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Preparation, Electronic structure and Luminescence Properties of Ce\textsuperscript{3+}-activated CaZnOS under UV and X-ray Excitation

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Abstract

The electronic structure of CaZnOS calculated using the CASTEP mode is an intermediate band gap semiconductor with a direct band gap of 2.4 eV. Ce\textsuperscript{3+}-activated CaZnOS samples were prepared by a solid-state reaction method at high temperature, and their luminescence properties under UV-visible and X-ray excitation were investigated. CaZnOS: Ce\textsuperscript{3+} exhibits a broad band emission in the wavelength range of 450 - 650 nm, originating from the 5d - 4f transition of Ce\textsuperscript{3+} for both under blue light (460 nm) and X-ray excitation. The mechanism of luminescence and concentration quenching of Ce\textsuperscript{3+} in CaZnOS have been investigated in detail. The results showed that the relative luminescence intensity reaches a maximum at 1 mol\% of Ce\textsuperscript{3+}, and the electric dipole - dipole interaction is the major mechanism for concentration quenching of Ce\textsuperscript{3+} emission in CaZnOS. The potential application of CaZnOS: Ce\textsuperscript{3+} has been pointed out.

Keywords: CaZnOS, luminescence, XEL

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1. Introduction

The white light-emitting diodes (LEDs) has attracted significant attention and developing rapidly because of their higher efficiency, lower power consumption, longer life time and environmental friendly compared to conventional lighting. The most common approach involves combining a blue LED chip (450 - 470 nm) with red and green emitting phosphors for an excellent color-rendering index, high power output and high color tolerance. Therefore, phosphors with strong absorption, desirable emission/excitation and high efficiency under blue excitation should be developed to advance this technology. Rare-earth doped alkali-earth sulfides, such as CaS: Eu$^{2+}$ (red), CaS: Ce$^{3+}$ (green), SrS: Eu$^{2+}$ (orange) and SrS: Ce$^{3+}$ (blue), are well-known phosphors for white LED applications because all of them show strong absorption in the blue region (450 - 470 nm) [1].

X-ray phosphors are solid-state inorganic materials, which can be incorporated into a variety of X-ray imaging devices, and widely used in medical and security applications. The role of these phosphors is designed to reduce the exposure time of the patients to X-rays while maintaining the structural features of the X-ray image [2]. This is done by amplifying every X-ray photon of high energy absorbed by a phosphor screen into hundreds of visible or UV-radiation photons of low energy, which are then recorded by a detector, such as a piece of photographic film.

The oxysulfide CaZnOS, first discovered by S. A. Petrova et al [3] in 2003 and then investigated in detail by J. Clarke et al [4] in 2007, crystallizes in hexagonal space group $P6_3mc$ (No. 186) with $a = 3.75726(3)$ Å, $c = 11.4013(1)$ Å, and $Z = 2$, as shown in Fig.1 (a). Its crystal structure is composed of layers of ZnS$_2$O tetrahedra all aligned with Zn-O bond vectors parallel and directed parallel to $c$-axis and linked at
all their S-containing vertices, yielding $\infty[ZnS_{3/3}O]^{2-}$ layers. Ca$^{2+}$ ions occupy distorted octahedral interstices between these $\infty[ZnS_{3/3}O]^{2-}$ layers (Fig.1 (b)). Zn$^{2+}$ is tetrahedrally coordinated by three S atoms and one O atom (ZnS$_3$O tetrahedron) with $C_{3v}$ point symmetry Fig.1 (c), and the resulting coordination for Ca$^{2+}$ cations is 6-fold with three S atoms and three O atoms, occupying distorted octahedral interstices between these layers Fig.1 (d). The band gap of CaZnOS is about 3.71 eV, making it a better semiconductor as a promising host lattice for activators, such as Mn$^{2+}$ and Eu$^{2+}$, etc. Recently, the photoluminescence properties of red-emitting CaZnOS : Mn$^{2+}$ and CaZnOS : Eu$^{2+}$ phosphors were investigated by Hintzen et al in 2009 [5] and Chen et al in 2010 [6], respectively. Mn$^{2+}$-activated CaZnOS phosphors show a single symmetric narrow red emission band in the wavelength range of 550 - 700 nm with the peak at about 614 nm. In addition, it can be efficiently excited under host lattice excitation (250 - 350 nm) and Mn$^{2+}$ itself ($d - d$ transitions, 350 - 500 nm) leading to the potential application as an alternative red-emitting LED conversion phosphor. CaZnOS : Eu$^{2+}$ reveals a strong broad absorption band between 450 - 500 nm, and exhibits a broad emission band with the peak at 650 nm. An intense white InGaN-based blue-LED, using red - emitting CaZnOS : Eu$^{2+}$, green - emitting (Ba, Sr)$_2$SiO$_4$ : Eu$^{2+}$, and yellow - emitting Y$_3$Al$_5$O$_{12}$ : Ce$^{3+}$ as light converters, was fabricated to exhibit a high color rendering index Ra of 85 with the color temperature of 4870 K.

