Synthesis and Optical Characterization of Oxygen-Incorporated ZnS$_{(1-x)}$O$_x$ for UV–Visible Color Palette Light-Emission Matter

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**ABSTRACT:** Single crystals of oxygen-incorporated ZnS (i.e., ZnS$_{(1-x)}$O$_x$ series) are environment-friendly wide-band-gap semiconductors available for light-emitting devices and solar cell use. The series of materials has considerable potential for use in visible ultraviolet areas with flexibility for palette emissions. In this study, we grow oxygen-incorporated ZnS series crystals by chemical vapor transport method with iodine (I$_2$) as the transport agent. Three different oxygen-incorporated crystals of undoped ZnS, ZnS$_{0.94}$O$_{0.06}$, and ZnS$_{0.88}$O$_{0.12}$ are studied. Through structural studies, ZnS doped with oxygen crystallizes in the main sphalerite phase and a little wurtzite structure. The lattice constants of the major cubic phase are determined to be $a = 5.43$ Å (ZnS), $5.41$ Å (ZnS$_{0.94}$O$_{0.06}$), and $5.39$ Å (ZnS$_{0.88}$O$_{0.12}$). Three band-edge excitonic transitions are simultaneously detected by thermorefraction measurement for the ZnS, ZnS$_{0.94}$O$_{0.06}$ and ZnS$_{0.88}$O$_{0.12}$ series samples. The energy positions of the band-edge transitions decrease as the oxygen content increases in the ZnS$_{(1-x)}$O$_x$ series. Defect-state and surface-state emissions, including sulfur vacancy, oxygen vacancy, zinc interstitial, and so forth, can emit approximately full-color spectra from the near band edge of the ZnS$_{(1-x)}$O$_x$ series crystals. With adjusting the oxygen content, the ZnS$_{(1-x)}$O$_x$ can be a series of color-palette luminescence matters that applied for fluorescent display or light-emitting device.

**INTRODUCTION**

In recent years, semiconductor optoelectronic and photovoltaic components have developed rapidly. People have growing demand for energy-saved lighting. The solid-state brightness sources have become next-generation illuminated and display light sources in daily life everywhere. To achieve that, light-emitting diodes and phosphors have attracted both science attention and commercial feasibility because their potential wide-scale use in, for example, architectural lighting, decorative lighting, flashlight, backlighting, fluorescent lamp, field emission display, plasma display panel, high-energy detector, and so forth. In addition, the application of biological light-emission devices and medical sterilization lamp development have also been concerned recently. Groups II–IV zinc sulfide (ZnS) is a direct semiconductor with band gap of $\sim 3.7$ eV$^{7-11}$, which is larger than that of ZnO ($\sim 3.3$ eV).$^{1,13}$ ZnS has generally two polymorphic phases, cubic (zinc-blende (ZB)) and hexagonal (wurtzite (W)), in the crystals.$^{14}$ Similar to zinc oxide, ZnS can easily form structural defects, such as sulfur vacancies, twins, stacking faults, and so forth, in the crystal for emitting defect lights. For the manufacture of II–VI solid-state lighting devices, defect emissions may play an important role in visible radiation for the human eye. For example, ZnO can emit green and red lights caused by oxygen vacancy and zinc defect. Nevertheless, ZnO lacks blue and purple emissions to achieve full-color lighting because its lower energy gap will result in longer-wavelength defect emissions. To attain blue and purple emissions, it is necessary to develop the series of ZnS$_{(1-x)}$O$_x$ related mixed compounds for widening and tuning band gap. However, such kinds of materials information for the ZnS$_{(1-x)}$O$_x$ series are still very rare up to date. One report claimed that the ZnS nanoparticles annealed over 400 °C will show ZnO structure in X-ray diffraction (XRD) measurement.$^{22}$ Nevertheless, no further optical measurement result was reported.

In this study, we employ chemical vapor transport (CVT) method to grow ZnS$_{(1-x)}$O$_x$ series crystals of undoped ZnS, ZnS$_{0.94}$O$_{0.06}$, and ZnS$_{0.88}$O$_{0.12}$ using iodine (I$_2$) as the transport agent. X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED) pattern, and energy-dispersive X-ray (EDX) spectroscopic analyses were used to characterize the structural phase and stoichiometry of the as-grown ZnS$_{(1-x)}$O$_x$ series crystals. The oxygen incorporated into ZnS will render the crystal mainly cubic zinc-blende (sphalerite) phase and a little wurtzite structure. Lattice constants of the ZnS$_{(1-x)}$O$_x$ series crystals of cubic phase were determined. The cubic lattice constant decreases with the increase in the oxygen content of the ZnS$_{(1-x)}$O$_x$ series. Raman scattering spectroscopy experiments of the ZnS, ZnS$_{0.94}$O$_{0.06}$ and ZnS$_{0.88}$O$_{0.12}$ crystals were performed at 300 and 4 K. The room-temperature Raman spectra show mainly the first-order longitudinal optical (LO)

