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# A Strategy for Synthesizing CaZnOS:Eu<sup>2+</sup> Phosphor and Comparison of Optical Properties with CaS:Eu<sup>2+</sup>



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#### 1. Introduction

In order to enhance a rendering index (Ra < 80) for W-LED based on a blue LED (GaN chip) precoated with a yellow phosphor (YAG:Ce) that lacks sufficient red emission, red-emitting phosphors with blue–green broad excitation band, such as Ca<sub>1-x</sub>Sr<sub>x</sub>-S:Eu<sup>2+</sup> [1,2] and (Ca,Sr,Ba)<sub>2-x</sub>Si<sub>5</sub>N<sub>8</sub>:xEu<sup>2+</sup> [3–7], have been used in the production process. To improve the sunlight conversion efficiency of the photosynthetic process in agriculture, the red-emitting phosphors Ca<sub>1-x</sub>Sr<sub>x</sub>S:Eu<sup>2+</sup> have been employed to manufacture sunlight-conversion plastic film to convert unused portions (green component) of sunlight to red light [8]. However, the main drawback of the alkaline earth sulfide-based phosphor is the sensitivity to water, resulting in the production of H<sub>2</sub>S. Meanwhile, the nitride-based red-emitting phosphor must be prepared in high press process. So, novel blue–green to red-emitting phosphor is still desirable.

Calcium zinc sulfide (CaZnOS) was first found as an intermediate product in recovery of zinc from its sulfide by carbothermal reduction in the presence of lime [9] and has been shown to be a semiconductor with a band gap of about 3.71 eV [10]. Later on, CaZnOS was first investigated as a novel phosphor doped with  $Mn^{2+}$  by Duan [11] and his coworkers who also proposed that  $Pb^{2+}$ ,  $Eu^{2+}$ ,  $Ce^{3+}$  and  $Tb^{3+}$  would be proper activators for CaZnOS host [12] in 2009. The next year, CaZnOS:Eu<sup>2+</sup> was reported as a high color rendering red-emitting phosphor applied for white LEDs [13].

#### ABSTRACT

The red-emitting phosphor CaZnOS:Eu<sup>2+</sup> was synthesized from CaCO<sub>3</sub>, ZnS, Eu<sub>2</sub>O<sub>3</sub> and CeCl<sub>3</sub> by controlling the sintering condition. It was found that Ce<sup>3+</sup> ions can play a role of reductant to contribute to the formation of Eu<sup>2+</sup> in CaZnOS matrix under inert protective atmosphere. While the gas flow changed to H<sub>2</sub>/ N<sub>2</sub>, the product turned to CaS easily. XRD, photoluminescence spectra, UV–vis and IR absorption spectra were evaluated to investigate the origin of the distinctions of the optical properties and stabilities between the two divalent europium ions doped phosphors CaZnOS:Eu<sup>2+</sup> and CaS:Eu<sup>2+</sup>. The similarities and differences between them were analyzed.

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Although a few CaZnOS phosphors have been found, the synthesis of a single-phase CaZnOS phosphor still remains a challenge for researchers to date because of the great difficulty in controlling the phase purity as well as good property. As a quaternary oxysulfide, the CaZnOS was not isolated in the individual state because of its partial decomposition [10,14]:

#### $ZnS + CaO \rightleftharpoons CaZnOS \rightleftharpoons ZnO + CaS$ (1)

As we know, zinc oxide (ZnO) will easily decompose to oxygen gas (O<sub>2</sub>) and zinc-vapor when it is heated above 1205 K under reducing atmosphere and the decomposition will accelerate with the addition of a carbonate salt such as CaCO<sub>3</sub> [15]. Besides, according to the literature [16–18], extraction of zinc-metal from the mixture of zinc sulfide (ZnS), carbon and calcium carbonate (or calcium oxide) reacts drastically over 1180 K and the sulfur content is captured by CaO as calcium sulfide (CaS). Furthermore, the yields of Zn recovery from both ZnO and ZnS increase as the temperature rises and the roasting time is prolonged. In the system of preparation of CaZnOS phosphors from ZnS, CaCO<sub>3</sub> and H<sub>2</sub>, the similar process of formation of zinc sublimation and CaS takes place during heating. This process can be illustrated by the formulas A.1–A.5 (Formulas A, Supplemental material).