The Ce$^{3+}$ ion, compared with Eu$^{2+}$ ion, is much simple because it contains only one electron in its excited configuration ($5d^1$) [7]. Similarly, the electron within the 5$d$ orbital of the excited Ce$^{3+}$ ion is also strongly dependent on the local structure of the host lattice. In the present work, we report the synthesis, the electronic structure of CaZnOS and the luminescence properties of Ce$^{3+}$-doped CaZnOS under UV and
X-ray excitation. In addition, the relationship between the luminescence properties and structural characteristics has been discussed.

2. Experimental section

2.1 Synthesis of Ca$_{1-2x}$Ce$_x$Li$_x$ZnOS ($0 \leq x \leq 0.15$)

Ca$_{1-2x}$Ce$_x$Li$_x$ZnOS ($0 \leq x \leq 0.15$) powder samples were prepared by solid-state reaction at high temperature. The starting materials were analytical grade CaO, ZnS, Li$_2$CO$_3$ and CeO$_2$ (99.99 % purity). Appropriate amounts of starting materials were weighed, thoroughly mixed and ground in an agate mortar. The powder mixtures were fired in molybdenum crucibles at 950 - 1050 °C for 48 h in a horizontal tube furnace under N$_2$ - H$_2$ (5 %) atmosphere. After firing, the samples were gradually cooled down in the furnace. After sintering, these samples were gradually cooled down to room temperature in the furnace. There was no apparent reaction of the prepared samples with the Mo crucibles. All processes were handled in a dry glovebox flushed with dry nitrogen because of air and water sensitivity of some starting materials.

2.2 Electronic structure calculation

The calculation of the electronic structures of CaZnOS was carried out with density functional theory and performed with the CASTEP code [8], which utilizes pseudopotentials to describe electron-ion interactions and represents electronic wave functions by means of a plane-wave basis set. The generalized gradient approximations (GGA) were chosen for the theoretical basis of density function. The code used the band-by-band conjugate-gradient technique to minimize the total energy with respect to the plane-wave coefficient. Two steps were necessary for
calculating the electronic band structure of CaZnOS. The first step was to optimize its crystal structure using the crystallographic data reported in the literature. There is only a small difference between the experimental unit cell parameters and the calculated ones after crystal structure optimization. The second step was to calculate the band structure and density of states (DOS) of CaZnOS. Lattice parameters and atom coordinates were fixed at the values obtained by the crystal structure optimization process in the first step. For the two steps, the following basic parameters were chosen in the setting up CASTEP: the kinetic energy cutoff = 400 eV, k - point spacing = 0.04 Å⁻¹, sets of k points = 2 × 1 × 5, SCF tolerance thresholds = 1.0 × 10⁻⁶ eV/atom, and space representation = reciprocal.

