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Warm white-light emission harvesting with enhanced color rendering index in conventional alloyed $\text{CdS}_{0.7}\text{Se}_{0.3}$ quantum dots

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ABSTRACT

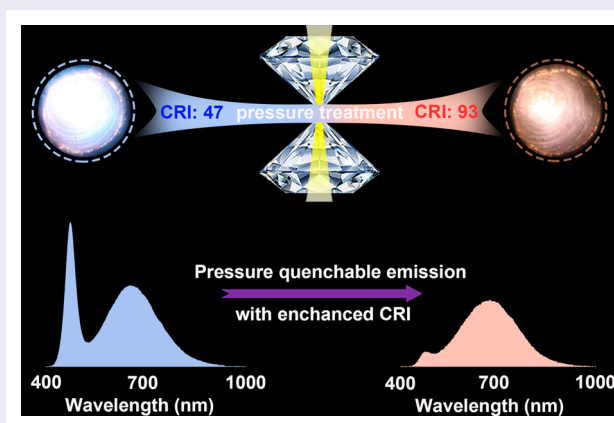
Warm WLED with high color rendering index (CRI) are greatly required for the widespread use of solid-state lighting especially indoors. Here, a remarkable improvement of CRI in alloyed $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs was achieved by pressure engineering. Notably, white light with enhanced CRI of 93, higher than pristine CRI of 47, was retained upon the complete release of pressure, accompanied by a color change from 'natural' (4298 K) to 'warm' white light (2170 K). Synchrotron ADXRD shows that $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs experienced an irreversible phase transition from the zinc blende phase to rocksalt structure.

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KEYWORDS

High pressure; phase transition; alloyed $\text{CdS}_{0.7}\text{Se}_{0.3}$; warm-white light emission; color rendering index



IMPACT STATEMENT

Warm white light with enhanced color rendering index of 93 is achieved by pressure processing, accompanied by a color change from 'natural' (4298 K) to 'warm' white light (2170 K).

1. Introduction

Semiconductor quantum dots (QDs) have emerged as a new technology platform with the potential to replace commercially used lamps [1–4]. Alloyed bichalcogenide CdSSe QDs showed promising potential in various light-emitting devices, such as white-light-emitting diodes (WLEDs) and photodetectors [5]. Reabsorption-associated losses and color rendering index (CRI) are two key photometric parameters to assess the performance of lighting devices. Considerable efforts, including boosting trap-assisted emission via partial ligand exchange or adopting the gradient composition, have been made to

control CRI values in CdSSe QDs [6,7]. Despite significant progress, the success in increasing the white-light quality has been limited and complex synthesis procedures are unfavorable for industrial production [8]. Increasing the CRI value for defect-induced trap-rich white-light nanocrystals still remains a crucial challenge.

High pressure is a powerful stimulus to regulate the physical and chemical properties of various functional materials, which broadens our fundamental understanding of structure–property relationships [9–12]. Moreover, metastable phases with novel properties upon compression could be retained under ambient conditions

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[13–16]. In addition, pressure can induce emission enhancement in compressed CdSe QDs as a result of the strengthened interactions between the capping organic acid molecule and the CdSe QDs at high pressure [17]. Motivated by these works, we have extended high-pressure effect to the alloyed bichalcogenide CdSSe QDs to investigate the structure–property behavior of CdSSe QDs and enhance their white-light properties.

In this regard, we systematically investigated the pressure-dependent optical properties of alloyed bichalcogenide $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs. Upon compression, the evolutionary behavior of band-edge emission and trap-assisted emission results in a persistently increscent CRI value up to 89 at 5.97 GPa. More importantly, the warm-white emission corresponding to the CIE coordinates (0.5041, 0.4085) with higher CRI of 93 is retained under ambient conditions upon the complete release of pressure, accompanied by a color change from ‘natural’ to ‘warm’ white light with 2170 K. The irreversible tuning of optical properties in $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs was highly associated with the retention of high-pressure rocksalt phase after pressure release. The high-resolution TEM images

revealed the distinct variation in morphology due to the pressure-induced ripening in $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs, which is possibly responsible for the irreversible phase transition. Our study deepens insights into comprehending the structure–property relationship and guiding future material design for promising applications through phase engineering.

