Short communication

Effect of activator distribution on photo- and X-ray excited luminescence properties of ZnS:Cu,Cl phosphors

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Abstract

ZnS:Cu,Cl phosphors were prepared by conventional solid state reaction with the aid of NaCl–MgCl$_2$ flux. The copper activator was introduced into the phosphor precursors by three different methods: co-precipitated with ZnS (CP), wet-coated onto ZnS powders (WC), and simply mixed with ZnS in a mortar (SM). The samples were characterized by X-ray powder diffraction, photoluminescence spectra and X-ray excited luminescence spectra. The results show that both photo- and X-ray excited luminescence intensities of the as-prepared ZnS:Cu,Cl phosphors are in the decreasing order of CP > WC > SM. The different copper activator distribution in the phosphors resulting from the different methods was the main reason responsible for the different luminescence intensity, and uniform distribution is beneficial to the luminescence of the phosphors.

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1. Introduction

The direct transition ZnS possesses the largest energy band gap (∼3.70 eV) among the IIB–VI semiconductors (3.2 eV for ZnO, 2.6 eV for ZnSe, 2.4 eV for CdS, etc.), even comparable with some III–V semiconductors (e.g. 3.4 eV for GaN) [1]. ZnS with some impurities as activators, such as certain transition or rare-earth metals, have been widely used as luminescent materials [2–6]. Among them, ZnS:Cu,Cl phosphors have attracted great attention and are extensively researched [6,7–11]. They have been applied in electronic display devices, CRTs, safety markers, pigments in phosphorescent paints and inks, and the LED phosphors [12]. In addition, ZnS:Cu,Cl may have potential applications in non-dynamic medical imaging due to its green emission spectrum, compatible with the sensitivity of many currently used photodetectors, and its high X-ray to light intrinsic conversion efficiency [13].

The conventional synthetic route for ZnS:Cu,Cl phosphors is the high-temperature solid-state method. In this process, ZnS host powders are mixed with copper salts and flux. The copper activator then diffuses into the host matrix during the subsequent annealing treatment. The activator distribution is an important factor determining the luminescence properties of the phosphors [14]. However, there are no systematic studies reported in the literatures.

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In this paper, we prepared three different phosphor precursors to control the copper distribution and uniformity inside ZnS particles. The photo- and X-ray excited luminescence properties were compared among the as-prepared phosphors. The present study illustrates that the luminescence properties are tightly related to the precursor preparation method and the resultant activator distribution. This research results are also significant and helpful to develop other high-performance phosphors.

2. Experimental

2.1. Preparation of the ZnS:Cu,Cl phosphors

All the reagents purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) were of high purity (>99.99%). ZnS:Cu,Cl phosphors were synthesized by a double-crucible method with the aid of 15 wt% 3NaCl–2MgCl$_2$ (in mole ratio) flux, whose eutectic melting point is about 460 °C [15]. The doping content of copper is 0.02%, 0.04% and 0.06% in molar ratio to Zn^{2+}. The phosphor precursors and the chloride flux were ground in a mortar, and then the reagents were placed in a small covered crucible, which was nestled in a large crucible. The space between the two crucibles was filled with carbon granules. The samples were fired at different temperatures in the range of 600–1100 °C for 1 h. The products were washed to remove chlorides with deionized water and dried at 120 °C in air.

In the preparation of phosphor precursors, copper activator was introduced by three different methods: (1) co-precipitated (CP) with Zn^{2+} to form ZnS:Cu powders. Zn(CH$_3$COO)$_2$·2H$_2$O and CuCl$_2$·2H$_2$O were firstly dissolved in deionized water, and then the solution was added to freshly prepared Na$_2$S·9H$_2$O aqueous solution under vigorous stirring. The resulting white suspension was filtered, washed several times with deionized water and then dried at 120 °C in air; (2) wet-coated (WC) onto precipitated ZnS powders with CuCl$_2$·2H$_2$O in alcohol solution; and (3) simply mixed (SM) precipitated ZnS with CuCl$_2$·2H$_2$O. After heat treatment, the as-prepared phosphors are denoted as CP, WC, and SM phosphors for abbreviation.