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phonon near ~351 cm$^{-1}$ and the transverse optical (TO) phonon at ~272 cm$^{-1}$ for all of the as-grown undoped and oxygen-doped ZnS crystals. It is the evidence that the ZnS$_{1-x}$O$_x$ series crystals are crystallized in the major zinc-blende phase. In particular, the surface optical (SO) phonon for the wurtzite phase$^{16}$ was also detected in the Raman spectra of the oxygen-incorporated ZnS$_{0.94}$O$_{0.06}$ and ZnS$_{0.88}$O$_{0.12}$ crystals. They are crystallized in major cubic and minor hexagonal mixed phases. With the temperature down to 4 K, the intensities of the LO and TO peaks greatly enhanced and peak energies also blue-shifted owing to the temperature effect in the ZnS$_{(1-x)}$O$_x$ lattice. The transmittance absorption edge of the ZnS$_{(1-x)}$O$_x$ series was also investigated by transmission measurement. The band edge is red-shifted from 3.69 eV (ZnS) and 3.65 eV (ZnS$_{0.94}$O$_{0.06}$) to 3.61 eV (ZnS$_{0.88}$O$_{0.12}$) owing to the increase in the oxygen content of the ZnS$_{(1-x)}$O$_x$ series. For more accurate study of the band-edge transitions (excitons), thermoreflectance (TR) and photoluminescence (PL) measurements were implemented. All of the band-edge or valence-band-splitting transitions $E_A$, $E_B$, and $E_C$ are clearly detected in the TR spectra of the ZnS$_{(1-x)}$O$_x$ series crystals. The PL results obviously show free-exciton (Fx) emission peak in each of the ZnS$_{(1-x)}$O$_x$ series crystals. The occurrence of PL band-edge emission verified good crystalline quality of the ZnS$_{(1-x)}$O$_x$ series crystals. At low temperatures, we can also observe strong visible defect lights from green and blue to purple through the ZnS$_{(1-x)}$O$_x$ series crystals. It provides the potential for the ZnS$_{(1-x)}$O$_x$ series of solids as a visible color-palette material for use in future full-color display.

## RESULTS AND DISCUSSION

Figure 1 shows the morphology and size of the as-grown bulk crystals of the ZnS$_{(1-x)}$O$_x$ series: (a) $x = 0$, (b) $x = 0.06$, and (c) $x = 0.12$. The pure ZnS crystal in Figure 1a essentially displays transparent and thicker outline. The ZnS$_{0.94}$O$_{0.06}$ crystal in Figure 1b shows a light yellowish rectangular shape. The ZnS$_{0.88}$O$_{0.12}$ crystal of the highest oxygen content shows a white crystal of hexagonal shape displayed in Figure 1c. The light yellow style of the transparent ZnS$_{(1-x)}$O$_x$ crystal indicates the existence of visible defect centers consisted in the as-grown crystals, whereas the hexagonal shape outline of the ZnS$_{0.88}$O$_{0.12}$ may be owing to the presence of wurtzite {0001} or zinc-blende {111} plane to the crystal. The size of the crystals in Figure 1a–c is in the order of several millimeters. To evaluate the stoichiometric content of the oxygen-incorporated ZnS, EDX measurements were implemented. Figure 1d–f shows the EDX spectral analysis of undoped ZnS, ZnS$_{0.94}$O$_{0.06}$ and ZnS$_{0.88}$O$_{0.12}$, respectively, and the corresponding as-grown crystals are shown in Figure 1a–c. For pure ZnS crystal, the atomic ratio of Zn to S is estimated to be 50.25:49.75 based on the EDX spectrum in Figure 1d. The result indicated that a little chalcogen deficiency existed in the as-grown ZnS crystal. For the oxygen-incorporated samples, the atomic ratio of Zn to S to O is $50.43:46.60:2.97$ for the ZnS$_{0.94}$O$_{0.06}$ crystal (i.e., O/(O + S) $\approx$ 6%). As for ZnS$_{0.88}$O$_{0.12}$, the stoichiometric ratio of Zn to S to O is $50.38:43.67:5.95$ (i.e., O/(O + S) $\approx$ 12%), as shown in Figure 1f. The oxygen peak (O) of the EDX spectrum in Figure 1f (i.e., ZnS$_{0.88}$O$_{0.12}$) also shows higher intensity than that of ZnS$_{0.94}$O$_{0.06}$ in Figure 1e. Within standard errors, the stoichiometric content of the oxygen-incorporated ZnS is hence defined as ZnS$_{0.94}$O$_{0.06}$ and ZnS$_{0.88}$O$_{0.12}$, as referring to Figure 1.

For structural analysis, the obtained transmission electron microscopy data of the ZnS$_{(1-x)}$O$_x$ samples are processed and converted using DigitalMicrograph software (version 3.7.4; Gatan Inc.). Figure 2a,d,g shows the SEAD pattern, fast Fourier
transform (FFT), and HRTEM image of undoped ZnS, Figure 2b,e,h are those of ZnS$_{0.94}$O$_{0.06}$, and Figure 2c,f,i are those of ZnS$_{0.88}$O$_{0.12}$, respectively. The zone axis of the electron beam was along the [222] direction. The SEAD pattern of each sample clearly reveals hexagon-shape dotted spots as the planes of (220), (202), (022), (220), and (202) in Figure 2. The FFT result (converted from the HRTEM image of each sample) also shows comparable dotted pattern to that of the corresponding SEAD pattern. This result reveals good crystalline quality of the as-grown ZnS$_{(1-x)}$O$_{x}$ series obtained by CVT. The cubic lattice constant $a$ of ZnS, ZnS$_{0.94}$O$_{0.06}$, and ZnS$_{0.88}$O$_{0.12}$ can be estimated from their corresponding HRTEM images (i.e., by atomic spacing) and verified by their SEAD patterns (i.e., using the dotted distances). The values are determined to be $a = 5.43$ Å for ZnS, 5.41 Å for ZnS$_{0.94}$O$_{0.06}$, and 5.39 Å for ZnS$_{0.88}$O$_{0.12}$. With the increase in oxygen content, the lattice constant decreases in the ZnS$_{(1-x)}$O$_{x}$ series.

