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Size-dependent structural phase transitions and their correlation with photoluminescence and optical absorption behavior of annealed $Zn_{0.45}Cd_{0.55}S$ quantum dots

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ABSTRACT

In this paper, we investigate the effect of thermally induced structural phase transitions on the photoluminescence (PL) and optical absorption behaviour of $Zn_{0.45}Cd_{0.55}S$ nanoparticles (NPs). Analysis of X-ray diffraction (XRD) patterns and high-resolution electron microscope (HRTEM) images reveal that the as-synthesized sample possesses zinc-blende-type cubic structure. In addition, at annealing temperature (T_a) 400 °C, the cubic structure transforms completely into the wurtzite-type hexagonal structure. Furthermore, the second phase transition of the as-synthesized sample has observed at 700 °C, where the cubic structure has transformed into mixed polycrystalline phases of hexagonal ZnO, cubic CdO, monoclinic $CdSO_3$, and orthorhombic $ZnSO_4$ structures. These new phases have also confirmed from the analysis of Raman and FTIR spectra. Analysis of UV–visible optical absorption spectra demonstrates that Increasing T_a results in the decrease of optical band gap due the improvement in crystallinity accompanied by the increase in the particle size. The PL emission bands at an excitation energy of 3.818 eV exhibit redshift and a decrease in the intensity with increasing T_a up to 500 °C. Meanwhile, further increase in T_a up to 700 °C results in the enhancement of green emission intensity. On the other hand, PL emission spectra at 3.354 eV and T_a 700 °C, reveal a dramatic increase in the emission intensity nearly by one-order of magnitude with respect to its value of the as-synthesized sample. This behaviour is ascribed to the incorporation of oxygen-related defects via thermal annealing in air, which act as additive radiative centers. Also, we have interpreted the observed spectral blue shift of PL emission spectrum with increasing excitation energy.

1. Introduction

Semiconductor quantum dots (QDs) have attracted great attention due to their novel and unique size-dependent physical, chemical and biomedical properties. It is found that a ternary alloy of $Zn_xCd_{1-x}S$ nanocrystals have a specific advantage since their properties can be tuned either by the variation of size or composition by changing Zn to Cd molar ratios [1–13]. They have been regarded as promising candidates for many applications such as photocatalytic hydrogen production [14], biological markers [15, 16], photovoltaic devices [17], field emitting devices [9], chemical sensors [18] and nonlinear optical devices [19].

Phase transformation of II-VI semiconductor bulk compounds from the cubic to the hexagonal structure takes place at transition temperature higher than that of the corresponding nanostructures, for example, the transition temperature of bulk ZnS at about 1023 °C [20]; meanwhile, phase transition in ZnS NPs takes place at lower temperatures 225 °C [21] and 400 °C [22]. In addition, the phase transformation from the cubic to the hexagonal structure in nanomaterials depends mainly on the crystallite size (**D**) and is different from that of the bulk crystals [23], where activation energy of phase transformation in bulk material is higher than that of the nanoparticles [22, 24]. In addition, structural defects in nanocrystals can be annealed out more easily at annealing temperature (T_a) lower than that in bulk [24, 25]. Huang et al. [21] suggested a model for the phase transformation, assuming that nucleation occurs at the surface and growth involves the collective movement of atoms at the cubic-hexagonal interface. It is well known that the optical absorption properties and PL emission behaviour of QDs

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are strongly dependent on the surrounding medium and surface conditions [26, 27]. Bhattacharjee et al. [28] found that increasing $\mathbf{T}_a$ leads to the increase of particle size associated with redshift and decrease in the intensity of ultraviolet and blue emission bands. Moreover, previously reported works showed that PL intensity of Cu [29] and Mn-doped ZnS NPs [30] decreases with increasing annealing temperature due to improvement in the crystallinity.

The structural phase transformation of II-VI semiconductor bulk compounds from cubic to hexagonal takes place at a transition temperature higher than the corresponding nanostructured compounds, where the low phase transition temperature of nanostructured materials is very useful in various important application photocatalysis [31], photoconduction [32, 33]. The structural transition temperature of ZnS bulk crystals was determined at about 1023 °C by Liu [20]; meanwhile, Huang et al. [21] have reported that the structural transformation of ZnS nanocrystals from cubic to hexagonal under hydrothermal condition occurred at nearly 225 °C. They suggested that hexagonal phase grows initially at the cubic-hexagonal interface and the crystal growth of hexagonal phase due to the collective movement of interior atoms toward the surface of the cubic structure is kinetically controlled by the particle size. On the other hand Qadri et al. [34] and Osman et al. [35] have observed the partial structure phase transition of ZnS nanocrystals from cubic to hexagonal structure at 400 °C due to the increase in the crystallite size by thermal annealing; whereas in the case of CdS nanostructure Osman et al. [35] found the thermally induced structural phase transition from cubic to hexagonal occurred completely at 300 °C. Qadri et al. [22] investigated the pressure-induced structural transformation of ZnS nanoparticles and found that the increase of the applied pressure results in the reduction of the crystallite size accompanied by the phase transition from cubic to hexagonal structure. Moreover, Banerjee et al. [23] demonstrated that nanostructured materials have lower activation energy than the corresponding bulk, which by turn leads to the reduction of required energy (i.e. transformation temperature) and for the movement of internal structural defects responsible for structural phase transition toward the cubic-hexagonal interface [24, 25]. In our previous work [36], we have investigated for the first time the excitation wavelength dependent PL emission behaviour, as well as, the effect of UV irradiation on the optical band gap and PL emission behaviour of $Zn_{0.45}Cd_{0.55}S$ NPs. We have found that the increase of excitation energy (i.e. wavelength decreasing) results in the blue shift of PL emission spectra accompanied by the improvement of PL emission intensity. In addition, the increase of UV irradiation dose leads to the increase of the optical band gap associated to with the improvement of the corresponding PL emission intensity.

