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Effect of processing on agglomeration and characteristics of cobalt doped zinc selenide nanoparticles synthesized by reactive solution method

Brett Setera, Ching Hua Su*, David Sachs, Bradley Arnold, Fow-Sen Choa, Brian Cullum and N. B. Singh
University of Maryland Baltimore County, 100 Hilltop Circle, Baltimore, MD 21250
*EM31, NASA Marshall Space Flight Center, Huntsville, AL 35812

Abstract. A reactive solution growth process was used to prepare pure and cobalt doped ZnSe nano crystals using zinc acetate and sodium selenite solution. Effect of the capping agent was studies for several concentrations of the dopant to evaluate agglomeration characteristics and size of nanoparticles. The concentration of the dopant affected the agglomeration significantly. Morphological studies demonstrated faceted ZnSe nanoparticles with a minimum grain size of 10 nm for both doped and undoped nanoparticles. Dynamic light scattering detected cluster formation of particles above 100 nm in the doped solutions. Large particles in excess of 100 nm sizes were attributed to grain growth and agglomeration. Measurements on fluorescence and UV-visual absorption showed a shift of the absorption and emission bands compared to bulk ZnSe bulk crystals. These Co-doped clustered nano crystals showed a wider bandgap than bulk ZnSe.

Keywords: Zinc selenide; cobalt; morphology; nanocrystals; physical vapor transport; optical properties

Correspondence: singna@umbc.edu

1. Background

Zinc sulfide (ZnS), zinc selenide (ZnSe) and their solid solutions have been grown and characterized because of multifunctionality and potential of wide scale applications in the bulk and quasi phase matched structures [1-6]. These two materials have low absorption coefficient, wide transparency range, large damage threshold and high breakdown voltage. Availability of large, high purity, bulk ZnS and ZnSe crystals grown by physical vapor transport method (PVT) has enabled doping to extend wider applications in optical industries. Su et al. have made significant progress on the growth and effect of vapor transport, fluid flow and convection driven effects on crystal growth [1, 3-6]. Werner et al.[7] used poly crystalline ZnSe material with

varying particle size powder to generate mid wave infrared (MWIR) laser emission. The approach of rare earth or transition metal doping in ZnSe crystals have been used for several applications. However, the doping of the of the single crystals with rare earth or transition-metal ion creates point and line defects in the matrix, which ultimately affects the performance [8]. The dopants have different sizes and oxidation states causing another complication which may result in voids, precipitates, and other defects. In a series of experiments, we have studied effect of growth condition and doping in the bulk [3,4] and nanocrystals [9] . The objectives of this study were to evaluate effect of doping and stage at which capping was added in solution grown on the agglomeration of Co-ZnSe particles.

2. Previous Methods, Materials Synthesis and Characterization

2.1 Synthesis of pure and doped ZnSe nanoparticles: A variety of growth approaches have been proposed to develop ZnSe nano crystals [10-17] in recent years including preparation using thermal treatment at different calcination temperatures in a nitrogen flow by Salem et al [11] in which they showed amorphous phase which transformed into crystalline structure. Zhu et al. [12] synthesized nanoparticles using sonochemical irradiation of aqueous solution of zinc acetate and selenourea. For low temperature process, Ravindranadth et al. [17] utilized zinc chloride, PVA solution in water and reacted with hydrogen selenide and they casted on glass plates and dried it to produce ZnSe nanoparticles. We used a different process and conditions which has some similarity to that of Deshpande et al [10]. Because of cobalt doping, time of refluxing, temperature, amount of each nutrient, drying conditions were significantly different. We used a reactive solution method using zinc acetate and sodium selenite as source materials for the synthesis. We dissolved 0.1 M zinc acetate in approximately 50.0 cc dimethylformamide and continuously stirred it for a period of 15-20 minutes. After complete dissolution, approximately 1cc thioglycerol capping agent was added to prevent the aggregation of precipitating particles. We added 15-20 cc sodium selenite solution prepared in water in the zinc acetate solution. The amount of sodium selenate depended on its concentration. For the 15-20 cc volume the strength of solution was approximately 0.5M in the water. Upon mixing both solutions, a cloudy precipitation of nanoparticle started immediately. A continuous stirring was provided, and an orange color product was observed. Solution was fluxed using a condenser and round bottom flask as shown in **Figure 1.** The solution was refluxed for a time of 3 hrs. We heated and

continuously stirred this solution and temperature was maintained between 95 and 100℃ to ensure the complete the reaction. Nanoparticles were formed and a grey-green colored colloidal precipitate on the bottom and a clear layer was observed on the top portion.