Figure 2a shows the X-ray diffraction (XRD) data, which are employed to identify the structure and crystalline phase of the ZnS$_{(1-x)}$O$_{x}$ series crystals. For pure ZnS, the diffraction peaks can be indexed as (111), (200), (220), (311), (222), (400), (331), (420), and (422) planes for zinc-blende (ZB) ZnS phase. The XRD pattern of ZnS matched well with that of the JCPDS No. 772100 (marked as the top green line in Figure 3a) for a cubic ZnS with zinc-blende structure. In addition, the XRD results of ZnS$_{0.94}$O$_{0.06}$ and ZnS$_{0.88}$O$_{0.12}$ indicated that
most of the crystal structures belong to ZB, whereas three additional peaks of W(101) at \( \approx 26.69^\circ \), W(002) at \( \approx 28.38^\circ \), and W(100) at \( \approx 30.68^\circ \) can be detected by the oxygen-contained samples of ZnS\(_{0.94}\)O\(_{0.06}\) and ZnS\(_{0.88}\)O\(_{0.12}\). The diffraction peaks are similar to those of the wurtzite (W) phase compound as referred to JCPDS No. 751534. Shown in Figure 3b is the comparison of the ZB(111) peak positions for the three compounds derived from Figure 3a. The diffraction angle of ZB(111) plane moves to higher value with respect to the increase of the oxygen content in the ZnS\(_{1-x}\)O\(_x\) series. The (111) peak positions are \( \theta = 28.43^\circ \) for ZnS, 28.54° for ZnS\(_{0.94}\)O\(_{0.06}\) and 28.63° for ZnS\(_{0.88}\)O\(_{0.12}\). It means lattice shrinkage with replacing sulfur atom with oxygen in the ZnS unit cell. The cubic lattice constant can be calculated to be \( a \approx 5.43\ \text{Å} \) for ZnS, 5.41 Å for ZnS\(_{0.94}\)O\(_{0.06}\) and 5.39 Å for ZnS\(_{0.88}\)O\(_{0.12}\), similar to those estimated in previous HRTEM results. It should be noticed that the ZB(111) peak of the ZnS\(_{1-x}\)O\(_x\) series in Figure 3 has nearly the same angle as that of W(002) in the wurtzite phase. In fact, the band structure and optical property of ZB\{111\} and W\{0001\} were claimed to be the same atomic arrangement and similar energy states in the II–VI compounds. The resemblance of material property between ZB\{111\} and W\{0001\} planes is maybe the turning point for phase transition from zinc-blende to wurtzite in growing the oxygen-incorporated ZnS.

Figure 4a shows the experimental Raman spectra of the ZnS\(_{1-x}\)O\(_x\) series crystals at 300 K. One ZnO bulk crystal grown by CVT was also included in Figure 4a for comparison. For undoped ZnS, a lot of peak modes have been detected at 300 K, which are all indexed to the cubic phase of zinc-blende ZnS. For the phase change of the ZnS\(_{1-x}\)O\(_x\) series, low-temperature Raman measurement at 4 K was also implemented. Figure 4c shows the Raman spectra of the ZnS\(_{1-x}\)O\(_x\) series crystals also implies that a little wurtzite ZnO is also incorporated into the formation of the ZnS\(_{1-x}\)O\(_x\) ternary compounds. The enhancement of peak intensity is due to the reduction of thermal broadening effect to the Raman peak features. The inset in Figure 4c clearly shows that the vibration energies of the LO, TO, and SO modes are reduced with increasing oxygen content in the ZnS\(_{1-x}\)O\(_x\) series. The values of Raman shift (LO, TO, and SO) versus oxygen content for the three samples at 4 K are also depicted in Figure 4d. The vibration energy of Raman mode also shows decrease with increasing oxygen content in the ZnS\(_{1-x}\)O\(_x\) series. For the phase change of the ZnS\(_{1-x}\)O\(_x\) crystal, we can also observe that the intensities of the TO and LO modes in the cubic ZnS (see inset in Figure 4c) decrease with increasing oxygen content. The LO and TO phonon peaks of the zinc sulfide will even completely disappear when the crystals are fully converted into zinc oxide, as shown in the lower part of the spectra in Figure 4a at 300 K. However, the appearance of the SO(W) peak in the ZnS\(_{0.94}\)O\(_{0.06}\) and ZnS\(_{0.88}\)O\(_{0.12}\) crystals also implies that a little wurtzite ZnO is also incorporated into the formation of the ZnS\(_{1-x}\)O\(_x\) ternary compounds.