On the other hand, as reported, the decomposition of CaZnOS commences beyond 1370 K under an inert atmosphere and, as a result, the CaS component forms substantially [14]. Consequently, it is key to accurately control the  $H_2/N_2$  flow rate, reaction temperature and heating time to make the CaZnOS-based phosphor the dominate phase. In fact, it is very difficult to obtain pure CaZnOS under reducing ( $H_2/N_2$ ) atmosphere even if firing temperature was controlled in lower level [13].

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In this paper, we report a strategy to prepare the single-phase CaZnOS phosphor doped with  $Eu^{2+}$ , co-doping with  $Ce^{3+}$  as the deoxidizer to promote the formation of  $Eu^{2+}$ , rather than reducing  $(H_2/N_2)$  atmosphere, followed by detailed characterization and comparison of its red properties with CaS: $Eu^{2+}$ .

#### 2. Experimental

#### 2.1. Sample preparation

CaZnOS host material and optimized nominal composition phosphors CaZnOS:Eu<sup>2+</sup>,Ce<sup>3+</sup> were synthesized by the conventional solid-state reaction method. CaCO<sub>3</sub> (A.R), ZnS (A.R), Eu<sub>2</sub>O<sub>3</sub> (99,99%) and CeCl<sub>3</sub> (99,95%) were used as raw materials. The nonedoped and doped CaZnOS, impure CaZnOS:Eu<sup>2+</sup> and pure CaS:Eu<sup>2+</sup> phosphors were designed as shown in Table 1. The relevant raw materials were weighed out according to the stoichiometric molar ratio of the composition (the doping concentrations were optimized as shown Fig. D1, Supplemental material), and subsequently mixed and ground together in an agate mortar. The mixtures were then sintered under a N2 flow atmosphere at 1270 K for 4 h. As for CaS:Eu2+, the same starting materials except CeCl3 were used and kept at 1420 K for 8 h under 5%H<sub>2</sub>/95%N<sub>2</sub> flow. In order to compare the optical properties of CaZnOS:Eu<sup>2+</sup> to CaS:Eu<sup>2+</sup>, a multi-phased phosphor CaZnOS:Eu<sup>2+</sup>,Ce<sup>3+</sup> with a CaS impurity was synthesized at some sintering condition at the present of 5%H<sub>2</sub>/95%N<sub>2</sub> flow. Finally, the as-synthesized phosphors were allowed to cool down naturally in the furnace. Besides, only Ce<sup>3+</sup> or Ce<sup>4+</sup>-doping CaZnOS samples were also prepared likewise in which CeCl<sub>3</sub> or CeO<sub>2</sub> were used as direct dopant.

#### 2.2. Characterization

The crystalline phase of the prepared samples was examined by X-ray diffractometry with Cu K $\alpha$  radiation at 40 kV and 30 mA (Rigaku D/MAX-2550 X-ray diffractometer, Tokyo, Japan). The elementary compositions were characterized by energy dispersive X-ray spectroscopy (EDX). The microstructure and morphology of the phosphors were observed by using JSM-5600LV scanning electron microscope (SEM). The photoluminescence excitation and emission spectra of the samples were measured using an Hitachi F-4500 luminescence spectrofluorometer equipped with a UV 390 nm filter, a 400 V photomultiplier tube voltage, and a 175 W Xenon lamp as the radiation source. And also solid-state UV-vis absorption spectra were recorded by means of a Hitachi U-3010 spectrometer. Finally, infrared spectroscopy was performed with a Fourier transform infrared spectrometer (AVA-TAR 370, Nicolet Company, America). All measurements were carried out at room temperature and in the air.