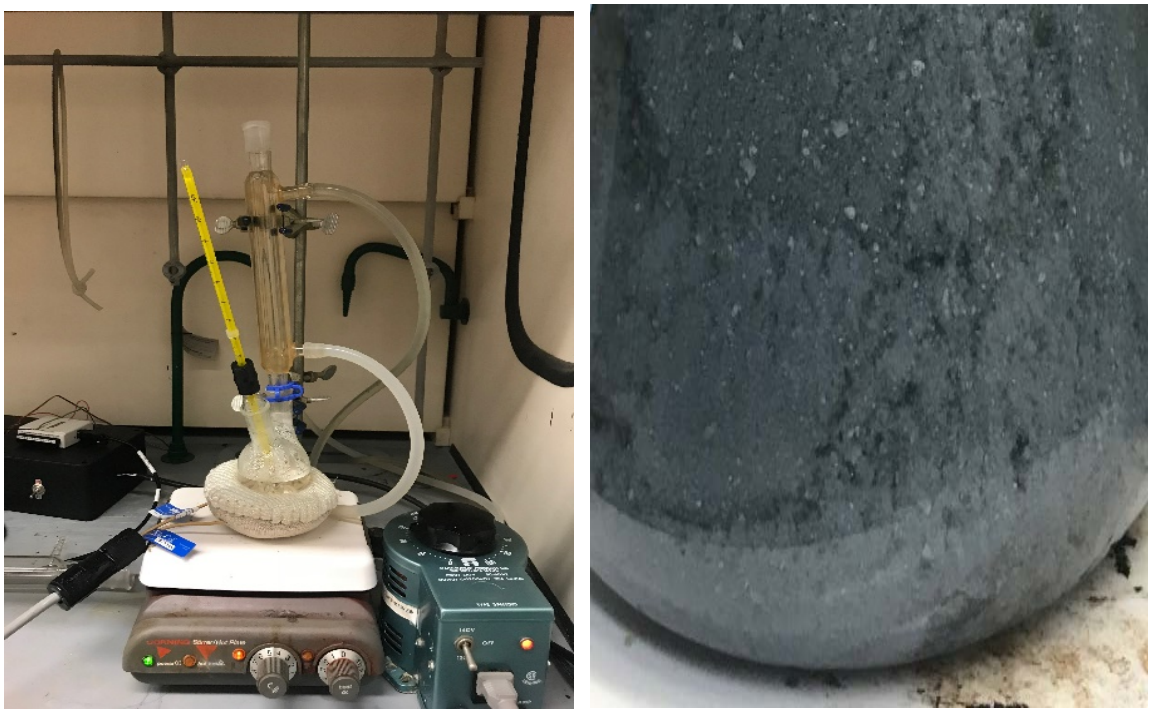

Figure 1. (a) Solution was refluxed for a period of three hours and **(b)** grey-green colored precipitate on the bottom.

For the cobalt doping, process was similar to that used for the preparation of pure ZnSe nanocrystals and approximately 0.1g of cobalt chloride hexahydrate was added and stirred continuously. To evaluate effect of doping level, we had experimented several amounts of doping up to 0.4g. A dense and coarse precipitate was observed with the increased doping. We prepared 50 cc of this solution. The temperature of the solution was raised to 95-100℃ and maintained for an hour. It was observed that the solution turned a dark magenta red color, which faded in few minutes. It was observed that the doped colloidal/precipitate layer was a green-grey light color in the bottom portion. The colloidal precipitate formation was observed as soon as the reaction started, and color changed to cloudy white. In the pre-capping experiment capping agent was added before adding cobalt chloride. Similar to the case of the post capping, the solution turned an orange red color during heating. The color of the reaction solution faded gradually during heating in approximately 30 minutes. The bottom precipitate layer was a green color, and

the solution layer was clearly separated**.** The color transition in the Co-doped ZnSe nanoparticles when pre-capping process was used was slightly different from the post capping case. A light green color after 30 minutes of refluxing was observed and the reaction solution produced a green precipitate.