To determine the band gap of the ZnS\(_{1-x}\)O\(_x\) series, optical transmission measurement has been implemented. It is a simple way to observe direct band edge of the mixed compounds. Figure 5 shows the transmittance spectra of ZnS\(_{0.88}\)O\(_{0.12}\), ZnS\(_{0.94}\)O\(_{0.06}\) and pure ZnS. The dashed lines are the
experimental data at low temperature (40 K), and the solid curves are those measured at room temperature. The energy value of the bottom edge in each transmittance spectrum is 3.69 eV for ZnS, 3.65 eV for ZnS$_{0.94}$O$_{0.06}$, and 3.61 eV for ZnS$_{0.88}$O$_{0.12}$ at 300 K. They are increased (blue-shifted) to 3.81 eV (ZnS), 3.76 eV (ZnS$_{0.94}$O$_{0.06}$), and 3.72 eV (ZnS$_{0.88}$O$_{0.12}$) at 40 K following a general semiconductor trend. The smooth variation of energy values in the bottom edge of the transmittance spectra (at 40 and 300 K) indicates the formation of ternary ZnS$_{0.94}$O$_{0.06}$ and ZnS$_{0.88}$O$_{0.12}$ compounds when the crystals were grown. This situation is similar to the gradual lattice-constant change measured by XRD and HRTEM in the cubic ZnS$_{(1-x)}$O$_x$ series of different oxygen contents.

To evaluate band-edge structure and excitonic transitions of the ZnS$_{(1-x)}$O$_x$ series crystals, TR measurements were carried out. Figure 6a,b shows the experimental TR spectra of ZnS, ZnS$_{0.94}$O$_{0.06}$, and ZnS$_{0.88}$O$_{0.12}$ at 300 and 40 K, respectively, near band edge. The experiments were done in the energy range of 3–4.3 eV in vacuum. TR has been proven to be a very powerful tool for the determination of direct interband transitions in semiconductor using a derivative line-shape.
The derivative line shape of TR feature suppresses unintentional spectral background and emphasizes the energy location at exact interband transition. As shown in Figure 6, the dashed lines are the experimental data and solid curves are the first-derivative Lorentzian line-shape fits obtained using an equation appropriate for band-edge excitonic transition expressed as:

$$\frac{\Delta R}{R} = \text{Re} \left\{ \sum_{i} A_i^\text{ex} e^{i\phi_i^\text{ex}} (E - E_i^\text{ex} + j\Gamma_i^\text{ex})^{-2} \right\}$$  \hspace{1cm} (1)$$

where $i$ is the respective transition, $A_i^\text{ex}$ and $\phi_i^\text{ex}$ are the amplitude and phase, respectively, and $E_i^\text{ex}$ and $\Gamma_i^\text{ex}$ are the energy and broadening parameters of the interband excitonic transition, respectively. The best fit by using eq 1 can be shown by the solid line on each of the TR spectra because the band-edge transition energies of the cubic {111} plane are similar to those of the wurtzite {0001} face to show three features of $E_A$, $E_B$, and $E_C$ excitons. The result is caused by crystal-field and spin–orbital coupling in the valence band of the II–VI compounds. The PL experiment is an effective tool for the evaluation of band-edge and defect emissions in a luminescent material. For ZnS$_{1-x}$O$_x$-related compounds, it is known that the appearance of band-edge emission is a high-quality index for the ZnS crystalline state. In combination with both TR and PL techniques, we can determine the energy positions of band-edge transition $E_A$ and free-exciton Fx emission. Figure 7a shows, from top to bottom, the TR and PL spectra of ZnS$_{0.88}O_{0.12}$ and ZnS$_{0.94}O_{0.06}$ and ZnS at 40 K. The PL band-edge emissions of ZnS$_{0.88}O_{0.12}$ include Fx and bound exciton complexes (BECs) at 3.7–3.8 eV. The BECs may contain biexciton XX (surface exciton SX), neutral-donor-bound exciton D$_0^X$, and neutral-acceptor-bound exciton A$_0^X$ that had ever been detected by previously pure ZnS. For the free-exciton emission Fx, the peak values are 3.784 eV for ZnS$_{0.88}O_{0.12}$, 3.787 eV for ZnS$_{0.94}O_{0.06}$, and 3.796 eV for ZnS. The appearance of Fx emission indicates high crystalline quality of the as-grown ZnS$_{1-x}$O$_x$ series crystals. For each of the ZnS$_{1-x}$O$_x$ compounds in Figure 7a, the energy positions of band-edge transition $E_A$ (in TR) and free exciton Fx (in PL) are similar, whereas the energies of $E_B$ and $E_C$ are larger than $E_A$. The $E_B$ and $E_C$ transitions are originated from valence-band splitting as indicated in the representative band-edge scheme in Figure 7c. The energy values of $E_A$, $E_B$, and $E_C$ obtained by TR using the spectral analysis of eq 1 are shown in Figure 7b. The emission energies of Fx of the ZnS$_{1-x}$O$_x$ series obtained by PL are also included for comparison. In general, the band-edge transition energy of $E_A$ in the wurtzite {0001} plane is higher than that in the cubic (zinc-blende) {100} plane due to the larger crystal-field and spin–orbital coupling. Because of the similarity of atomic arrangement in ZB{111} and W{0001}, the transition energy $E_A$ of ZB{111} is similar to that of W{0001}.