2. Results and discussion

As shown in Figure 1(a and b), the synthesized samples exhibit a spherical shape with an average diameter of 4.41 nm. The zinc-blende (ZB) phase structure of alloyed $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs can be evidenced by the well-resolved lattice fringes with an interplanar spacing of 0.34 nm, which lies between the (111) lattice spacing of cubic CdS (0.336 nm) and that of cubic CdSe (0.352 nm) [18]. Figure 1(c) presents the absorption and PL of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs with a strong narrow emission (NE), at 475 nm and a broad emission (BE) at ~ 658 nm. The NE, which is only a few nanometer Stokes-shift, is clearly a result of excitonic recombination at the band edge. The large

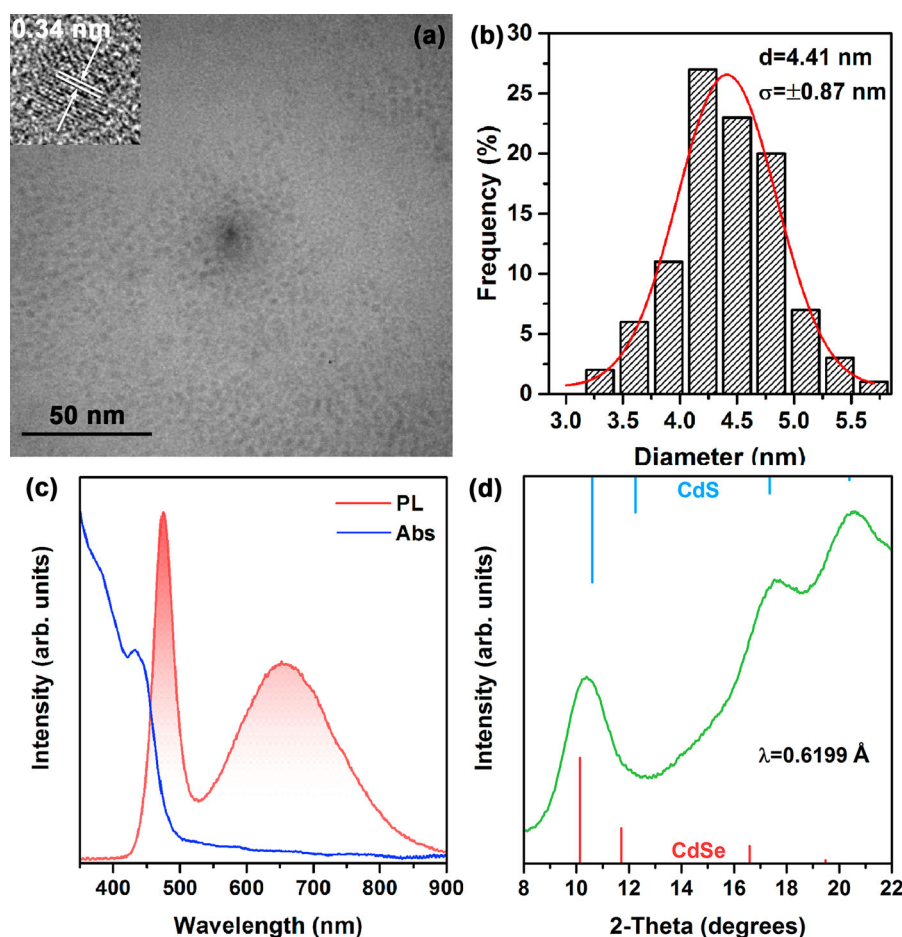


Figure 1. (a) TEM and HRTEM images of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs. (b) Corresponding size distribution. (c) Absorption and PL spectra. (d) XRD pattern of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs. The vertical red and blue lines show the reflections corresponding to CdSe and CdS.