2.3 Characterization

All measurements were performed on finely ground samples, which were analyzed by X-ray powder diffraction (Bruker, D4 Endeavor X-ray Diffractometer) using Cu Kα radiation at 40 kV and 40 mA with a graphite monochromator. The 2θ ranges of all the data sets are from 10 to 80 ° using step scan with a step size of 0.02 ° in 2θ and a count time of 1 second per step. The XRD measurements were performed at room temperature in air. The cell parameters of Ca₁₋ₓCeₓLiₓZnOS (0 ≤ x ≤ 0.15) were determined from the X-ray powder diffraction patterns using the indexing program Fullprof [9]. Thermal analysis (TG/DTA) using Mettler Toledo TGA/SDTA 851 was carried out on precursor powder in 70 ml Al₂O₃ crucibles from 300 to 1200 °C with a heating rate of 5 K/min in flowing nitrogen (50 ml/min). The morphology was determined by using field emission scanning electron (FE-SEM, JEOL JSM-6700F) microscopy. The diffuse reflectance, emission and excitation spectra of the samples were measured at room temperature by a Perkin Elmer LS 50B
spectrophotometer equipped with a Xe flash lamp. The reflection spectra were calibrated with the reflection of black felt (reflection 3 %) and white barium sulfate (BaSO$_4$, reflection ~ 100 %) in the wavelength region of 230 - 700 nm. The excitation and emission slits were set at 15 nm. The emission spectra were corrected by dividing the measured emission intensity by the ratio of the observed spectrum of a calibrated W-lamp and its known spectrum from 300 to 900 nm. Excitation spectra were automatically corrected for variations in lamp intensity (and thus for the spectral dependence of the excitation energy) by a second photomultiplier and a beam-splitter. All luminescence spectra were measured with a scan speed of 400 nm/min at room temperature in air. The X-ray excited luminescence (XEL) of the sample was performed under room temperature using an X-ray excited spectrometer (Fluormain), in which an F-30 X-ray tube (W anticathode target) was used as the X-ray source operating at 30 kV (peaking voltage) and 4 mA.

3. Results and discussion

3.1 The electronic structure of CaZnOS

Fig. 2, part (a) and (b) show the band structure and density of states of CaZnOS, respectively. As shown in part (a), CaZnOS exhibits a direct band gap, and the gap between the lowest energy of the conduction band and the highest energy of the valence band is about 2.4 eV, which is much lower compared to the experimentally determined value (3.88 eV, which will be shown in section 3.3). It should be noticed that the calculated value of the band gap is usually underestimated due to the well-known DFT reason using GGA as the exchange-correlation potential [10]. Therefore, the experimental gap of CaZnOS is expected to be larger than the
calculated one, making it a good host for many luminescent activators. Fig. 2 (b) shows the total density of states and partial density of states of CaZnOS in the energy range between - 40 eV and 10 eV, where four ranges can be recognized. At an energy below - 30 eV, the DOS is determined by Ca 4s states. The bonding band from - 25 eV to - 10 eV is mainly formed by Ca 3p, S 3s and O 2s states, indicating considerable interactions between Ca and S/O. The top of the valence band is dominated by O 2p and S 3p states, and it may hybridize with Zn 3d states. In addition, the bottom of the conduction band is mainly composed of Ca 3p and Zn 3p states.

3.2 Phase formation, morphology and thermal stability of Ca$_{1.2-x}$Ce$_x$Li$_x$ZnOS (0 ≤ x ≤ 0.15)

According to the powder X-ray diffraction patterns, the samples with the composition of Ca$_{1.2-x}$Ce$_x$Li$_x$ZnOS (0 ≤ x ≤ 0.15) were obtained as nearly single phase material of CaZnOS (ICSD no. 24 - 5309). Like CaZnOS : Eu$^{2+}$ reported by Kuo et al, in which Eu$^{2+}$ substitution for Ca$^{2+}$ has the same formal charge and the ionic radius of Eu$^{2+}$ (r = 1.17 Å, CN = 6) is much larger than that of Ca$^{2+}$ (r = 1.01 Å, CN = 6), leading to a marked expansion of the unit cell volume [6]. As we know, the ionic radius of Ce$^{3+}$ (r = 1.01 Å, CN = 6) is similar to that of Ca$^{2+}$ (r = 1.00 Å, CN = 6), but much larger than that of Zn$^{2+}$ (r = 0.6 Å, CN = 4, r = 0.74 Å, CN = 6) [11]. Thus, it is expected that the expansion of the unit cell volume could be clearly observed if Zn$^{2+}$ sites are occupied by Ce$^{3+}$. However, the unit cell volume of CaZnOS : Ce$^{3+}$ slightly increase to $x = 0.15$ with increasing the Ce$^{3+}$ concentration (i.e. 0 - 15 mol % with respect to Ca), as shown in Fig. 3, indicating that Ca$^{2+}$ sites instead of Zn$^{2+}$ sites are
substituted by Ce$^{3+}$ ions. The site occupation of Ce$^{3+}$ in CaZnOS is different from that of Mn$^{2+}$ in MZnOS ($M = \text{Ca, Ba}$) [5, 12], and Cu$^{2+}$ in BaZnOS [13].