#### 3. Results and discussion

Fig. 1 shows the representative X-ray diffraction (XRD) patterns of pure CaZnOS (A) and doped CaZnOS samples. All of the diffraction peaks of the samples can be basically indexed to pattern card PDF67-0788. For that synthesized under N<sub>2</sub> flow, only a trace impurity belonging to CaO is detected in the doped sample (B), which can be scoured off by acetic acid [9,14] and is independent of the optical property of CaZnOS phosphors. However, the compound obtained under 5%H<sub>2</sub>/95%N<sub>2</sub> flow is composed of CaZnOS with CaS impurity (C) or single-phase CaS (D) due to excessive reduction and increase of temperature. To further confirm the elementary compositions of the as-obtained samples, Energy Dispersive X-ray Spectroscopy (EDX) (Fig. B1 and Table B1, Supplemental material) was used to analyze the elementary compositions of the as-obtained samples are been as not contained samples, which revealed that zinc was not contained

#### Table 1

The nominal composition (mol%) and synthesized conditions of the samples.

No.	Raw materials n <sub>CaCO3</sub> :n <sub>ZnS</sub> :n <sub>Eu2O3</sub> :n <sub>CeCl3</sub>	Atomosphere	Temperature (K)	Roasting time (h)	Main phases
Α	1:1(no Eu or Ce)	N <sub>2</sub>	1270	4	CaZnOS
В	1:1:0.05%: 0.5%	N <sub>2</sub>	1270	4	CaZnOS
С	1:1:0.05%: 0.5%	$5\%H_2/95\%N_2$	1270	4	CaZnOS,
					CaS
D	1:1:0.05% (no Ce <sup>3+</sup> )	5%H <sub>2</sub> /95%N <sub>2</sub>	1420	8	CaS
Е	1:1(: none): 0.5%	N <sub>2</sub>	1270	4	CaZnOS
F	1:1(: none): 0.5% (CeO <sub>2</sub> )	N <sub>2</sub>	1270	4	CaZnOS



**Fig. 1.** The representative XRD patterns of samples: single phase CaZnOS (A) and CaZnOS: $Eu^{2+}$ , $Ce^{3+}$  phosphor (B) synthesized under N<sub>2</sub> flow; CaZnOS: $Eu^{2+}$ , $Ce^{3+}$  containing CaS (C) and CaS: $Eu^{2+}$  phosphor (D) synthesized under H<sub>2</sub>/N<sub>2</sub> flow.

in CaS:Eu<sup>2+</sup> phosphors made from CaCO<sub>3</sub> and ZnS. And the morphology of Eu<sup>2+</sup>-doped CaZnOS phosphor were examined by SEM (Fig. 2). It can readily be seen that the phosphor powders are composed of aggregated spherical particles with size smaller than 5  $\mu$ m.

The results show that Eu<sup>2+</sup> and Ce<sup>3+</sup> codoped CaZnOS under nitrogen flow was prepared and pure CaS can be made from CaCO<sub>3</sub> and ZnS. And the contrast samples CaZnOS:Eu<sup>2+</sup>,Ce<sup>3+</sup> with impurity CaS were also obtained by controlling the roasting time and the hydrogen flow rate.

As shown in Fig. 3, host material CaZnOS primarily absorbs ultraviolet light asymmetrically peaked at 378 nm assigned to host lattice absorption and transfers to a wide green light emission at about 500 nm. We could propose that Eu<sup>2+</sup> and Ce<sup>3+</sup> are both expected to occupy the Ca<sup>2+</sup> sites preferably because the ionic radii of Eu<sup>2+</sup> (1.17 Å) and Ce<sup>3+</sup> (1.03 Å) are close to that of Ca<sup>2+</sup> (1.0 Å) with six coordination [19]. With Ce<sup>3+</sup> ions codoped, the red band emission ascribed to  $4f^{6}5d^{1} \rightarrow 4f^{7}$  transition of Eu<sup>2+</sup> is detected. It has to be mentioned that the major excitation band of CaZnOS:Eu<sup>2+</sup> and emission band of CaZnOS host entirely overlap so as to energy transfer from the host to Eu<sup>2+</sup> to the utmost. Only a feeble



Fig. 2. SEM image of CaZnOS:Eu<sup>2+</sup> powder.