2.2 Measurement of particle size: Particle size of the prepared material was determined by light scattering experiments using the dynamic light scattering apparatus Malvern Zetasizer Nano-ZS.

2.3 Nano and Micromorphology: Scanning electron microscope (SEM) model NOVA NANOSEM 450 under a voltage of 5 and 10 kV determined the morphology of crystals.

2.4 Optical Evaluation: To evaluate effect of agglomeration on the optical properties, measurements were performed using an Edinburg F920 fluorescence spectrometer with xenon source and cadmium selenide detector for the emission and photoluminescence studies. The Acton SpectraPro 500i software was used for this study and software developed by Princeton Instrument was utilized. For excitation we used power in the range of 35mW at room temperature. All studies were performed for the 10 accumulations using 1-second acquisition time and one nm steps.

3. Results and Discussion

Doping of ZnSe caused complexity such as precipitation, clustering/agglomerations, and reactions between nutrients in the solution during synthesis at low temperature. **Figure 2** shows morphology of cobalt doped ZnSe nanoparticles synthesized by reactive solution growth method. Nano and micro particles were jointed together and binded strongly. We observed that grains grew in few micrometer sizes and grew in the same orientation. The detailed morphological evaluation showed that grains were faceted and jointed together. The aging effect of the material was studied by placing for a period of one months at room temperature to evaluate stability and segregation. It was observed that large number of clusters were grouped together**.** This indicates some type of very slow coarsening occurring at room temperature in the doped material as function of time. These agglomerates were expected since the solution was kept for a term of one month and grains grew due to nutrients from the solution. This data corroborates the SEM morphology. It showed