SEM was used to characterize the morphology of the products. Fig. 4 shows electron microscope images of a typical Ce$^{3+}$-doped CaZnOS sample. Most of the particles are distributed in the crystal size range of 10 - 15 μm, together with some larger particles up to 50 μm. In addition, some small equiaxed crystals grow together and form larger aggregates, which can be partially broken up again in a mortar.

TG/DTA was used to characterize the thermal stability of CaZnOS. Fig. 5 shows the TG/DTA curves of CaZnOS powder in the flowing N$_2$ atmosphere. The TG profile indicated that, weight loss occurs mainly in two steps between 25 and 1200 °C accompanied by one endothermic effect that was recorded at about 1000 °C in the DTA profile. This broad endothermic peak and almost 50 % weight loss in the TG can be ascribed to the degradation of decomposition of the CaZnOS to a mixture of CaS, CaO and ZnS which is supported by the XRD analysis, as shown in Fig. 1S.

3.3 Luminescence properties of Ca$_{1-x}$Ce$_x$Li$_x$ZnOS ($0.005 \leq x \leq 0.15$)

The undoped CaZnOS shows a drastic drop in the reflection in the UV range below 290 nm, according to the diffuse reflection spectrum of CaZnOS as shown in Fig. 6. It is essentially corresponding to the valence-to-conduction band transitions of the CaZnOS host lattice. The intense reflection in the visible spectral range is in agreement with the fact that undoped CaZnOS exhibits white body color. The absorption spectrum of CaZnOS, obtained from the reflection spectrum by using the Kubelka - Munk function, is used to better localize the thresholds for host lattice
absorption:

\[ F(R) = (1-R)^2/2R = K/S \]  \hspace{1cm} (1)

where \( R, K, \) and \( S \) are the reflection, absorption, and scattering coefficient, respectively. The absorption \((K/S)\) function of \( \text{CaZnOS} \) derived with the Kubelka-Munk function is shown in the inset in Fig. 6. The value of the optical band gap of \( \text{CaZnOS} \) is calculated by extrapolating the Kubelka-Munk function to \( K/S = 0 \). There is one absorption band with peak at 250 nm, and the optical band gap is calculated to be about 3.88 eV (i.e. 320 nm), which is in-between the values reported by Sambrook (3.7 eV) [4] and Hintzen (4.0 eV) [5].