Stokes-shifted BE can be attributed to the surface-related midgap states. The emission of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs under ambient conditions is determined as (0.3519, 0.2926), which provides a correlated color temperature (CCT) of 4298 K. The XRD spectra confirm that the $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs occupy the ZB structure (Figure 1d). The reflections of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs slightly shift toward the lower angles with respect to the reflections of CdS, indicating the existence of lattice expansion owing to the larger Se^{2-} ionic radius compared with that of S^{2-} . In addition, the emission properties can be modulated via S:Se ratios due to the existence of two different surface chalcogenide atoms within CdSSe QDs (Figure S1).

When the pressure increased to 2.02 GPa, the NE of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs exhibited a blue shift, accompanied by a slight pressure-induced emission enhancement, while the BE underwent a persistent dropping in its intensity and a similar blue shift to that of NE. Upon further

compression, the NE and BE intensities decreased and were finally quenched at 8.75 GPa. The CCT gradually increased up to 6516 K at 4.37 GPa, followed by a persistent decrease up to 3947 K. The corresponding optical micrographs of the emission clearly displayed the variation in the PL brightness of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs upon compression, accompanied by the color change from neutral to warm white light (Figure 2c). Meanwhile, the obvious improvement of CRI was able to be achieved, and the CRI reached to a maximum of 89 at 5.97 GPa, which is almost twice than the initial counterpart (Figure 2d). Impressively, considerably different emission profile and intensity appeared upon decompression with the emergence of warm-white light (Figure 2e). The CRI was promoted from the initial 47 to the maximum value of 93 after pressure processing. The corresponding quantum yields of quenched $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs was estimated to be about 12.02%. On the basis of the CIE chromaticity