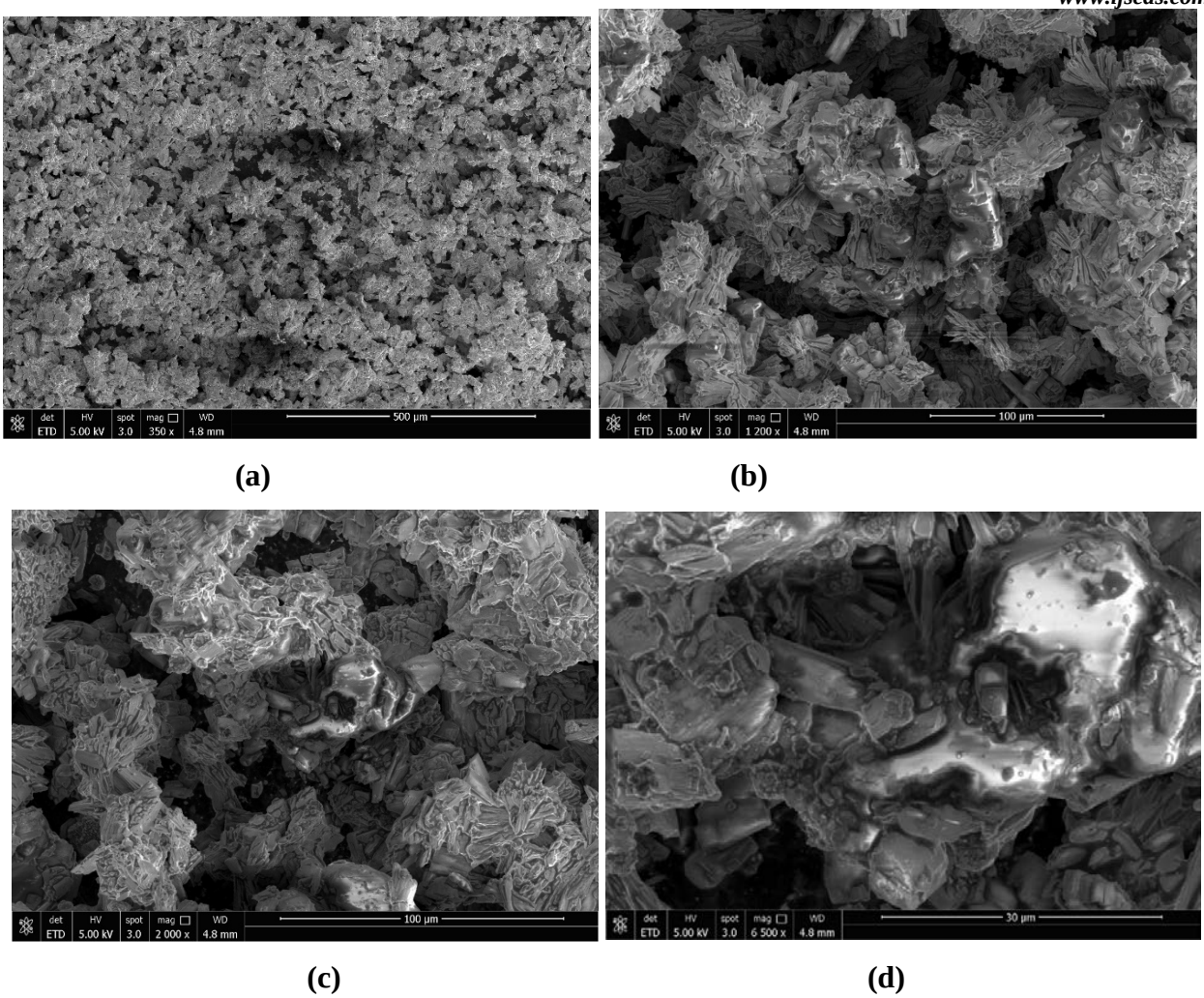

Figure 2. (a) Micromorphology of a high concentration Co doped ZnSe nanoparticles (b) transition of particles and stabilization into faceted shapes. (c) Stable morphology showed facetted grains aggregated together when high concentration of cobalt doping was used and (d) effect of aging of high concentration material at room temperature,

clusters and coarsened particles of different sizes (**Figure 2a, b)**. These were observed as small, faceted needles or plates. Each grain are totally separated. There are sharp boundaries, and we did not see large range of attached boundaries. The surfaces look very rough, and it appears as a disc before it forms rectangular crystallite. This also indicates that strong faceting may be due to cobalt doping which may have altered the surface anisotropy of the solution grown ZnSe particles. With increasing concentration of cobalt aggregation increased significantly. As shown from the size measurements also, with increasing concentration larger size clusters of particles

were observed. To understand the formation of particles we had performed short term refluxing experiments. **Figure 2 (c)** also shows transition of morphologies to facetted and bunched structures. The effect of aging was studied by placing the particles in the grown container for a period of three weeks. As shown in this **Figure 2 (d)**, coarsening of particles was observed. Small particles Co-ZnSe of various shapes started dissolving and nucleated and stabilized into large, faceted shapes and join to form aggregates. It is clear that larger grains are growing at the expense of dissolution of small grains by channeling mechanism which creates localized solution to provide nutrients. White shiny region shown at high magnification in **Figure 2d** shows meta stable regions for driving grain growth and coarsening of materials.

The effect of dopant concentration on the size of particle was studied by synthesizing Co-ZnSe with concentration of cobalt solution of 1.0, 2.3, 4.5 and 5.0 $x10^{-3}$ mole. Doping did not have significant change in shape of particles. All solutions has identical faceted morphology with a significant difference in sizes and aggregation. The higher concentrations of cobalt in the solution resulted in larger aggregates which was confirmed by DLS. For the lowest concentration we observed average size of 186-426 nm with a main peak at 216 nm and other smaller peaks observed at roughly 0.7 nm and 1 nm. The peak at 2931 nm was due to large clusters of nanoparticles. There was no major difference between main peak around 216 nm for this sample and the $2.3x10^{-3}$ mol cobalt doped solution. Similarly, for the ZnSe doped with $4.5x10^{-3}$ mol cobalt solution the average size was 350-900 nm with a peak at 600 nm. The average size for highest concentration doping was in the range of 3151-5213nm with a peak at 4182nm, indicating significant aggregation. This solution also showed a very week peak below 1 nm. We observed that the concentration of the dopant affected the agglomeration characteristics significantly. We observed that with increasing cobalt concentration, overall particle size also increased. It was observed that pre-addition of capping agent before the growth of ZnSe nanoparticles in both undoped and doped cases produced significantly lower clustering of nanoparticles. This was helpful in achieving reduced formation of needles in the solution and indicates that it may be changing the anisotropy thus producing faceted structures. Further studies on the pre and post capping agent and their amount may clarify this issue.