Fig. 3. Excitation and emission spectra of CaZnOS (A), CaZnOS: $Eu^{2+}$ , $Ce^{3+}$  (B), CaZnOS: $Eu^{2+}$ , $Ce^{3+}$  containing CaS (C) and CaS: $Eu^{2+}$  (D) phosphors.

absorption peak at 378 nm attributed to host lattice is found when the Eu ions concentration is low. Besides, whether  $Ce^{3+}$  ions exist or not, the luminescence spectrum profile of CaZnOS:Eu<sup>2+</sup> has no change. That is to say,  $Ce^{3+}$  ions play a role of deoxidizer to promote the formation of Eu<sup>2+</sup> and also transfer energy to Eu<sup>2+</sup> so that no obvious emission of the sensitizer can be detected.

Phosphors co-doped with Ce<sup>3+</sup> and Eu<sup>2+</sup> have been investigated under reducing (H<sub>2</sub>/N<sub>2</sub>) atmosphere, such as YAG:Ce<sup>3+</sup>,Eu<sup>2+</sup> [20], Ba<sub>2</sub>ZnS<sub>3</sub>:Ce<sup>3+</sup>,Eu<sup>2+</sup> [21], and Li<sub>2</sub>SrSiO<sub>4</sub>:Eu<sup>2+</sup>,Ce<sup>3+</sup> [22]. As we know, Eu can exist as Eu<sup>2+</sup>/Eu<sup>3+</sup> and Ce as Ce<sup>3+</sup>/Ce<sup>4+</sup> [23]. It is assumed that Ce<sup>3+</sup> ions undergo easy oxidation to induce the formation of Eu<sup>2+</sup>/Ce<sup>4+</sup> [23,24] during heating Eu<sup>3+</sup> and Ce<sup>3+</sup> co-existent mixture so that energy transfer occurs from Ce<sup>3+</sup> to Eu<sup>2+</sup> resulting in the enhancement of the emission of Eu<sup>2+</sup>. Hence, the redox reaction would spontaneously happen in an enclosed system without reducing gas. This process can be illustrated by the following formulas [20,23,24]:

$$Ce^{3+} \to e^{\cdot} + Ce^{4+} \tag{2}$$

$$\mathrm{Eu}^{3+} + \mathrm{e}^{\mathrm{\cdot}} \to \mathrm{Eu}^{2+} \tag{3}$$

Therefore, we can infer from the above analysis that the red-emitting phosphor (B) with composition CaZnOS:0.1%Eu<sup>2+</sup>, 0.1%Ce<sup>4+</sup>, 0.4%Ce<sup>3+</sup> was formed. In fact, CaZnOS materials just doped with  $Ce^{3+}$  or  $Ce^{4+}$  were synthesized also under N<sub>2</sub> flow when  $CeCl_3$  or CeO<sub>2</sub> was used as direct dopant. As shown in Fig. C1 (Supplemental material), CaZnOS:Ce<sup>3+</sup> phosphor shows similar optical property as pure host material but the intensity of luminescence is obviously enhanced. It is assumed that the doping level of Ce<sup>3+</sup> is located at the bottom of the conduction band of CaZnOS. The emission band of CaZnOS:Ce<sup>3+</sup> locates at the region of green light which almost completely overlaps with the excitation band of Eu<sup>2+</sup>-doping CaZnOS phosphor. Eu<sup>2+</sup> and Ce<sup>3+</sup> ions are f-d and d-d electron configurations, respectively. The energy transfer would occur between activator/coactivator couples by efficient resonant type. Moreover, when  $Ce^{3+}$  and  $Eu^{3+}$  ions co-exist in the matrix,  $Ce^{3+}$  can undergo easy oxidation to  $Ce^{4+}$  during heating and the electron released during the oxidation is used to convert Eu<sup>3+</sup> to Eu<sup>2+</sup> species. According to the charge-transfer from Ce to Eu, energy transfer  $Ce^{3+} \rightarrow Eu^{2+}$ must happen and luminescence quenching of Ce<sup>3+</sup> ions should take place [25]. However, doping with Ce<sup>4+</sup>, nearly no obvious luminescence phenomenon related to  $Ce^{4+}$  was detected in CaZnOS. The electron configuration of  $Ce^{4+}$  is composed of  $5d^0$  so that d-f transition is impossibility. Consequently, it is believed that Ce<sup>3+</sup> ions are partially as deoxidizer, and partially as sensitizer for Eu<sup>2+</sup> ions.