![Figure 6](image-url)
Figure 7. (a) TR and PL spectra of the ZnS(1−x)Ox series crystals at 40 K. The energy positions of $E_A$ and $F_X$ are indicated with arrows. The HRTEM image of ZB–ZnS in the inset shows that the ZnS simultaneously consisted of ZB{111} and ZB{100} planes caused by stacking fault. (b) Excitonic transition energies ($E_A$, $E_B$, and $E_C$) vs sulfur content in the ZnS(1−x)Ox series. (c) Schematic diagram of band-edge structure for ZB{111} or wurtzite {0001} in the ZnS(1−x)Ox series. (d) Energy separations of $E_C - E_B$ and $E_B - E_A$ vs sulfur composition change in the ZnS(1−x)Ox series.

Figure 8. Wide-energy-range PL spectra and the corresponding visible-light images of ZnS(1−x)Ox caused by defect and band-edge emissions at 10 K. The sample emission lights clearly show purple, blue, and green colors that are available for future color-palette emission device’s fabrication.
but higher than that of ZB\{100\}. That is why, the ZB–ZnS simultaneously having the mixed \{111\} and \{100\} planes will widen (broaden) the \(E_A\) feature of TR, as shown in Figure 7a. The HRTEM image of ZnS shown in the inset of Figure 7a clearly demonstrates that the ZnS has the \{111\} and \{100\} mixed planes (i.e., existence of stacking fault).\(^{30}\) For ZnS, the PL emission of \(F_x\) is coming from the lowest-energy states’ recombination (i.e., from \{100\} plane), whereas the TR optical transition \(E_A\) may originate from the higher-energy states’ absorption (i.e., from the \{111\} plane). The energy separation of \(E_A - F_x\) in ZnS is therefore larger than that in ZnS\(0.94\)\(O_{0.06}\) and ZnS\(0.88\)\(O_{0.12}\) as shown in Figure 7b. For the highest oxygen-contained sample ZnS\(0.88\)\(O_{0.12}\), the wurtzite-phase composition is the largest in the ZnS\(1-x\)O\(_x\) series. The energies of \(E_A\) and \(F_x\) are nearly the same as shown in Figure 7b. The TR and PL spectra of ZnS\(0.88\)\(O_{0.12}\) in Figure 7a even show additional spectral features from wurtzite ZnO at \(\sim 3.4\) eV. Figure 7d shows the energy separations of \(E_B - E_A\) and \(E_C - E_B\) (\(E_{BC}\)) of the ZnS\(1-x\)O\(_x\) series caused by valence-band splitting from crystal-field and spin–orbital coupling.\(^{31}\) The results are obtained by TR measurements. For ZnS, the values of \(E_{AB}\) and \(E_{BC}\) are \(4\) and \(80\) meV in Figure 7d. With increased oxygen content, the energy separations of \(E_{AB}\) and \(E_{BC}\) are gradually reduced in the ZnS\(1-x\)O\(_x\) series. The reduction is maybe owing to the decrease of crystal field in the crystal environment of the oxygen-incorporated ZnS.

The as-grown ZnS\(1-x\)O\(_x\) series compounds have a band gap larger than that of ZnO (see the PL and TR result of ZnS\(0.88\)\(O_{0.12}\) in Figure 7a). It is reasonable that the defect emissions of the ZnS\(1-x\)O\(_x\) series can have a higher energy value than ZnO. It can be expected that the ZnS\(1-x\)O\(_x\) compound emits blue defect light for overcoming the drawback of ZnO defect emission (i.e., energy lower than green emission). Figure 8 shows, from left to right, the PL spectra and emission colors (image) of the ZnS, ZnS\(0.94\)\(O_{0.06}\) and ZnS\(0.88\)\(O_{0.12}\) samples at low temperature for further demonstrating color-palette light-emission capability. It is noticed that the color emissions can also be observed at room temperature, but they are weakened owing to thermal effect. We have therefore taken color images at low temperature due to the stronger PL intensity. As shown in the upper part of Figure 8, all of the full-PL spectra emit not only the defect emission but also the band-edge emission to show high crystalline quality of the ZnS\(1-x\)O\(_x\) series crystals. For ZnS, strong purple light is emitted. A violet luminescence peak appeared at 375 nm (3.31 eV), which is an electronic transition from conduction band to the Zn interstitial defect (\(V_{Zn^+}\) responsible for an acceptor level),\(^{32}\) as shown in the inset in Figure 8, for ZnS. A strong blue light can be emitted from the ZnS\(0.88\)\(O_{0.12}\) sample, as displayed in the middle-part image of Figure 8. Radiative recombination of electrons from sulfur vacancy (\(V_S\)) to holes in valence band leads to evolution of blue-component PL peak that positioned at around 430 nm (2.88 eV).\(^{33}\) For green-light emission of the ZnS\(0.88\)\(O_{0.12}\) sample (see right-part image), an emission band around 500 nm (2.48 eV) is arisen when the photogenerated holes were trapped in the deep level by oxygen vacancy (\(V_{O^\cdot}\)).\(^{34}\) The electron–hole recombination will occur when an electron in a shallow level below conduction band recombines with a hole in the \(V_{O^\cdot}\) level.\(^{35}\) The higher-energy colorful emissions of the ZnS\(1-x\)O\(_x\) series of green, blue, and purple together with the intrinsic green, orange, and red defect emissions in ZnO will render a full-color light emission from \(\sim 380\) to \(\sim 620\) nm. The ZnS\(1-x\)O\(_x\) series compounds may hence derive the advantage for application in visible-light fluorescent material, light-emitting device, or display component.