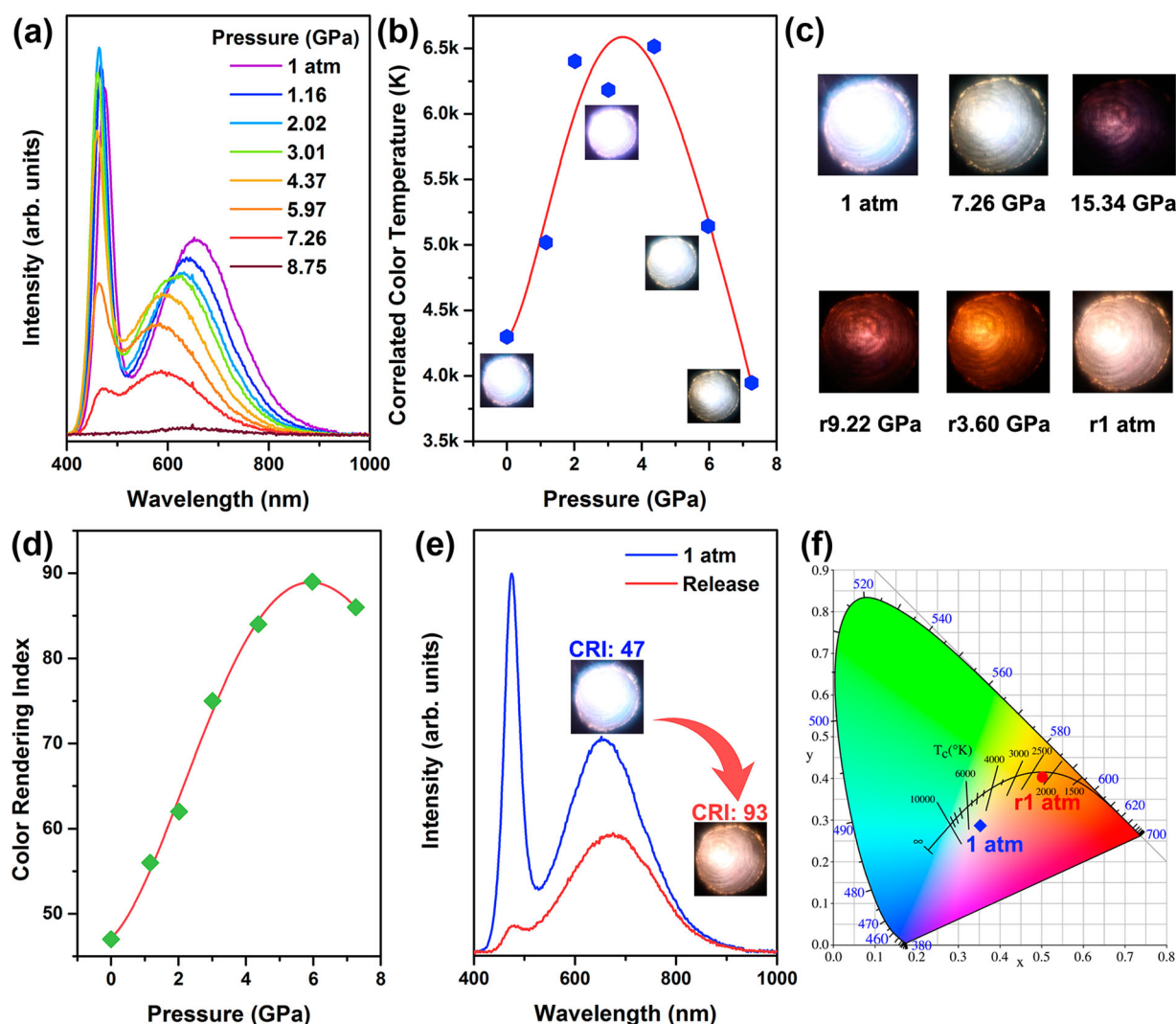


Figure 2. (a) Evolution of the PL spectra under pressures from 1 atm to 8.75 GPa. (b) Pressure-dependent correlated color temperatures of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs. (c) Evolution of the microphotographs under selected pressures. (d) CRI changes as a function of pressure. (e) PL spectra of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs at 1 atm and after pressure release from 15 GPa. (f) Chromaticity coordinate diagram for 1 atm and decompression.

diagram, as shown in Figure 2(f), the initial emission with CIE chromaticity coordinate of (0.3519, 0.2926) and CCT of 4298 K can be tuned by pressure, converting to 2170 K with CIE chromaticity coordinate of (0.5041, 0.4085). Moreover, the quenched CRI was able to remain the value of above 90 after aging time up to one week at ambient conditions (Figure S2). We further collected the PL spectra of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs upon decompression from different pressures. The CRI values of quenched emission were 49, 92 and 93 from 5.07 GPa, 10.02 and 15.03 GPa, respectively (Table S2). When the applied pressure exceeded 10 GPa, the quenched NE intensity weakened apparently, whereas the quenched BE intensity was almost unchanged (Figure S3). CRI and CCT are important parameters for white emissive materials, and the reflect the ability of a light source to accurately render the colors of an object compared with daylight.

Therefore, high-pressure technology as a simple and clean method achieves high-quality white-light emission. Looking forward, we can use the large volume press to achieve large-scale preparation of white emissive CdSSe QDs with high CRI for practical application [19].

The PL spectra selected were split into two subbands attributed to NE and BE to assess the high-pressure PL property more accurately (Figure 3a). Based on the deconvolution of the PL spectra using Gaussian functions, we deduced the high-pressure evolution of the FWHM, intensity, and position of each PL peaks. The FWHM of NE displayed a slight narrowing before 4.37 GPa and a slow broadening with further increase in pressure (Figure 3b). By contrast, the FWHM of the BE first increased when the pressure increased from ambient to 4.37 GPa (Figure 3b). Subsequently, the FWHM declined with pressure increasing