The emission and excitation spectra of \( \text{Ca}_{1-x}\text{Ce}_x\text{Li}_x\text{ZnOS}\) \((x = 0.01)\) are presented in Fig. 7. Under 460 nm excitation, \( \text{Ca}_{0.98}\text{Ce}_{0.01}\text{Li}_{0.01}\text{ZnOS} \) displays obviously doublet emission bands in the wavelength range of 450 - 650 nm with the peaks center at about 505 and 563 nm, respectively. It can be believed that these two emission sub-bands are the characteristic splitting of the emission bands of \( \text{Ce}^{3+} \) due to the spin-orbit split of ground state, and can be well decomposed into two Gaussian components (inset in Fig. 7 (b)). These bands should correspond to the \( 5d \rightarrow ^2F_J (J = 7/2, 5/2) \) transitions of \( \text{Ce}^{3+} \). The \( F_J (J =7/2, 5/2) \) energy gap of \( \text{Ce}^{3+} \) in \( \text{CaZnOS} \) is 2,040 cm\(^{-1}\), which is very close to the \( F_J (J =7/2, 5/2) \) energy gap of \( \text{Ce}^{3+} \) (2,000 cm\(^{-1}\)) in most \( \text{Ce}^{3+} \) activated phosphors [7]. There is one principle excitation band in the excitation spectra of \( \text{Ca}_{1-x}\text{Ce}_x\text{Li}_x\text{ZnOS}\) \((x = 0.01)\) located in the wavelength range of 400 - 500 nm with the peak centered at 460 nm, regardless of the monitoring wavelength. The broad excitation band is assigned to the transition from the \( ^2F_{5/2} \) ground state of \( \text{Ce}^{3+} \) to the lowest level of the \( 5d \) configuration split by the crystal field interactions. As a comparison, some characteristics of the \( \text{CaZnOS} : \text{Ce}^{3+} \) and other typical \( \text{Ce}^{3+} \)-activated (oxy)sulfide phosphors are presented in table 1 [14-19].
The typical X-ray excited luminescence spectra of CaZnOS : Ce$^{3+}$ at room temperature are presented in Fig. 8. The broad band emission extending from 450 nm to 700 nm is attributed to the $5d \rightarrow {^2}F_J (J = 7/2, 5/2)$ transitions of Ce$^{3+}$, which can be well decomposed into two Gaussian components with the maxima at 19,763 cm$^{-1}$ and 17,730 cm$^{-1}$ (corresponding to 506 nm and 564 nm, respectively) on an energy scale. The ratio between the luminescence intensity of these two sub-bands (higher energy ($^2F_{5/2}$) vs. lower energy ($^2F_{5/2}$)) increases with increasing Ce$^{3+}$ concentration. It is worthwhile to note that both the XEL spectra of CaZnOS : Ce$^{3+}$ and Bi$_4$Ge$_3$O$_{12}$ (BGO) have the similar broad emission band, as shown in Fig. 8. CaZnOS : Ce$^{3+}$ fulfills the requirements for a potential green-emitting phosphor. Its dominant emission is located at 505 nm, more importantly, it can be easily excited by 460 nm and X-ray excitation.

It is well known that the relative energy of the first $f$ - $d$ transition for different RE$^{3+}$ ions is almost independent of host, and the $5d$ level of RE$^{3+}$ ions in the defined crystal show somewhat lower energies compared with the $5d$ orbital energy of the free RE$^{3+}$ ions. Therefore, it is easy to predict that the decrease of $5d$ energy for the different RE$^{3+}$ ions in a similar lattice must exhibit some relationship. Dorenbos has provided the $4f$ - $5d$ transition energies of triply ionized lanthanides in various compounds and proposed that the crystal field decrease $D(Ln, A)$ for the energy of the $4f^{n-1}5d$ levels of a lanthanide ion in compound $A$ relative to the same level energies in the free ion, i.e.

$$D(Ln, A) = E(Ln, \text{free}) - E(Ln, A)$$

(1)

is almost independent of the nature of lanthanide ion doped.

Here, $E(Ln, \text{free})$ is the energy of the first $f$ - $d$ transition of Ce$^{3+}$ as free (gaseous)
ions. $E(Ln, A)$ is the $f - d$ energy difference of the lanthanide ions $Ln^{3+}$ doped in compound $A$. The lowest $4f - 5d$ excitation transition of $Ce^{3+}$, $E(Ce^{3+}, CaZnOS)$ was found to be $460 \text{ nm}$ (i.e. $21,740 \text{ cm}^{-1}$). The $5d$ level of free $Ce^{3+}$ was $49,340 \text{ cm}^{-1}$ [20]. Thus, the $f - d$ transitions energy of $Ce^{3+}$ in $CaZnOS$ was decreased by $27,600 \text{ cm}^{-1}$, compared with that of free $Ce^{3+}$ ion. It is implied that $D(Ce^{3+}, CaZnOS)$ was $27,600 \text{ cm}^{-1}$.

According to the excitation spectra with increasing $Ce^{3+}$ concentration (Fig. 9), only a slight red shift of less than $7 \text{ nm}$ can be observed, i.e. starting at $433 \text{ nm}$ for $x = 0.005$ and ending at $440 \text{ nm}$ for $x = 0.1$. This phenomenon can be ascribed to the changes of the host lattice cell parameters, similar to the situations in $CaAlSiN_3: Ce^{3+}$ [21], and $M_2Si_3N_8: Ce^{3+}$ ($M = Ca, Sr, Ba$) [22]. The slight change in the position and shape of the excitation spectra with increasing $Ce^{3+}$ concentration indicates that there are no significant changes in crystal field strength around $Ce^{3+}$. It is well known that the red shift in the emission spectra can be ascribed to the change of crystal field strength, Stokes shift, reabsorption, and so on. The red shift in the emission spectra is hardly observed with an increase in the studied $Ce^{3+}$ concentration (Fig. 9), which is similar to that observed in the excitation spectra. In our case, the changes in crystal field strength, introduced by the expansion or shrinkage of the unit cell parameters when incorporating activators into the host lattice, is thought to be less important since there is no significant change in the position and shape of excitation spectra.