As we already know, with temperature rising,  $CaCO_3$  decomposed to CaO at first. Then CaZnOS was formed through a combination of CaO and ZnS. Keep the temperature climbing up beyond 1370 K and the equilibrium of formula (4) would be shifted toward the right side substantially. Meanwhile, the drastic decomposition of ZnO and zinc vaporization grew up under  $H_2/N_2$ . As a result, phase-pure CaS was formed:

$$\begin{split} & \mathsf{CaCO}_3 + \mathsf{ZnS} + 0.05\% \mathsf{Eu}_2 \mathsf{O}_3 + \mathsf{H}_2 \rightarrow \mathsf{CaS} : 0.1\% \mathsf{Eu}^{2+} + \mathsf{Zn} \\ & \uparrow + 1/2\mathsf{O}_2 \uparrow + \mathsf{CO}_2 \uparrow + \mathsf{H}_2\mathsf{O} \uparrow \end{split} \tag{4}$$

where  $H_2$  was supplied by  $5\%H_2/95\%N_2$  flow and considered as the reductant for Eu<sup>3+</sup> ions as well as an assistant for decomposition of ZnO. The excitation and emission spectra of the as-obtained CaS:Eu<sup>2+</sup> samples make no odds with those reported phosphors [2,8,26]. It indicates that the method in this paper can provide a new strategy to synthesize calcium sulfide based material.

It is interesting that similar spectra profiles emerge from both CaS:Eu<sup>2+</sup> and CaZnOS:Eu<sup>2+</sup>. However, due to the change of the crystal structure and crystal field, some unique phenomena appear as for the two Eu<sup>2+</sup> ion activated substances. Compared with CaS:Eu<sup>2+</sup>, several differences of the spectra can be easily found. Firstly, the ultraviolet excitation bands in Fig. 3 reveal the biggest variance. CaS:Eu<sup>2+</sup> possesses a prominent UV excitation band which locates at about 327 nm attributed to  $4f^7({}^8S_{7/2}) \rightarrow 4f^65d^1(t_{2g})$  [2,26] transition of Eu<sup>2+</sup> ions, while the weak UV band of CaZnOS peaks at 378 nm attributed to host lattice (HL) absorption of CaZnOS. In addition, the main excitation band of CaS:Eu ranges from 400 to 630 nm. For CaZnOS:  $Eu^{2+}$ , the absorption at the visible region, more abruptly, starts at about 420 nm. Nevertheless, the profiles of the red emission bands of the two phosphors are nearly the same except for the locations at 650 nm of CaS:Eu and 645 nm of CaZnOS:Eu<sup>2+</sup>, respectively. On the other hand, the luminescence intensity of CaZnOS:Eu<sup>2+</sup> is relatively a guarter of that of CaS:Eu<sup>2+</sup>. And because of this, once the impurity CaS forms, the luminescence of CaS:Eu<sup>2+</sup> would be absolutely dominant so that the characteristic luminescence of CaZnOS:Eu<sup>2+</sup> is difficult to be detected as shown by phosphor C in Fig. 3.