In the present work, ternary alloy $Zn_{0.45}Cd_{0.55}S$ NPs have synthesized by a simple and low-cost chemical precipitation method at room temperature. We study the effect of thermal annealing in the air on the structure, morphology, optical absorption and photoluminescence emission behaviour of $Zn_{0.45}Cd_{0.55}S$ nanoparticles. In addition, we investigate the mechanism of thermally induced structural phase transformation of $Zn_{0.45}Cd_{0.55}S$ NPs from Zincblende-type cubic to wurtzite-type hexagonal structure, which has not investigated yet. Moreover, the role of structural phase transformation on the tuning of the optical band gap and PL emission behaviour has been discussed. For more understanding, the role of defect states related emission we have investigated the dependence of PL emission spectra on excitation wavelength (λ_{ex}) changes, which revealed the applicability of using our materials in many optoelectronic applications such as optical memory

2. Preparation and Characterization of $Zn_{0.5}Cd_{0.5}S$ Alloyed Nanoparticles

2.1. Samples Preparation

Chemical precipitation method has been used to synthesize $Zn_{0.5}Cd_{0.5}S$ alloys nanoparticles at room temperature under the same conditions described in our previous works on CdS [37] and ZnS [35] nanoparticles, where 0.4 M (6.72 g) of $Zn(CH_3COO)_2{\cdot}2H_2O$ (MW = 219.5 g·mol^{-1}, assay 98%), and 0.4 M (8.08 g) of Cd $(CH_3COO)_2{\cdot}2H_2O$ (MW = 266.52 g·mol^{-1}, assay 99%), were dissolved in 75 ml double distilled water and 0.08 M (1.76 g) EDTA ($C_{10}H_{16}N_2O_8$, MW = 292.25 g·mol^{-1}, assay 99.5%) was added to the mixed solution as stabilizer to either prevent or reduce further coalescence and agglomeration of the nanoparticles, then (0.8 M, 12.78 g), of $Na_2S{\cdot}3H_2O$ (MW = 132.05 g·mol^{-1}, 62%) was dissolved in 75 ml double distilled water and added in the form of dropwise to the solution containing Cd^{2+} and Zn^{2+} ions sources at continuous stirring of 400 rpm for 1 h. The precipitate was filtered out and washed several times with double distilled water and ethanol to remove unwanted impurities formed during the preparation process. Finally, the product was dried at 100 °C for 3 h in the atmospheric air then cooled to room temperature at the rate of 10 °C/min by research oven [model FV-40, MK-15, AC 220 V, P25 KW, UGAWA SEIKI CO LTD]. For studying the annealing effect on the structural phase transitions of $Zn_{0.45}Cd_{0.55}S$ NPs, 0.5 g of the as-prepared was used for annealing at each temperature in the range 200–700 °C.

2.2. Samples Characterization

Structural changes of as prepared $Zn_{0.5}Cd_{0.5}S$ nanoparticles (NPs) samples due to thermal annealing process in air in the temperature range 100–700 °C were characterised by PW 1700 X-ray diffractometer (XRD) with Cu K_α radiation $\lambda = 0.154056$ nm at diffraction angle (2θ) in the range 20–70° with a step of 0.06° and refined by crystal structure Celref Software. The morphological changes in $Zn_{0.5}Cd_{0.5}S$ NPs at different annealing temperatures (T_a) were investigated by using a high-resolution transmission electron microscope (HRTEM) Jeol Jem 2100 microscope at operating voltage 200 kV, where small amount of the powder was dispersed in absolute ethanol using ultrasonic cleaner and then a small drop was deposited on carbon-coated Cu grid (200 mesh, carbon thickness ranging from 15 to 25 nm, TED PELLA INC.) and left to dry on air, after that the deposited sample on the grid was placed into the customized microscope holder and various image have been recorded at different resolution. The obtained TEM Images were analyzed using built-in software called pro plus version 6.0. Measurements of optical absorption and transmittance spectra were carried out using UV–vis Perkin-Elmer Lambda 750 spectrophotometer, where 2 mg from the powder was dispersed in 10 ml double distilled water for 15 min in ultrasonic cleaner for obtaining homogeneous colloidal solution, then 5 ml quartz cuvette (1 cm × 1 cm × 5 cm) was filled from the colloidal solution and placed in the customized holder in the spectrophotometer and both of absorbance and transmittance spectra were recorded after baseline correction in the range 200 to 700 nm. Photoluminescence (PL) emission spectra were recorded by JASCO FP-6300 spectrofluorometer at excitation wavelengths 325 and 370 nm and the deconvoluted PL spectra were deconvoluted by Origin Software to identify the exact peak position of the emission bands. To determine the exact molar fractions of the constituents of the as-synthesized product an elemental analyser x-ray fluorescence (XRF) spectrometer (JEOL, JSX-3222) was used. Fourier transform infrared (FTIR) spectra of the as-prepared and annealed samples were measured by using Nicolet™ iS™10 FTIR spectrometer in the wave number range 400–4000 cm^{-1}. Raman spectra were recorded by Bruker Senterra Raman microscope (Bruker Optics Inc., Germany) with an excitation wavelength of 785 nm, 1200 rulings/mm holographic grating, a charge-coupled device (CCD) detector, and the acquisition time was 3 s with the power of 50 mW.