### CONCLUSIONS

High-quality oxygen-incorporated ZnS\((1-x)O_x\) with different oxygen contents of \(x = 0, 0.06\), and 0.12 have been synthesized and grown by CVT method. The EDX measurement verified stoichiometric content of the ZnS\(1-x)O_x\) series crystals. The analyses of XRD, HRTEM, SAED, FFT, and Raman measurements reveal that the as-grown ZnS\(1-x)O_x\) series crystals possess high crystalline quality and that a main zinc-blende phase was present in the pure ZnS, whereas the mixed phase of major zinc-blende and minor wurtzite existed in the oxygen-incorporated ZnS\(0.94)O_{0.06}\) and ZnS\(0.88)O_{0.12}\) samples. The cubic lattice constants were determined to be \(a = 5.43\) Å (ZnS), 5.41 Å (ZnS\(0.94)O_{0.06}\)), and 5.39 Å (ZnS\(0.88)O_{0.12}\)). With increasing the oxygen content, the lattice constant was decreased in the crystal series. Optical measurements of transmission, TR, and PL are carried out to characterize the band-edge structure and defect emissions of the ZnS\(1-x)O_x\) series crystals. The appearance of band-edge excitonic emissions in the ZnS, ZnS\(0.94)O_{0.06}\) and ZnS\(0.88)O_{0.12}\) samples reflects high quality of the crystals. Owing to the similarities in the atomic arrangement and optical properties of ZB\{111\} and W\{0001\} planes, the \(E_A, E_B,\) and \(E_C\) excitonic transitions caused by crystal-field and spin–orbital coupling can be simultaneously detected by the ZnS, ZnS\(0.94)O_{0.06}\) and ZnS\(0.88)O_{0.12}\) samples using TR experiment. The energy of \(E_B\) is close to that of free-exciton emission Fx detected by PL. Because of the coexistence of ZB\{111\} and ZB\{100\} planes in the ZnS by stacking fault, the energy of free-exciton emission Fx by PL (dominated by lower-energy \{100\} plane) is lower than that of \(E_A\) by TR (dominated by higher-energy \{111\} plane). The energies of Fx and \(E_A\) are comparable for the wurtzite ZnS\(0.94)O_{0.06}\) of highest oxygen content. The energy separations of valence-band splitting between \(E_{AB}\) and \(E_{BC}\) transitions show decrease with increasing oxygen content owing to the reduction of crystal field. At low temperature, strong blue light by sulfur vacancy to valence band (\(\sim 430\) nm) in ZnS\(0.94)O_{0.06}\) and enhanced purple light by conduction band to the Zn interstitial (\(\sim 375\) nm) in ZnS are emitted from the samples. The blue-violet defect emission of ZnS\(1-x)O_x\) will amend ZnO that lacks higher-energy visible-light defects. The ZnS\(1-x)O_x\) series of crystals is highly desirable for use in a light-emitting or display assembly of a color-palette-emitting device.

### EXPERIMENTAL SECTION

#### Crystal Growth and Structural Characterization

Single crystals of ZnS\((1-x)O_x\) series with various oxygen content of \(x = 0, 0.06,\) and 0.12 were grown by CVT method\(^{17}\) using I\(_2\) as the transport agent. Such kind of CVT growth was performed in a horizontal three-zone tube furnace with a temperature gradient setting as 950 °C \(\leftarrow 1000\) °C \(\rightarrow 950\) °C\(^{18}\) for simultaneously growing two sealed quartz ampoules (22 mm o.d., 17 mm i.d., 20 cm length).\(^{19}\) The temperature gradient was about \(2.5\) °C/cm to the quartz ampoules. Prior to the crystal growth, pure elements of Zn (99.99% pure) and S (99.999% pure), ZnO powder (99.999% pure), and a small amount of transport agent were put into the quartz ampoule, which was then cooled with liquid nitrogen, evacuated to \(\sim 10^{-6}\) Torr, and sealed. The ratio and weights of Zn, S, and oxygen must be...
measured in proper stoichiometric composition. For growing 10 g of ZnS\(_{0.94}O_{0.06}\), the weights of the starting elements must be Zn = 6.776 g, S = 3.123 g, and ZnO > 0.056 g to achieve the desired stoichiometry of ZnS\(_{0.94}O_{0.06}\). The growth kinetics of the CVT with the auxiliary of transport agent can be described as \(iA(t) + jB(t) \rightarrow kC(t)\), where A is the synthesized material, B is the transport agent, and C is the gaseous synthesized compound (A, C = ZnS\(_{1-x}\)O\(_x\), B = Zn). The formation of ZnS must undertake the reversed reaction of the above equation, and keeps 480 h for growing large single crystals. For X-ray transmission or reflection (XRD) measurements, Cu K\alpha line (\(\lambda = 1.5418 \) Å) was the X-ray light source and a silicon standard used for experimental calibration. The structures and stoichiometry of the ZnS\(_{1-x}\)O\(_x\) series crystals were characterized by HRTEM, XRD, and EDX techniques.