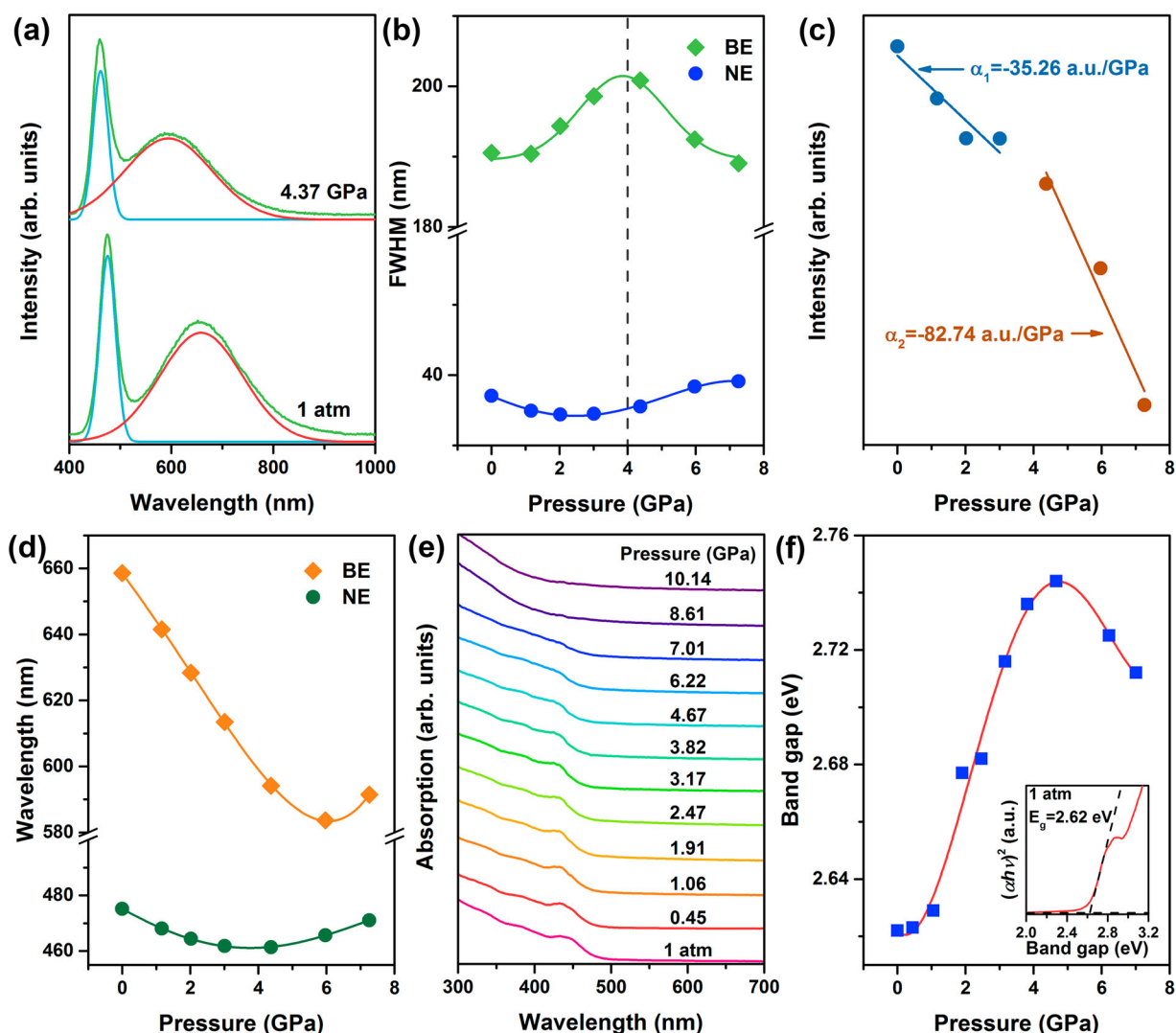


Figure 3. (a) Fitted PL spectra at 1 atm and 4.37 GPa. (b) Pressure-dependent FWHM of NE and BE. (c) Intensity of BE as a function of pressure. (d) Pressure-dependent position variations of BE and NE. (e) Absorption spectra as a function of the pressure. (f) Pressure dependence of band gap.

