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**Effect of Se concentration on mixed phonon modes and spin orbit splitting in thermally evaporated CdSxSe1−x (0 ≤ *x* ≤ 1) films using CdS–CdSe nano-composites**

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**Highlights**

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CdSxSe1−x films are prepared by [thermal evaporation](https://www.sciencedirect.com/topics/physics-and-astronomy/thermal-evaporation) of nanocomposite powder.

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SO splitting decreases with decrease in Se concentration.

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Observed [phonon](https://www.sciencedirect.com/topics/physics-and-astronomy/phonon) modes frequency and intensity change with Se concentration.

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FWHM and intensity of the disorder ZE phonons decrease with Se content.

**Abstract**

[Thin films](https://www.sciencedirect.com/topics/materials-science/thin-films) of CdSxSe1−x (0 ≤ *x* ≤ 1) are prepared by simple [thermal evaporation](https://www.sciencedirect.com/topics/physics-and-astronomy/thermal-evaporation) technique using CdS–CdSe nanocomposite powder. Though the starting powder had been a nanocomposite, the structural and [optical properties](https://www.sciencedirect.com/topics/materials-science/optical-property) of the films confirm that these are [ternary alloys](https://www.sciencedirect.com/topics/materials-science/ternary-alloy) CdSxSe1−x. Systematic shifts in position of diffraction peaks in X-ray [diffraction pattern](https://www.sciencedirect.com/topics/physics-and-astronomy/diffraction-pattern) and absorption edge in transmission spectra is observed as the concentration of S and Se atoms changes in the films. A plot of (αhν)2 *vs* hν exhibit two linear regions for films containing Se atoms corresponding to two direct transitions; (�8�→�6�) and (�7�→�6�) due to spin orbit (SO) splitting of the valence band. The SO splitting decreases with decrease in Se concentration in the films. Raman measurements on the [ternary alloys](https://www.sciencedirect.com/topics/physics-and-astronomy/ternary-alloy) exhibit two [phonon](https://www.sciencedirect.com/topics/physics-and-astronomy/phonon) modes corresponding to CdS and CdSe LO vibration, with a small shift in peak position with composition. In addition, signature of disorder induced zone edge phonons are also observed in all the films containing S atoms.

**Introduction**

CdSe and CdS are well known II–VI binary compound semiconductors widely used as photoconductors in various electronic devices and as an *n*-type layer in CdTe and ZnTe based heterojunction solar cells owing to their suitable direct band gaps [1], [2], [3], [4], [5], [6], [7]. Several low cost techniques such as chemical bath deposition [8], spray pyrolysis [9], physical thermal evaporation [10], solvothermal [11], [12], hydrothermal [13], etc., have been successfully used to synthesize these binary compounds in the form of thin films as well as nanostructures. Alloying of these two binary compounds to form new ternary CdSxSe1−x (0 ≤ *x* ≤ 1) alloys has also been contemplated and achieved through several techniques such as laser ablation [14], mechanical alloying [15], chemical bath deposition [16], etc. The structural and optical properties of the resulting CdSxSe1−x (0 ≤ *x* ≤ 1) material lie between the respective properties of the end binary compounds. Reported literature [17], [18], [19] have shown that the material properties can be properly tuned by controlling the material composition. This ability to tune the band gap and electrical properties by varying the composition of ternary alloys opens up a huge possibility of fabricating of a number of devices for specific applications.

Besides being technologically important, binary and ternary alloys of II–VI compounds also exhibit interesting physical phenomenon. For example, a single absorption edge is observed in transmission spectra of pure CdS crystals [20], whereas in case of CdSe crystals, optical transitions corresponding to two direct transitions (�8�→�6�) and(�7�→�6�), have been reported [21], [22], [23]. The occurrence of two direct optical transitions at k = 0 are referred due to spin orbit splitting of the valence band introduced by heavier Se atoms. Direct experimental observation of spin orbit splitting, however, has not been much explored for CdS/CdSe binary and ternary alloys, single crystals and thin films.

Another interesting feature which has been observed in II–VI ternary alloy system is occurrence of two phonon modes corresponding to two binary alloys. For example, in case of CdSxSe1−x alloys, Raman spectra show peaks due to vibrational modes of both CdS and CdSe bonds. This is quite different than the observation of single phonon modes for ionic crystals such as NixCo1−xO, KClxBr1−x, NaxRb1−xI, etc [24], [25]. A few reports, both theory and experimental, on Raman scattering studies on these ternary alloys system are available in literature [24], [25], [26]. However, the experimental work is mostly limited to nanocrystallites of these compounds dispersed in glass matrix [27] and sometimes on nanocrystals having nearly equal concentration of S and Se atoms in CdSxSe1−x alloys [14].

In the present paper, we report structural and optical studies on films of CdSxSe1−x alloys (0 ≤ *x* ≤ 1). The films are prepared using simple thermal evaporation technique with starting material as nanocomposites of CdS/CdSe, which were synthesized using solvo-thermal route. It therefore, has a much better control on the composition of the films. The XRD and UV–Vis–NIR transmission studies show that the films are uniform in thickness and unlike starting material, have single phase. The Se containing films also exhibit two optical absorption edges, corresponding to (�8�→�6�) and(�7�→�6�), arising as a result of spin orbit splitting due to presence of Se atoms. The difference in band gap corresponding to two absorption edge decreases with the decrease in Se concentration in the films. Raman scattering studies suggest the presence of phonon modes corresponding to both CdS and CdSe, however, a shift in vibrational frequencies is observed with composition. In addition to dual phonon modes, deconvolution of asymmetric peak corresponding to CdS LO mode indicates the presence of disorder induced zone edge phonons in films containing S atoms. To the best of our knowledge, this is the first systematic study of structural and optical properties of CdSxSe1−x ternary alloy thin films having a large range of composition variation.

**Section snippets**

**Experimental section**

CdSxSe1−x thin films (with x = 0, 0.17, 0.35, 0.64, 1) are prepared on corning 1737 glass by thermal evaporation of solvothermally synthesized CdS, CdSe and CdS–CdSe composite powders. In this solvothermal process, cadmium acetate [(CH3COO)2Cd. 2H2O], sodium sulfite [Na2SO3] and sodium selenite [Na2SeO3] are used as precursor for cadmium, sulfur and selenium ions respectively. A mixed solution made up of appropriate amount of ammonia (NH3. H2O), hydrazine hydrates (N2H4. H2O) and de-ionzed

**Results and discussion**

The elemental composition of the synthesized CdS–CdSe nanocomposite powders along with the SEM images and the corresponding EDX spectra are given in Fig. 1. Though it is not possible to get the crystallite size using SEM images, the elemental compositions shown in the figures were obtained by taking the average of the values measured at 2–3 different locations. The XRD patterns (Fig. 2) of two of the synthesized composite powders exhibit diffraction peaks corresponding to the hexagonal planes

**Conclusion**

Though, the preparation technique of CdSxSe1−x (0 ≤ *x* ≤ 1) thin films developed in this work is a bit lengthy as it involves two step processes, it, however, does not require sophisticated instruments and the starting compound is prepared using already well established low cost processes. The thin films have uniform deposition with good crystallinity and tunable structural and optical properties. Valance band splitting due to Spin orbit coupling, as reported for binary CdSe compound has also

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