**Optical Measurements.** Optical transmission and TR measurements were carried out from 3 to 4.2 eV. A 150 W xenon-arc lamp acted as the white-light source. The light was dispersed and filtered by a photon technology international 0.2-m monochromator to provide the monochromatic light. A 1200 grooves/mm ruled grating acted as the dispersion unit. The transmission or reflected light from the sample (>80 μm in thickness) was detected by a photomultiplier tube and signal was recorded via an EG&G model 7265 dual-phase lock-in amplifier. The μ-Raman measurements of the ZnS\(_{1-x}\)O\(_x\) series crystal were carried out using a RAMAker integrated micro-Raman-PL identified system (Protrustech Co. Ltd., Taiwan) equipped with one 532 nm solid-state diode-pumped laser as the excitation source. A light-guiding microscope was equipped with an Olympus objective lens (50×, working distance ~ 8 mm) for interconnection and coupling the ZnS\(_{1-x}\)O\(_x\) sample, incident light, scattered light, and the charge-coupled device (CCD) spectrometer. A Janis liquid-helium open-cycle cryostat with thermometer controller assists low-temperature measurement of the oxygen-incorporated ZnS crystals. The PL measurements were implemented in a spectral measurement system, where a TRIRAX 550 imaging spectrometer equipped with a 1200 grooves/mm grating acting as the dispersion unit. The CCD array detection was employed in the PL measurement. The pumping light source was a Q-switched diode-pumped solid-state laser of \(\lambda = 266\) nm, and the spot size reduced to ~100 μm. A set of neutral-density filters changed the sample, incident light, scattered light, and the charge-coupled device (CCD) spectrometer. A Janis liquid-helium open-cycle cryostat with thermometer controller assists low-temperature measurement of the oxygen-incorporated ZnS crystals.

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**References**

(1) Nizamoglu, S.; Ozel, T.; Sari, E.; Demir, H. V. White Light Generation using CdSe/ZnS Core–Shell Nanocrystals Hybridized with InGaN/GaN Light Emitting Diodes. *Nanotechnology* 2007, 18, No. 065709.

(2) Era, K.; Shionoya, S.; Washizawa, Y. Mechanism of Broad-Band Luminescences in ZnS Phosphors—I. Spectrum Shift During Decay and with Excitation Intensity. *J. Phys. Chem. Solids* 1968, 29, 1827–1841.

(3) Sebastian, J. S.; Swart, H. C.; Trottier, T. A.; Jones, S. L.; Holloway, P. H. Degradation of ZnS Field-Emission Display Phosphors During Electron-Beam Bombardment. *J. Vac. Sci. Technol., A* 1997, 15, 2349–2353.

(4) Kim, C.-H.; Kwon, L.-E.; Park, C.-H.; Hwang, Y.-J.; Bae, H.-S.; Yu, B.-Y.; Pyun, C.-H.; Hong, G.-Y. Phosphors for Plasma Display Panels. *J. Korean Chem. Soc.* 1998, 42, 588–595.

(5) Lin, K. B.; Su, Y. H. Photoluminescence of Cu:ZnS, Ag:ZnS, and Au:ZnS Nanoparticles Applied in Bio-LED. *Appl. Phys. B* 2013, 113, 351–359.

(6) Yamamoto, O.; Sawai, J.; Ishimura, N.; Kojima, H.; Sasamoto, T. Change of Antibacterial Activity with Oxidation of ZnS Powder. *J. Ceram. Soc. Jpn.* 1999, 107, 853–856.

(7) Velumani, S.; Ascencio, J. A. Formation of ZnS Nanorods by Simple Evaporation Technique. *Appl. Phys. A* 2004, 79, 153–156.

(8) Nadeem, M. Y.; Ahmed, W. Optical Properties of ZnS Thin Films. *Turk. J. Phys.* 2000, 24, 651–659.

(9) Yes, S.; Schwarz, U.; Christensen, N. E.; Syassen, K.; Cardona, M. Cubic ZnS Under Pressure: Optical-Absorption Edge, Phase Transition, and Calculated Equation of State. *Phys. Rev. B* 1990, 42, 9113.

(10) Davar, F.; Mohammadi-kish, M.; Loghman-Estarki, M. R.; Hamidic, Z. Synthesis of Spherical ZnS Based Nanocrystals Using Thioglycolic Assisted Hydrothermal Method. *CrystEngComm* 2012, 14, 7338–7344.

(11) Plassler, R.; Griebel, E.; Riepl, H.; Lautner, G.; Bauer, S.; Preis, H.; Lischka, K.; et al. Temperature Dependence of Exciton Peak Energies in ZnS, ZnSe, and ZnTe Epitaxial Films. *J. Appl. Phys.* 1999, 86, 4403–4411.

(12) Guo, L.; Ji, Y. L.; Xu, H.; Simon, P.; Wu, Z. Regularly Shaped, Single-Crystalline ZnO Nanorods, With Wurtzite Structure. *J. Am. Chem. Soc.* 2002, 124, 14864–14865.

(13) Ho, C.-H.; Chen, Y.-J.; Jhong, H.-W.; Du, J.-H. Optical Anisotropy of ZnO Nanocrystals on Sapphire by Thermoreflectance Spectroscopy. *Opt. Lett.* 2007, 32, 2765–2767.

(14) Tiwary, C. S.; Saha, S.; Chattopadhyay, K. Observation of Combined Effect of Temperature and Pressure on Cubic to Hexagonal Phase Transformation in ZnS at the Nanoscale. *Cryst. Growth Des.* 2014, 14, 4240–4246.