2.2. Characterization of the as-prepared phosphors

X-ray powder diffraction (XRD) patterns were determined on a Rigaku D/max-2550 V diffractometer at 40 kV and 40 mA using Cu Kα radiation (λ = 0.15418 nm). The content of copper activator in the phosphor product was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Varian Vista AX, USA). Photoluminescence (PL) spectra were obtained on a Shimadzu RF-5301PC spectrofluorophotometer with a Xe lamp as the excitation source at room temperature. X-ray excited luminescence (XEL) spectra were examined using an X-ray excited spectrometer (Fluormain), and an F-30 X-ray tube (W anticathode target) was used as the X-ray source operating at 30 kV and 4 mA.

3. Results and discussion

3.1. X-ray powder diffraction and composition

XRD patterns of the co-precipitated ZnS:0.06%Cu samples before and after the heat treatment are presented in Fig. 1. The unfired sample exhibits three broad peaks, corresponding to 1 1 1, 2 2 0 and 3 1 1 diffractions of cubic ZnS, respectively. The crystalline grain size estimated from Scherrer formula is about 2.7 nm. The samples fired at 600, 1000 and 1100 °C are pure cubic phase, while the samples fired at 700, 800 and 900 °C are mixed cubic and hexagonal phases. So the samples undergo phase transitions from cubic to hexagonal and again to cubic phase with increased firing temperature. The ratios of cubic to hexagonal phase estimated using the method proposed by Huang et al. are included in Fig. 1 [16]. In our experiments, the transition temperature (about 700 °C) from cubic to hexagonal structure is much lower than 1020 °C in bulk ZnS material. This phenomenon can be ascribed to the large surface area effect of the nanometer-sized ZnS powders [17].

It should be pointed out that the copper solubility limit may influence the formation of ZnS (cubic and hexagonal) and Cu$_x$S phases which would then initiate the hexagonal to cubic transformation [18–21]. Nien and co-workers experimentally found by transmission electron microscope (TEM) that Cu$_x$S precipitates were only observed in ZnS:Cu,Cl phosphors with copper concentrations equal to or larger than 400 ppm (0.04 wt%) [20]. The maximum
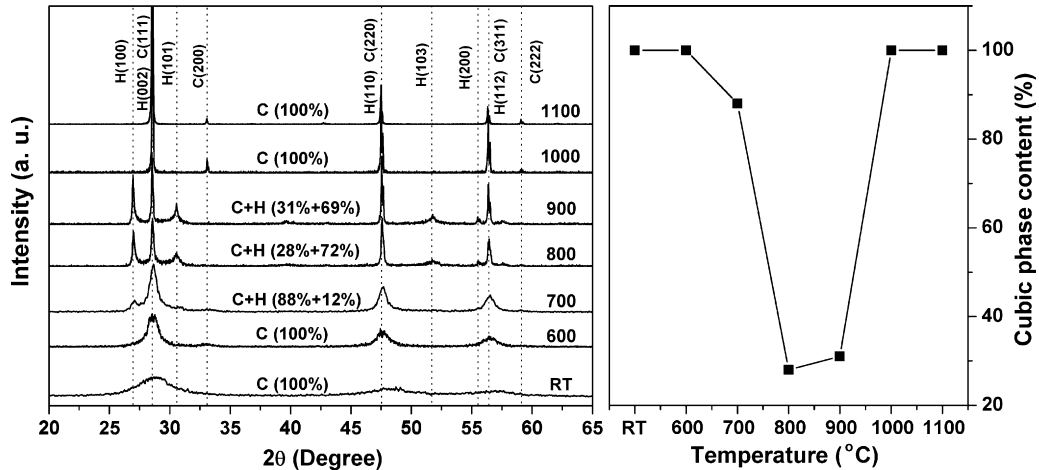
Fig. 1. XRD patterns of the co-precipitated ZnS:0.06%Cu samples before and after the heat treatment. H and C denote cubic and hexagonal, respectively. The right part of the figure exhibits relationship between cubic phase content and the firing temperature.