Fig. 10 shows the overall emission intensity of $Ca_{1-x}Ce_xLi,ZnOS$ ($0.005 \leq x \leq 0.15$) as a function of the $Ce^{3+}$ concentration under an excitation wavelength of $460 \text{ nm}$. The maximum overall emission intensity is observed for $CaZnOS$ doped with $x = 0.01$ (i.e. $1 \text{ mol}\%$) of $Ce^{3+}$. The emission intensity declines gradually as the concentration of $Ce^{3+}$ exceeds $x = 0.01$ because of the concentration quenching effect.
From Fig. 10, it is clear that 1 mol% is the critical concentration of Ce$^{3+}$, from which a rough estimation of the critical distance ($R_c$) for energy transfer can be made using the formula proposed by Blasse [23]:

$$R_c \approx 2[3V/(4\pi x_c Z)]^{1/3} \quad (2)$$

in which $V$ is the volume of the unit cell, $x_c$ is the critical concentration of the activator ion, and $Z$ is the number of formula units per unit cell. In the CaZnOS : Ce$^{3+}$ phosphor, $Z$ equals 2, $V$ and $x_c$ are taken approximately as 139.12 Å$^3$ and 0.01, respectively. The value of $R_c$ is estimated to be about 24 Å. Since the luminescence of Ce$^{3+}$ in CaZnOS is the allowed 4f-5d electric-dipole transition, the process of energy transfer should be controlled by electric multipole-multipole interaction according to Dexter’s theory [24]. Therefore, the intensity of electric multipolar interaction can be determined from the change of the emission intensity from the emitting level which has the electric multipolar interaction. The emission intensity ($I$) per activator ion follows the equation [25]:

$$I/x = K [1 + \beta(x)Q^{2/3}]^{-1} \quad (3)$$

Where $I$ is the emission intensity, $x$ is the activator concentration, $K$ and $\beta$ are constant for the same excitation conditions for a given host crystal, and $Q$ is the function of electric multipole - multipole interaction for 6 (dipole - dipole), 8 (dipole - quadrupole), 10 (quadrupole - quadrupole), respectively. The plot of $\lg I/x$ as a function of $\lg x$ in CaZnOS : Ce$^{3+}$ is shown in the inset of Fig. 10. The dependences of the emission intensity of CaZnOS : Ce$^{3+}$ excited at 460 nm as a function of the corresponding Ce$^{3+}$ concentration is determined. It can be seen clearly that the dependence of $\lg I/x$ on $\lg x$ is linear and the slope is -1.882. The value of Q can be calculated as 5.646 which is approximately equal to 6, indicating the electric dipole - dipole interaction is the major mechanism for concentration quenching of Ce$^{3+}$.
emission in CaZnOS.

In Fig.11, the fluorescence decay curves of Ce$^{3+}$-doped CaZnOS powder samples under UV excitation were presented, together with their single exponential decay fit curves. The monitoring excitation and emission wavelengths were fixed at the effective 4$f$ - 5$d$ transitions of Ce$^{3+}$ (i.e. $\lambda_{\text{ex}} = 460$ nm and $\lambda_{\text{em}} = 505$ nm), respectively. The solid curves of these samples in the interval from 20 - 180 ns can be well fitted with a single exponential decay $I(t) = I_0 \exp(-t/\tau)$, where $I_0$ is the initial spectral intensity and $\tau$ is the decay time constant of the emission. The fitting decay time is 37.75 ns ($\chi^2 = 0.992$), 33.13 ns ($\chi^2 = 0.992$), 29.42 ns ($\chi^2 = 0.994$), corresponding to the 0.5 mol%, 1 mol%, 2 mol% Ce$^{3+}$-doped CaZnOS, respectively. The decay time of Ce$^{3+}$ in CaZnOS features the typical decay time value of Ce$^{3+}$ 5$d$ - 4$f$ emission in many other host lattices [26, 27].