The UV–vis absorption spectra of the as-synthesized phosphors are plotted in Fig. 4. The absorption band of CaZnOS host material is concentrated in the near-UV region which well matches with the excitation spectrum of pure CaZnOS as depicted in Fig. 3. By contrast, the absorption band of CaZnOS:Eu<sup>2+</sup>,Ce<sup>3+</sup> stretches to the visible region so that a fairly wide excitation band of the phosphor covered the whole green light region is observed. In comparison with the pure CaZnOS:Eu<sup>2+</sup>,Ce<sup>3+</sup>, a remarkably uplift at a range of 430–630 nm turns up in impure CaZnOS: Eu<sup>2+</sup>,Ce<sup>3+</sup> and CaS:Eu<sup>2+</sup> phosphors. This result can support the phenomenon about higher luminescence intensity of CaS than CaZnOS doped with Eu<sup>2+</sup> ions. Especially, the center of the UV absorption of CaS:Eu<sup>2+</sup> shifts to about 330 nm in accordance with the excitation band.

To better understand the differences of the optical spectra between CaZnOS:Eu<sup>2+</sup> and CaS:Eu<sup>2+</sup>, a infrared (IR) test was also carried out. Fig. 5 exhibits the IR spectra of different materials. Comparison between pure CaZnOS and CaS (synthesized by the method referred to Ref. [8]) suggests an assignment to a Ca–S stretching model at 650, 931, 980, 1099, 1143 and 1213 cm<sup>-1</sup> as the black arrows pointed which exist only in samples containing CaS component. The atoms in CaZnOS are located in layers stacked along the [001] irection so that Ca–O layers are inserted in the aligned parallel [ZnS<sub>3</sub>O] layers attached to the O atom. In the polar structure, the Ca–O layer and the other adjacent [ZnS<sub>3</sub>O] layer links through van der Waals and consequently the interaction force between Ca and S atoms are quite weak. The peaks at 1414, 1501 and



**Fig. 4.** UV-vis absorption spectra of host CaZnOS, CaZnOS:Eu<sup>2+</sup>,Ce<sup>3+</sup>, CaZnOS:Eu<sup>2+</sup>,-Ce<sup>3+</sup> containing CaS and CaS:Eu<sup>2+</sup> phosphors.

1628 cm<sup>-1</sup> as the blue arrows pointed would belong to S-S bending vibration in that them appear in both of CaZnOS and CaS. Whereas, through a contrast with the spectra between CaZnOS:Eu<sup>2+</sup>,Ce<sup>3+</sup> and CaZnOS host, we can speculate the IR peaks at 872, 1398 and 2505  $\text{cm}^{-1}$  come from the Eu–O stretching vibration as the red arrows pointed. Further support is the sharply drop of these peaks in those samples containing CaS. Then, for all the Eu<sup>2+</sup> doped phosphors, the significant peak at 1480 cm<sup>-1</sup> ought to be bound up with the distortion of crystal lattice after the replace of  $Ca^{2+}$  by larger  $Eu^{2+}$ , which leads to the enhancement of S–S bending viration. As the increase of the content of CaS impurity within the phosphors, the peaks ranging from 650 to  $1220 \text{ cm}^{-1}$ regularly gradually change with the decrease of Eu–O vibration and increase of Ca-S stretching. And the intensities of the absorption decline progressively for the formation of cubic CaS with high symmetry.