from 4.37–7.27 GPa. The sudden decrease in the FWHM of BE could be attributed to the pressure-induced ripening of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs, which reduces the number of trapped states from the surface of QDs. We also divided the BE intensity as a function of pressure into two regimes associated with dramatic change in slope (Figure 3c). The coefficient α of -35.26 GPa^{-1} from the linear function $E(P) = E_0 + \alpha P$ at the low-pressure regime was smaller than that of -82.74 GPa^{-1} at high-pressure regime. This finding could be attributed to the faster reduction in the number of trapped states. As depicted in Figure 3(d), the position of NE showed an initial blue shift upon compression to about 4.37 GPa. When higher pressure was applied, it exhibited a redshift to 7.26 GPa, at which point the PL intensity completely disappeared. With the increase in pressure to 5.97 GPa, the BE peak showed continuously blue-shift. The BE started to display a red-shift tendency.

The pressure-dependent absorption spectra of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs were recorded, as shown in Figure 3(e). Under ambient conditions, $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs exhibited an obvious exciton absorption peak around 433 nm. At relatively low pressure, the exciton absorption peak initially displayed a gradual blueshift in wavelength due to the compression of the unit cell. At around 4.67 GPa, the original exciton absorption peak suddenly presented

a slight redshift, consistent with the NE behavior upon compression, indicating the intrinsic band-edge transition feature. In addition, the defect states depended on the host media, their transition energy should be not directly related to the change of host's band gap. Beyond 7.01 GPa, the vanishing of the exciton absorption peak indicated that the $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs possibly underwent a structural phase transition. After completely releasing pressure to ambient conditions, the exciton absorption peak become seriously weakened compared with the original state, explaining the reduction in the NE intensity for the quenched samples (Figure S4). Detailed evolution of the band-gap energy for $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs under high pressure was displayed in Figure 3(f). The variation in band gap energy (E_g) for the $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs was estimated by a Tauc plot, fitting the linear portion of $(\alpha h\nu)^2$ versus $h\nu$, where α and $h\nu$ are the absorption coefficient and photon energy, respectively. In addition, similar absorption behavior upon compression for $\text{CdS}_x\text{Se}_{1-x}$ QDs ($x = 0.5$ and 0.3) indicates that the inflexion had nothing to do with the changes of S/Se ratios (Figure S5).

To evaluate the structure–property relationship, in situ high-pressure angle-dispersive X-ray diffraction (ADXRD) experiments were performed (Figure 4a). With increasing pressure, all diffraction peaks shifted toward high angles without any new peaks occurring