(15) Ma, C.; Moore, D.; Li, J.; Wang, Z. L. Nanobelts, Nanocombs, and Nanowindmills of Wurtzite ZnS. *Adv. Mater.* 2003, 15, 228–231.

(16) Xiong, Q.; Wang, J.; Reese, O.; Lew Yan Voong, L. C.; Eklund, P. C. Raman Scattering from Surface Phonons in Rectangular Cross-Sectional W-ZnS Nanowires. *Nano Lett.* 2004, 4, 1991–1996.

(17) Tafreshi, M. J.; Dibaei, B.; Fazi, M. Growth of ZnS Single Crystals by CVT Technique Under Different Mass Transport Stability Conditions. *Iran. J. Mater. Sci. Eng.* 2012, 9, 51–61.

(18) Hartmann, H. Studies on the Vapor Growth of ZnS, ZnSe and ZnTe Single Crystals. *J. Cryst. Growth* 1977, 42, 144.

(19) Ho, C.-H. Enhanced Photocatalytic-Conversion Yield in Niobium-Incorporated In\(_2\)S\(_3\) with Intermediate Band. *J. Mater. Chem.* 2011, 21, 10518–10524.
(20) Ho, C.-H.; Lin, M.-H. Synthesis and Optical Characterization of a High-quality ZnS Substrate for Optoelectronics and UV Solar-Energy Conversion. RSC Adv. 2016, 6, 81053.

(21) Okeil, S.; Krausmann, J.; Dönges, I.; Pfleger, S.; Engstler, J.; Schneider, J. J. ZnS/ZnO@CNT and ZnS@CNT Nanocomposites by Gas Phase Conversion of ZnO@CNT. A Systematic Study of Their Photocatalytic Properties. Dalton Trans. 2017, 46, 5189−5201.

(22) Qadri, S. B.; Skelton, E. F.; Hsu, D.; Dinsmore, A. D.; Yang, J.; Gray, H. F.; Ratna, B. R. Size-Induced Transition-Temperature Reduction in Nanoparticles of ZnS. Phys. Rev. B 1999, 60, 9191.

(23) Northrup, J. E.; Ihm, J.; Cohen, M. L. Electronic Structure of Zinc-Blende-Wurtzite Interfaces: ZnS−ZnS (111-0001) and ZnSe−ZnSe (111-0001). Phys. Rev. B 1980, 22, 2060−2065.

(24) Serrano, J.; Cantarero, A.; Cardona, M.; Garro, N.; Lauck, R.; Tallman, R. E.; Ritter, T. M.; Weinstein, B. A. Raman Scattering in β-ZnS. Phys. Rev. B 2004, 69, No. 014301.

(25) Cheng, Y. C.; Jin, C. Q.; Gao, F.; Wu, X. L.; Zhong, W.; Li, S. H.; Chu, P. K. Raman Scattering Study of Zinc Blende and Wurtzite ZnS. J. Appl. Phys. 2009, 106, No. 123505.

(26) Cusco, R.; Alarcón-Lladó, E.; Ibáñez, J.; Artús, L.; Jiménez, J.; Wang, B.; Callahan, M. J. Temperature Dependence of Raman Scattering in ZnO. Phys. Rev. B 2007, 75, No. 165202.

(27) Aspnes, D. E. Modulation Spectroscopy/Electric Field Effects on the Dielectric Fuction of Semiconductors. In Handbook on Semiconductors 2; Balkanski, M., Ed.; North Holland: Amsterdam, 1980; Chapter 4A, pp 109−154.

(28) Schleife, A.; Rödl, C.; Fuchs, F.; Furthmüller, J.; Bechstedt, F. Strain Influence on Valence Band Ordering and Excitons in ZnO: An ab Initio Study. Appl. Phys. Lett. 2007, 91, No. 241915.

(29) Yamada, Y.; Yamamoto, T.; Nakamura, S.; Taguchi, T.; Sasaki, F.; Kobayashi, S.; Tani, T. Biexciton Luminescence from Cubic ZnS Epitaxial Layers. Appl. Phys. Lett. 1996, 69, 88−90.

(30) Ryskin, A. I.; Suslina, G. L.; Khilko, G. I.; Shadrin, E. B. Excitons in ZnS Crystals with Stacking Faults. Phys. Status Solidi B 1972, 49, 875−884.

(31) Areshkin, A. G.; Vasiljeva, L. I.; Fedorov, D. L.; Markov, L. S. Exciton Piezospectroscopy of A2B6 Compounds with Structural Phase-Transition Zinc Blende-Wurtzite. J. Opt. Soc. Am. B 1998, 15, 41−46.

(32) Bansal, N.; Mohanta, G. C.; Singh, K. Effect of Mn2+ and Cu2+ Co-Doping on Structural and Luminescent Properties of ZnS Nanoparticles. Ceram. Int. 2017, 43, 7193−7201.

(33) Zeng, H.; Duan, G.; Li, Y.; Yang, S.; Xu, X.; Cai, W. Blue Luminescence of ZnO Nanoparticles Based on Non-Equilibrium Processes: Defect Origins and Emission Controls. Adv. Funct. Mater. 2010, 20, 561−572.

(34) Das, D.; Mondal, P. Photoluminescence Phenomena Prevailing in c-Axis Oriented Intrinsic ZnO Thin Films Prepared by RF Magnetron Sputtering. RSC Adv. 2014, 4, 35735−35743.