieber, *Nature* 409 (2001) 66.
- [3] V.Z. Mordkovich, H. Hayashi, M. Haemori, T. Fukumura, M. Kawasaki, *Adv. Funct. Mater.* 13 (2003) 519.
- [4] D.A. Schwartz, N.S. Norberg, Q.P. Nguyen, J.M. Parker, D.R. Gamelin, *J. Am. Chem. Soc.* 125 (2003) 13205.
- [5] Y.S. Wang, P.J. Thomas, P. O'Brien, *J. Phys. Chem. B* 110 (2006) 21412.
- [6] N.Y. Garces, L. Wang, L. Bai, N.C. Giles, L.E. Halliburton, G. Cantwell, *Appl. Phys. Lett.* 81 (2002) 622.
- [7] N. Ohashi, N. Ebisawa, T. Sekiguchi, I. Sakaguchi, Y. Wada, T. Takenaka, H. Haneda, *Appl. Phys. Lett.* 86 (2005) 091902.
- [8] S.M. Liu, F.Q. Liu, Z.G. Wang, *Chem. Phys. Lett.* 343 (2001) 489.
- [9] A. Ishizumi, Y. Kanemitsu, *Appl. Phys. Lett.* 86 (2005) 253106.
- [10] K. Vanheusden, W.L. Warren, J.A. Voigt, C.H. Seager, D.R. Tallant, *Appl. Phys. Lett.* 67 (1995) 1280.
- [11] K. Minegishi, Y. Koiwai, Y. Kikuchi, K. Yano, M. Kasuga, A. Shimizu, *Jpn. J. Appl. Phys.* 36 (1997) L1453.
- [12] D.C. Look, D.C. Reynolds, C.W. Litton, R.L. Jones, D.B. Eason, G. Cantwell, *Appl. Phys. Lett.* 81 (2002) 1830.
- [13] K.K. Kim, H.S. Kim, D.K. Hwang, J.H. Lim, S.J. Park, *Appl. Phys. Lett.* 83 (2003) 63.
- [14] D.C. Look, B. Clafin, Ya.I. Alivov, S.J. Park, *Phys. Status Solidi (a)* 201 (2004) 2203.
- [15] Z.P. Wei, Y.M. Lu, D.Z. Shen, Z.Z. Zhang, B. Yao, B.H. Li, J.Y. Zhang, D.X. Zhao, X.W. Fan, Z.K. Tang, *Appl. Phys. Lett.* 90 (2007) 042113.
- [16] S.Y. Bae, H.W. Seo, J. Park, *J. Phys. Chem. B* 108 (2004) 5206.
- [17] G.Z. Shen, J.H. Cho, J.K. Yoo, G.C. Yi, C.J. Lee, *J. Phys. Chem. B* 109 (2005) 5491.
- [18] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, *J. Appl. Phys.* 79 (1996) 7983.