The schematic configurational coordination diagram of Ce$^{3+}$ in CaZnOS deduced from the excitation and emission spectra is depicted in Fig. 12. The excitation spectrum has a peak at 460 nm, which is ascribed to the excitation from the 4$f$ ground state to the excited 5$d$ state of Ce$^{3+}$ (red arrow). There are two peaks at about 502 and 565 nm, corresponding to the transition from 5$d$ state to $^2F_{7/2}$ and $^2F_{5/2}$ of Ce$^{3+}$ (blue arrows).

Conclusions

The luminescence properties of Ce$^{3+}$ in CaZnOS were investigated. Luminescence results show that CaZnOS : Ce$^{3+}$ can be efficiently excited by blue light from 430 to 475 nm and exhibits a broad band emission in the range of 450 - 650 nm originating from the 5$d$ - 4$f$ transition of the Ce$^{3+}$ ions. The relative luminescence intensity reaches maximum at $x = 0.01$ (i.e. 1 mol%) of Ce$^{3+}$. In addition, the obvious red shift of the excitation and emission spectra with increasing Ce$^{3+}$ concentration has
not been observed. The concentration quenching takes place by the mechanism of electric dipole - electric dipole interaction.

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**References**


Figure Captions

Fig. 1 Crystal structure of CaZnOS. The projection of the CaZnOS lattice on the (001) plane (a), and diagram (b) shows the ZnS₃O tetrahedra. Zn is tetrahedrally coordinated by three S atoms and one O atom (c), Ca is distortedly octahedrally coordinated by three S and three O atoms (d).

Fig. 2 Band structure (a), partial and total density of states (b) of CaZnOS.

Fig. 3 The relationship between unit cell volume of Ca₁₋₂ₓCeₓLiₓZnOS and the Ce³⁺/Li⁺ concentration (x value).

Fig. 4 SEM images of Ca₀.⁹₈Ce₀.₁Li₀.₀₁ZnOS.

Fig. 5 TG/DTA curves of CaZnOS powder in the flowing N₂ atmosphere.

Fig. 6 Diffuse reflection spectrum of CaZnOS (The inset shows the absorption spectra as calculated by the Kubelka-Munk formula).

Fig. 7 Typical excitation and emission spectra of Ca₀.⁹₈Ce₀.₁Li₀.₀₁ZnOS.

Fig. 8 The normalized X-ray excited luminescence spectra of Ca₁₋₂ₓCeₓLiₓZnOS (solid line), and Bi₄Ge₃O₁₂ (BGO) (dash line) measured at room temperature.

Fig. 9 Excitation and emission spectra of Ca₁₋₂ₓCeₓLiₓZnOS (0.005 ≤ x ≤ 0.15).

Fig. 10 The relative integrated Ce³⁺ emission intensity under 460 nm excitation as a function of x in Ca₁₋₂ₓCeₓLiₓZnOS (0.005 ≤ x ≤ 0.15). The inset shows the plot of lg (I/I₀) as a function of lg x in Ca₁₋₂ₓCeₓLiₓZnOS (0.005 ≤ x ≤ 0.15) (λex = 460 nm).

Fig. 11 Fluorescence decay curves of Ce³⁺ 5d - 4f emission (λem = 505 nm) for Ca₁₋₂ₓCeₓLiₓZnOS (a: x = 0.005, b: x=0.01, c: x=0.02) at room temperature.

Fig. 12 Schematic configurational coordination diagram deduced from the luminescence spectra of CaZnOS: Ce³⁺, Li⁺.
Table Captions

Table 1. Characteristics of Ce$^{3+}$-doped CaZnOS as compared to typical Ce$^{3+}$-doped (oxy)sulfide phosphors at room temperature.
High lights:

1. The direct band gap of CaZnOS is calculated to be 2.4 eV using the CASTEP mode.
2. CaZnOS : Ce$^{3+}$ exhibits a broad band emission in the wavelength range of 450 - 650 nm.
3. The mechanism of luminescence and concentration quenching of Ce$^{3+}$ have been investigated in detail.
Table 1. Characteristics of Ce$^{3+}$-doped CaZnOS as compared to typical Ce$^{3+}$-doped (oxy)sulfide phosphors at room temperature.