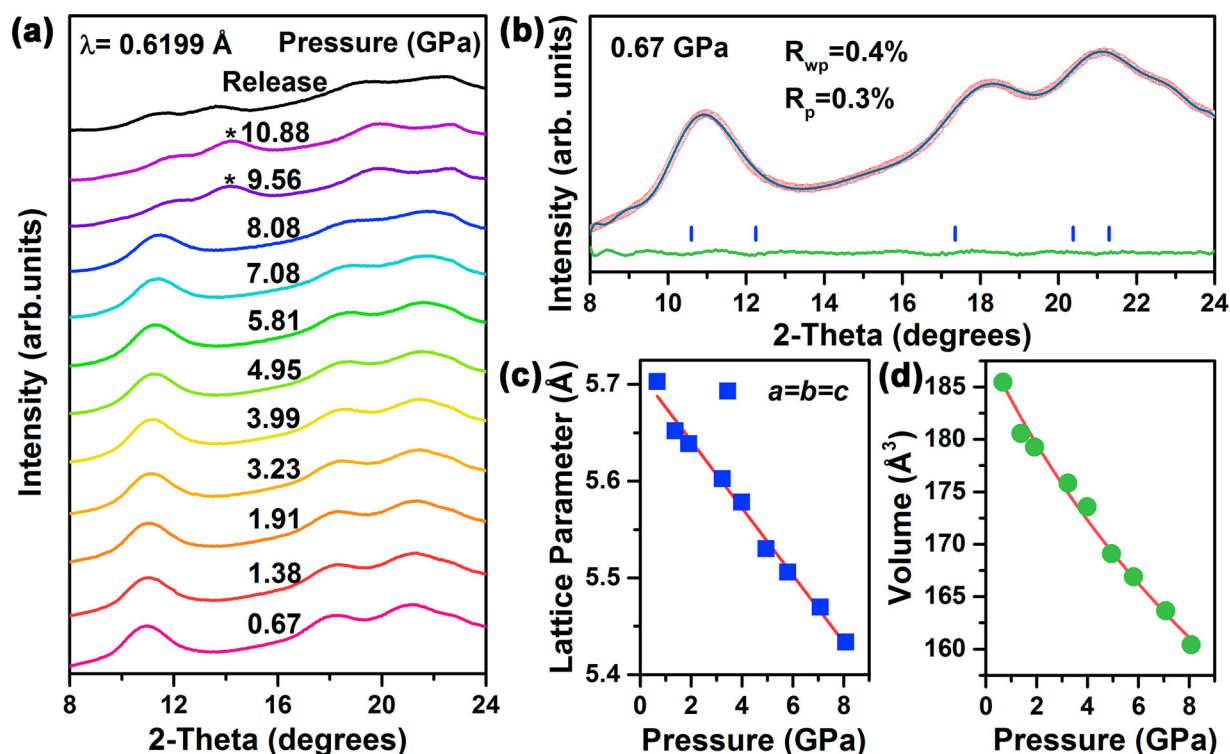


Figure 4. (a) ADXRD patterns of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs at pressures. (b) Refinements of ADXRD pattern with the experiment (red fork), simulation (gray profile), and difference (green line). Therein, blue vertical markers indicate the corresponding Bragg reflection. (c, d) Pressure dependence of lattice parameter and volume.

below 8.08 GPa. The rietveld refinement confirmed that the initial structure was the ZB phase with the space group of $F43m$ (Figure 4b). As the $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs were subjected to pressure beyond 8.08 GPa, the appearance of a new diffraction peak at about 14° (marked by asterisk) suggested that the $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs underwent a structural phase transition to the RS structure. The phase transition from a direct band gap ZB structure to an indirect band gap RS structure explained why the BE and NE were basically quenched above 7.01 GPa. Note that when completely releasing the pressure, some diffraction peaks of high-pressure RS phase can be maintained (Figure 4a). The refinements of quenched ADXRD pattern indicated that the proportions of ZB and RS are 46.5% and 53.5%, respectively (Figure S6). This partially irreversible phase transition eventually resulted in the irreversible change in the PL and absorption spectra. Figure 4(c and d) depicts that lattice constants decreased linearly without sudden change before 8.08 GPa.

First-principles calculations demonstrated that the bonds of Cd-S and Cd-Se experienced a persistent decrease with a similar rate under high pressure (Figure S7). The simulated electronic structure with a direct band gap feature exhibited a linear increase without any turning point upon compression (Figure S8). The HRTEM images show that the morphology of $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs was no longer uniform and some of QDs were sintered together after decompression (Figure S9). The decompressed $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs exhibited larger particle size, consistent with the result of CdSe QDs [20]. Therefore, the increase in size associated with pressure-induced ripening would result in stark discontinuity at ~ 4 GPa in the PL and absorption spectra. Because the stability of high-pressure phase was affected by the morphology of nanoparticles [21], the effective shape modification of alloyed $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs through pressure engineering could be responsible for the irreversible phase transition. Eventually, alloyed $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs with enhanced properties can be anticipated at room temperature and ambient pressure.

3. Conclusion

The CRI values of alloyed $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs were remarkably improved by pressure treatment at room temperature. Of particular importance is the retention of the white-light emission with high CRI of 93 upon the complete release of pressure, accompanied by a distinct color change from 'natural' (4298 K) to 'warm' white light with 2170 K. Synchrotron ADXRD patterns indicated that $\text{CdS}_{0.7}\text{Se}_{0.3}$ QDs experienced an irreversible phase transition from cubic ZB phase to the RS structure. This work provides a promising strategy for rational material design

by pressure treatment to retain novel properties, thus greatly facilitating its potential in solid-state lighting.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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