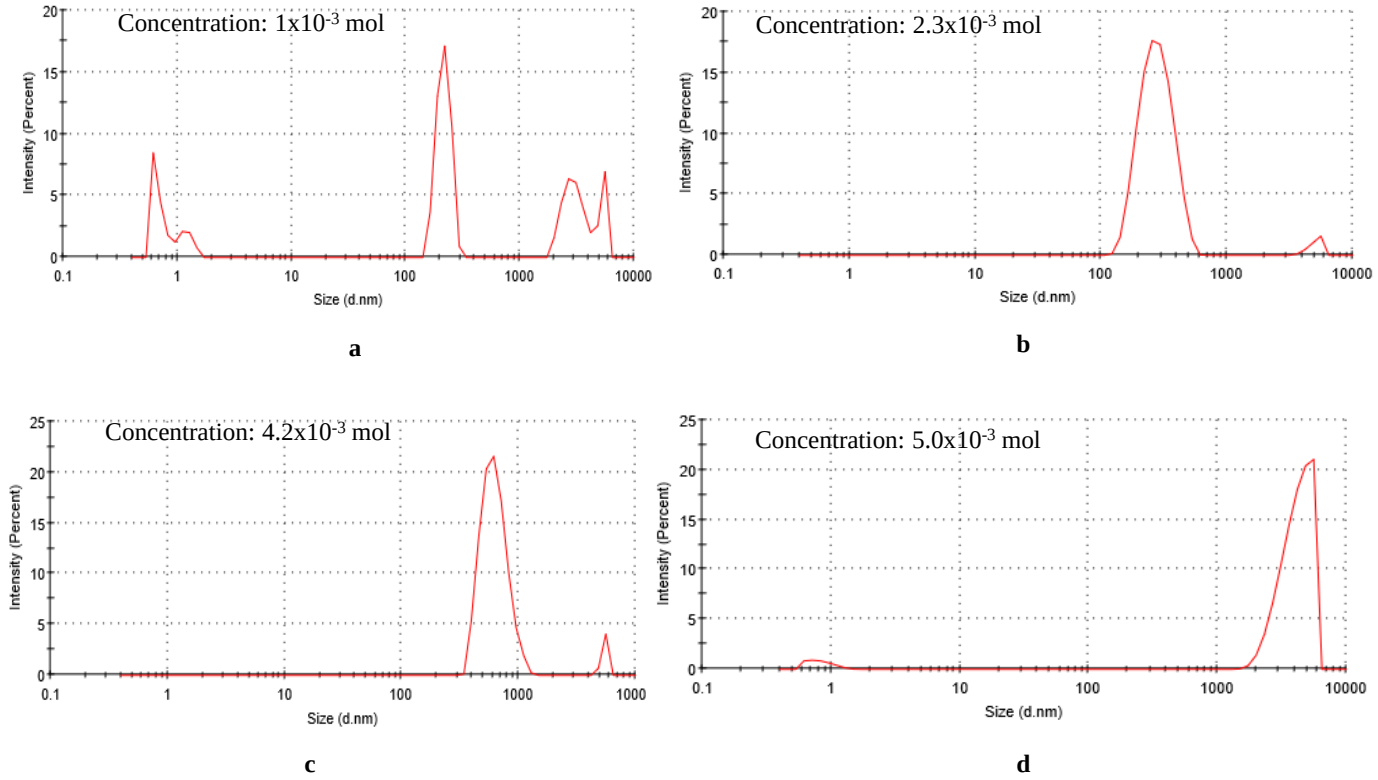

Figure 3. DLS characterization of nanoparticle size of Co:ZnSe with varying cobalt incorporation. **(a).** ZnSe doped with $1.0x10^{-3}$ mol Cobalt chloride solution. (b) ZnSe doped w/ $2.3x10^{-3}$ mol Cobalt chloride solution. (c) ZnSe doped w/ $4.5x10^{-3}$ mol Cobalt chloride concentration.(d) ZnSe doped with $5.0x10^{-3}$ mmol Cobalt chloride concentration..

3.2 Optical Characteristics

The transmission curves for ZnSe and Co:ZnSe nanoparticles are shown in **Figure 4**. Using the cutoff wavelength of the transmission curve, the bandgap can be estimated using the relationship:

$$E_g = \frac{1.240}{\lambda_{Cutoff}}$$

The bandgap of the pure ZnSe nanoparticles was estimated as 4.6 eV and 4.8 eV for the Co:ZnSe nanoparticles. This indicates that Co doping increases particle size and also bandgap. This requires more experiments to determine if the bandgap widening is based only on changes in nanoparticle size or other factors. It is important to note that these are estimations used to identify trends in the material and that the actual band gaps may be smaller.