doping content of copper in our experiments is 0.06% in molar ratio to Zn^{2+} (0.039 wt%), lower than 0.04 wt%. It is worth noting the ZnS raw materials used therein are micrometer-sized, while in our experiment the ZnS host synthesized by co-precipitation method is nano-sized ($\sim$2.7 nm). The smaller particle is favorable for copper ions to diffuse into ZnS matrix and ultimately to result in a relatively homogeneous distribution of copper. On the other hand, the copper source was CuS therein [20], while we adopted $CuCl_2$ as raw material. It is conceivable that CuS will lead to a higher probability of forming Cu_xS in the phosphor product. Based on the above discussion, it can be concluded that there is no Cu_xS separate phase in the ZnS:Cu,Cl phosphors prepared by us. The phases of ZnS:Cu,Cl phosphors (CP) with the copper addition of 0.02 and 0.04% prepared at 1000 and 1100 °C are all pure cubic just like the 0.06% sample. In order to ascertain the origin of the hexagonal to cubic transformation at high temperature, ZnS synthesized by co-precipitation method, and ZnS with 15 wt% $3NaCl–2MgCl_2$ (in mole ratio) flux were also fired at 1000 and 1100 °C. The latter was washed to remove chlorides with deionized water and dried at 120 °C in air (denoted as ZnS:Cl). It is found that ZnS possesses hexagonal structure while ZnS:Cl is pure cubic. Therefore the phase transition should not be ascribed to the Cu addition. The transformation mechanism is not well understood and will be investigated in our later work.

It was revealed by ICP-AES analysis that concentrations of copper in the as-prepared ZnS:0.04%Cu,Cl samples by the CP, WC and SM mixing method were 0.038%, 0.039% and 0.039%, respectively. Thus the real compositions of the phosphors are almost identical, and the very slight difference is believed not to influence the comparability.

3.2. Luminescence properties

3.2.1. Photoluminescence spectra

PL excitation spectra of the ZnS:0.06%Cu,Cl phosphors prepared at 900 °C were obtained by monitoring the green emission peak at 512 nm. As shown in Fig. 2, the spectra are similar and consist of two bands. The high-energy band has the maximum at about 335 nm. It coincides well with the band gap of ZnS ($\sim$3.70 eV), indicating that the energy absorbed by the host materials is transferred to the unexcited Cu^+ ions with certain efficiency. The low-energy band with the maximum at about 365 nm corresponds to the absorption of the impurities [22]. The impurity excitation of Cu^+ ions is less efficient than the excitation by the host absorption.