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>CaS:Ce$^{3+}$</th>
<th>SrS:Ce$^{3+}$</th>
<th>ZnS:Ce$^{3+}$</th>
<th>Ba$_2$ZnS$_3$:Ce$^{3+}$</th>
<th>RbLuS$_2$:Ce$^{3+}$</th>
<th>Y$_2$O$_2$S:Ce$^{3+}$</th>
<th>Lu$_2$O$_2$S:Ce$^{3+}$</th>
<th>CaZnOS:Ce$^{3+}$</th>
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<tbody>
<tr>
<td>Crystal system</td>
<td>Cubic ($Fm\bar{3}m$)</td>
<td>Cubic ($Fm\bar{3}m$)</td>
<td>Hexagonal ($P6\bar{3}mc$)</td>
<td>Orthorhombic ($Pnma$)</td>
<td>Rhombohedral ($R\bar{3}m$)</td>
<td>Hexagonal ($P\bar{3}m1$)</td>
<td>Hexagonal ($P\bar{3}m1$)</td>
<td>Hexagonal ($P6\bar{3}mc$)</td>
</tr>
<tr>
<td>Host absorption edge (nm)</td>
<td>280</td>
<td>290</td>
<td>338</td>
<td>370</td>
<td>310</td>
<td>260</td>
<td>235</td>
<td>320</td>
</tr>
<tr>
<td>Excitation bands (nm)</td>
<td>280 / 450</td>
<td>274 / 433</td>
<td>316 / 325 / 330</td>
<td>430</td>
<td>490</td>
<td>460</td>
<td>460</td>
<td>460</td>
</tr>
<tr>
<td>Emission bands (nm)</td>
<td>515 / 570</td>
<td>482 / 535</td>
<td>478 / 530</td>
<td>555 / 620</td>
<td>578 / 660</td>
<td>577 / 652</td>
<td>619 / 706</td>
<td>502 / 565</td>
</tr>
<tr>
<td>FWHM (nm)</td>
<td>45 / 70</td>
<td>50 / 70</td>
<td>40 / 60</td>
<td>80 / 70</td>
<td>80 / 85</td>
<td>110 / 205</td>
<td>100 / 155</td>
<td>60 / 75</td>
</tr>
<tr>
<td>Ref</td>
<td>[1]</td>
<td>[1]</td>
<td>[14]</td>
<td>[15, 16]</td>
<td>[17]</td>
<td>[18]</td>
<td>[18, 19]</td>
<td>This work</td>
</tr>
</tbody>
</table>
Figure 9

\[ \lambda_{em} = 505 \text{ nm} \]

\[ \lambda_{ex} = 460 \text{ nm} \]

**Ca\textsubscript{1-2x}Ce\textsubscript{x}Li\textsubscript{x}ZnOS**
Figure 10
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Relative PL intensity (%)

$\text{Ca}_{1-2x} \text{Ce}_x \text{Li}_x \text{ZnOS}$

$\lambda_{\text{ex}} = 460 \text{ nm}$
Figure 11

(a) 

$\tau = 34.75 \text{ ns (} \chi^2 = 0.991 \text{)}$

- Exp.
- Fit.

Instrumental response

$\lambda_{ex} = 460 \text{ nm}$

(b) 

$\tau = 33.13 \text{ ns (} \chi^2 = 0.992 \text{)}$

- Exp.
- Fit.

Instrumental response

$\lambda_{ex} = 460 \text{ nm}$

(c) 

$\tau = 29.42 \text{ ns (} \chi^2 = 0.994 \text{)}$

- Exp.
- Fit.

Instrumental response

$\lambda_{ex} = 460 \text{ nm}$

Time (ns)
Figure 12

- $\lambda_{em} = 502$ nm
- $\lambda_{ex} = 460$ nm
- $5d^1$
- $502$ nm
- $565$ nm
- $2F_{7/2}$
- $2F_{5/2}$

$10^3$ cm$^{-1}$ vs. $R$