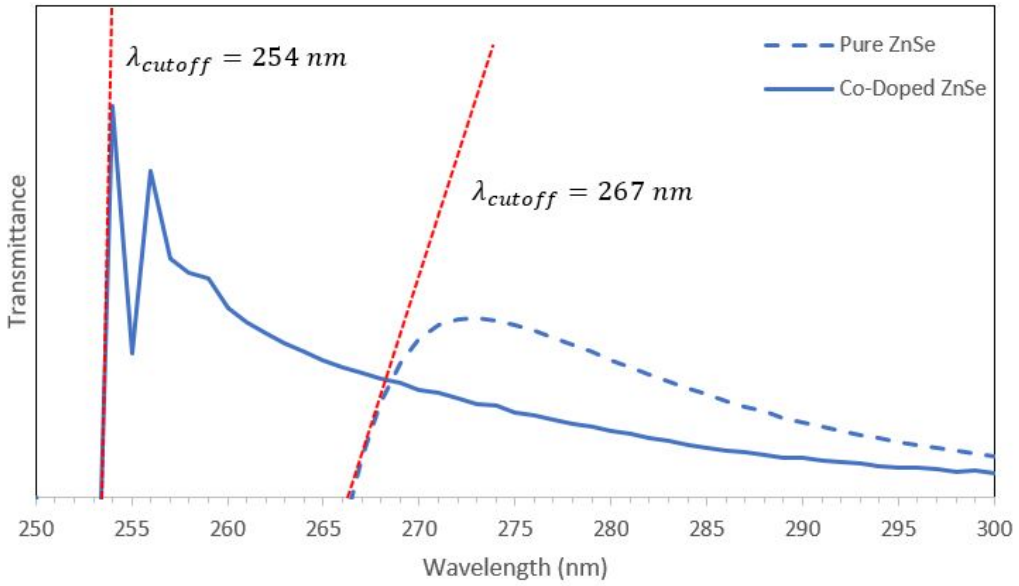

Figure 4. Transmittance of Co:ZnSe colloidal nanoparticles. Cutoff wavelength of 268.2 nm is used in estimation of bandgap of material.

The fluorescence spectra of pure ZnSe and Co-ZnSe materials synthesized determined at room temperature in solution using a 280 nm wavelength excitation source. The pure ZnSe spectrum shows main peak at 337 nm. The main peaks for ZnSe and Co-ZnSe are observed at 337 nm and 274 nm, respectively. The separation between the doped and undoped materials peaks increased from 13 nm to 63 nm, that is 0.2 eV to 0.8 eV. This increased separation is caused by nanoparticle agglomeration and further experimentations will determine if this is indeed a large stokes shift. This does not negate the trend of increased Co doping concentration increasing the nanoparticle size because this size discrepancy is purely due to aggregation of the pure ZnSe nanocrystals after synthesis. Also, it is possible that in case of the nanoparticles in solvent, the increase in the size of the solvation cage due to agglomeration may cause new bands that appear. It is expected that the rearrangement energy for potentially broad structures is altered with changes of particle size. The Co-doped nanoparticles ZnSe showed has higher intensity of emission. Future work will be focused for nanoparticles of similar sizes to clarify the dominant factor in band gap tunability, as well as the impact of Co-doping on nanoparticle growth rate by adjusting the concentration of the thioglycerol capping agent to prevent aggregation of particles in solution.

4. Summary

A low temperature reactive solution growth process was used to synthesize pure and cobalt doped ZnSe nanocrystals using zinc acetate and sodium selenite as the source materials. Cobalt dopant was determined to be 1.0, 2.3, 4.5 and 5.0 $x10^{-3}$ mole in the solution. The concentration of the dopant affected the agglomeration significantly. The grown particles showed significant difference in the size of the particles between the cobalt doped ZnSe nanoparticles and undoped bulk ZnSe crystals. It was observed that the addition of a capping agent before the growth of ZnSe nanoparticles in both undoped and doped cases significantly reduced agglomerates. The morphology of the cobalt doped particles were faceted, and clustering was significantly higher as the function of the doping concentration . ZnSe nanocrystals of both pure and Co-doped ZnSe yielded much higher bandgap compared to that of reported value for the bulk ZnSe crystals.

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