In addition, the crystal structure and coordination environment of the two matrixes are different as well as the crystal field strength. As shown in Fig. 6, CaZnOS consists of isotypic puckered hexagonal ZnS and CaO layers and crystallizes in hexagonal space group P6<sub>3</sub>mc (No. 186) [10]. Strikingly, Ca is surrounded by three O and three S atoms, where the O and S atoms are offered, respectively, by two parallel adjacent ZnS<sub>3</sub>O layers. Looking at a close-up of the environment of Ca site, we can easily find a distorted octahedra formed around Ca with S1 and O1 as vertexes. It is assumed that complex layered oxychalcogenides can offer scope for the



Fig. 6. The crystal structure CaZnOS.

realization of novel and unusual properties complementary to those found in chalcogenides and oxides as a result of control of the electronic communication between the chalcogenide and oxide layers. As we know, the Ca site locates at the octahedral center position with 6 S around in cubic CaS crystal. As a consequence, when  $Eu^{2+}$  ions displace the Ca<sup>2+</sup> sites, the similar luminescence phenomena arise up for both CaZnOS: $Eu^{2+}$  and CaS: $Eu^{2+}$ .

However, since the symmetry and the amount of covalency of CaZnOS are relatively lower, the energy difference between the  $4f^7$  and  $4f^65d^1$  configurations of Eu<sup>2+</sup> ions increases so that the emission band of CaZnOS:Eu<sup>2+</sup> shifts to a shorter wavelength than that of CaS:Eu<sup>2+</sup> [27].

It is generally known that CaS compound will easily deliquescence exposed to the air. Although Ca ions are coordinated with S atoms as well, the interatomic distance of Ca–S in CaZnOS crytal lattice is about 3.0346 Å larger than that in CaS single crystal (2.8445 Å, calculated by the data from Ref. [28]). In the oxygensulfide, Ca ions are more closer to O rather than S atoms and the interaction force between the Ca and S is quite weak. Hence, we can speculate that the thermodynamic stability of CaZnOS would be better than that of CaS. In order to investigate the chemical and



**Fig. 5.** Infrared spectroscopy of CaZnOS, pure CaZnOS:Eu<sup>2+</sup>,Ce<sup>3+</sup>, impure CaZnOS:Eu<sup>2+</sup>, impure CaZnOS:Eu<sup>2+</sup>.Ce<sup>3+</sup>, CaS:Eu<sup>2+</sup> and CaS.



338

**Fig. 7.** PL and PLE spectra of CaZnOS with and without chemical and heat treatment. The inset: XRD patterns of CaZnOS after chemical and heat treatment.

thermodynamic stabilities of CaZnOS, some host material were immersed in acetic acid for 24 h and then thermally treated in boiling water until the dry powders were gotten. It was found that the composition and optical property of CaZnOS had no change (Fig. 7), which indicates that CaZnOS has good chemical and thermal stability performance. Similar work was also done to doped CaZnOS phosphors and the results also support the above conclusion. So the results suggest that the CaZnOS-based phosphors are insensitive to the environment and can maintain good properties in application.

#### 4. Conclusions

A new strategy for synthesizing CaZnOS: $Eu^{2+}$  red-emitting phosphor by co-doping with  $Ce^{3+}$  as deoxidizer rather than  $5\%H_2/$  $95\%N_2$  flow as reducing atmosphere is introduced in the present work. The redox reaction ( $Ce^{3+} + Eu^{3+} \rightarrow Eu^{2+} + Ce^{4+}$ ) would spontaneously happen when the high-temperature solid-state reaction takes place in the system of  $Eu^{3+}$  and  $Ce^{3+}$  co-existent host (CaZnOS) without reducing gas, and also energy transfer occurs from  $Ce^{3+}$  to  $Eu^{2+}$  resulting in the enhancement of the emission of  $Eu^{2+}$ . It has been discovered that the nominal composition (mol%) CaZnOS: $0.1\%Eu^{2+}$ ,  $0.5\%Ce^{3+}$  phosphor has the optimal green-to-red composition. Because CaZnOS has good thermal and chemical stability we have evaluated its effectiveness in enhancing sunlight harvesting for increasing agricultural production and deemed it to be better than the CaS: $Eu^{2+}$  phosphor.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2013. 08.162.

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