PL emission spectra of the ZnS:0.06%Cu,Cl phosphors under the host excitation of 335 nm are also given in Fig. 2. The spectra of all SM phosphors prepared at different temperatures, and CP and WC phosphors fired at 800 °C exhibit symmetric and broad emission bands with an intensity maximum at about 512 nm. In contrast, CP and WC phosphors fired at 900 and 1000 °C possess the asymmetric emission bands, which imply superposition of multiple emission bands. Lorentzian curve fitting was applied to de-convolute the emission curves and the presence of two emission bands was found. The two peaks are centered at 512 and 443 nm for the phosphors prepared at 900 °C, while 510 and
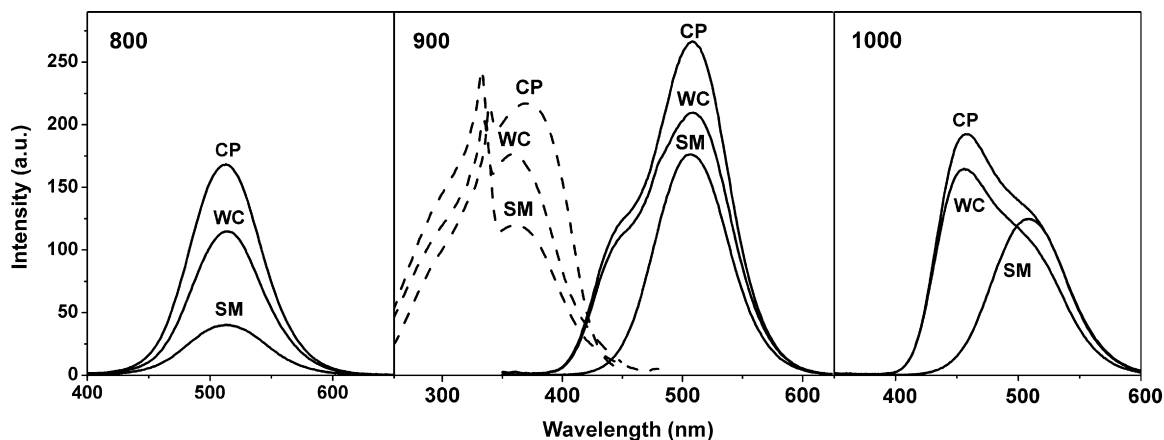
Fig. 2. PL excitation spectra (dotted lines, λ_{em} = 512 nm) and emission spectra (solid lines, λ_{ex} = 335 nm) of the ZnS:0.06%Cu,Cl phosphors. CP, WC and SM phosphors denote that whose precursors were prepared by co-precipitating, wet-coating and simple-mixing methods, respectively.

451 nm for those prepared at 1000 °C. It is generally accepted that copper can form two types of acceptor centers in ZnS. The Cu-green centers Cu_{Zn}^- were formed by Cu substitutionally sitting at the Zn^{2+} site, while the Cu-blue centers $Cu_{Zn}^-Cu_i^+$ were formed by tight binding of nearest neighbor pair of Cu_{Zn}^- and interstitially situated copper, Cu_i^+ [23,24]. The green and blue emissions observed in our experiments may originate from the Cu-green and Cu-blue centers, respectively.

PL emission spectra of the ZnS:0.02%Cu,Cl and ZnS:0.04%Cu,Cl phosphors prepared at 800 °C were also investigated and they are similar to those of the ZnS:0.06%Cu,Cl phosphors synthesized at 800 °C. The dependence of luminescence intensity on copper concentration is shown in Fig. 3. Apparently, the phosphors doped with 0.04% copper have the highest luminescence intensities. With further increment of copper concentration, the emission intensity decreases due to the concentration quenching. When the copper concentration exceeds the critical value, the non-radiative energy transfer between neighboring copper ions weakens the fluorescence.

3.2.2. XEL spectra

Comparisons among XEL spectra of the ZnS:0.06%Cu,Cl phosphors synthesized at 900 °C are displayed in Fig. 4. The phosphors all exhibit a broad emission band in the range of 400–650 nm with the peak center at about 516 nm. By calculating the integral areas of the emission bands for these phosphors, it can be seen that the light yields of CP and WC phosphors are about 138% and 109% as large as that of SM phosphor, respectively.
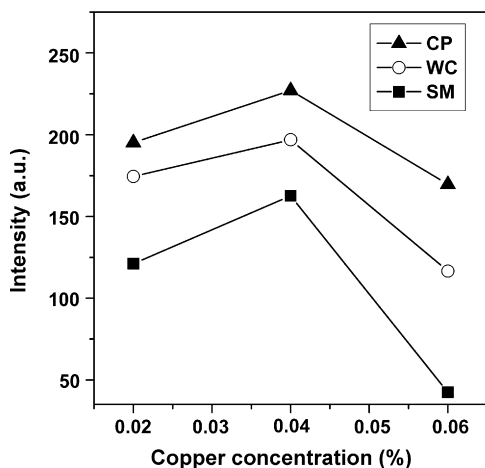

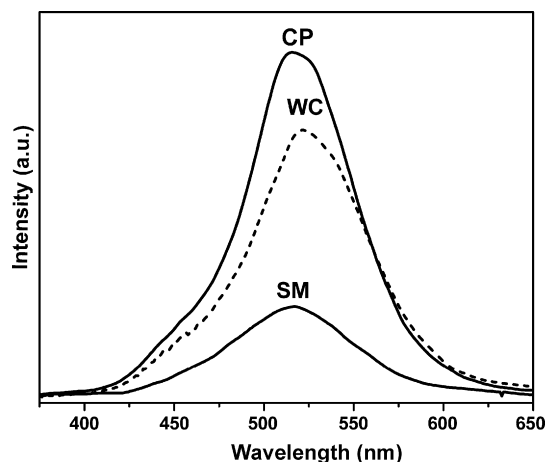Fig. 3. The dependence of luminescence intensity on copper concentration.

Fig. 4. XEL spectra of ZnS:0.06%Cu,Cl phosphors synthesized at 900 °C.

Phosphor excited by UV light and X-ray generally exhibits different luminescent characters, including spectra shape and relative intensity of emission peaks [25–27]. In our experiment, the shoulder band (blue band) in Fig. 2 was higher compared that in Fig. 4. The different luminescent properties may result from the excitation sources of UV light and X-ray with two distinct energies. When the phosphor is irradiated by X-ray with high energy, a very large number of free charge carriers or excitons are generated due to photoelectric effect [25]. The energy absorbed by these free charge carriers or excitons can be transported through the crystal lattice. They could be trapped in the impurity levels, and then the radiative recombinations are followed. The case is different from that excited by UV light and may be responsible for the phenomenon.

3.2.3. Copper distribution in the phosphors

From Figs. 2–4, it can be concluded that both photo- and X-ray excited luminescence intensities of the as-prepared ZnS:Cu,Cl phosphors are in the decreasing order of co-precipitating (CP) phosphor > wet-coating (WC) phosphor > simple-mixing (SM) phosphor. The result must be ascribed to the different methods of introducing copper activator into the phosphor precursors because other aspects to prepare the phosphors are the same. During the doping process of co-precipitation, the copper activator and ZnS host were mixed at the atomic level. The wet-coating method mixed the raw materials in the alcohol medium while the simple-mixing method in the solid-state system. So the efficacy of mixing is in the decreasing order of co-precipitating > wet-coating > simple-mixing. During the subsequent annealing treatment, the difficulty of copper activator diffusing into the ZnS host lattices is in the increasing order of co-precipitating < wet-coating < simple-mixing. Thus it is conceivable that the uniformity degree of copper activator distribution is in the deceasing order of CP phosphor > WC phosphor > SM phosphor. The uniform activator distribution may reduce the migration of excitation energy to the quenching sites in the phosphors, so uniform distribution is beneficial to the luminescence intensity. This was the main reason for the difference of luminescence intensities. Therefore, the precursor preparation and the resultant activator distribution exhibit strong influences on the luminescence properties. Different activator uniformity can lead to large variation of luminescence intensity, as though the average activator concentration remains the same.

4. Conclusions

ZnS:Cu,Cl phosphors were prepared by conventional solid state reaction with the aid of NaCl-MgCl$_2$ flux. The copper activator was introduced into the phosphor precursors by three different methods. Both PL and XEL spectra reveal that luminescence intensities of the as-prepared phosphors are in the decreasing order of co-precipitating (CP) phosphor > wet-coating (WC) phosphor > simple-mixing (SM) phosphor. The copper activator distribution in the phosphors resulting from the initial precursor preparation was the main reason responsible for the different

luminescence intensity, and uniform distribution is beneficial to the luminescence intensity. This research results are also significant and helpful to develop other high-performance phosphors.

Acknowledgments

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