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Elucidating the Relationship between Crystallo- Chemistry and Optical properties of CIGS Nanocrystals

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ABSTRACT

The performance of solar cells fabricated using Cu(In,Ga)(S,Se)_2 nanocrystal (NC) inks synthesized using the hot injection method has yielded efficiencies up to 12% recently. The efficiency of these devices is highly dependent on the chemical composition and crystallographic quality of the NCs. The former has been extensively discussed as it can be easily correlated to the optical properties of the film, but detailed crystallographic structure of these NCs has scarcely been discussed and it can influence both the optical and electrical properties. Hence both chemical composition and crystal structure should be explored for these NCs in order for this material to be further developed for application in thin film solar cells. In this work, a thorough investigation of the composition and crystal structure of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs synthesized using the hot injection method over the entire composition range ($0 \leq x \leq 1$) has been conducted. Raman spectroscopy of the NCs complements the information derived from x-ray diffraction (XRD) and electron probe microanalysis (EPMA). EPMA, which was carried out for the first time, indicates good controllability of the NC Ga/(In + Ga) ratio using this synthesis method. Raman spectroscopy reveals that CuInSe_2 NCs are a mixture of chalcopyrite and sphalerite with disordered cations, whereas CuGaSe_2 NCs are purely chalcopyrite. The lattice parameters determined from XRD were found to deviate from those calculated using Vegard's law for all compositions. Hence, it can be deduced that the lattice is distorted in the crystal. The optical and electrochemical band gap of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs increases as the Ga content increases. The energy band gap deviates from the theoretical values, which could be related to the contribution from cation disordering and strain. These results help to tailor the opto-electrical properties of semiconductors, which inherently depend on the crystalline quality, strain and composition.

1. Introduction

The fundamental physical/electrical properties of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ make it uniquely suited for solar cell applications [1]. To date the maximum efficiency achieved for $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ thin film solar cells is 22.6% [2]. Current manufacturing processes for these thin film solar cells involve the use of vacuum deposition, which makes the cost of commercial production of this type of solar cell relatively high. Therefore, a solution to tackle this issue has to be found.

The hot injection method has been successfully adapted to the synthesis of a wide range of semiconducting chalcogenide nanocrystals (NCs) for low cost solution processable solar cells [3]. Recently, device performance testing of solar cells made using $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (abbreviated as CIGS and CIGSe for sulfur and selenium anions, respectively) NCs from nanocrystal inks has yielded efficiencies up to 12% [4]. However, this field is still at its early stage of research and further improvement is needed. One of the major problems in the development of solution-processed inks is the ability to obtain CIGSe films with uniform and well-controlled composition profiles over large areas. Because of the complexity of CIGSe, device performance can be significantly affected by local composition, non-uniformity and impurity phases. Other than that, grain boundaries are active recombination centers for photo-generated carriers and CIGSe films must exhibit either large or passivated grains in order to achieve attractive device performance for commercial applications (>10%) [4]. Although considerable progress has been made in the development of bulk ternary and quaternary $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ systems, improved crystallo-chemical understanding of this system, particularly in NC form, is still required to understand how to optimize the properties for solar cell applications.

The fundamental chemical and physical properties of quaternary $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ materials can be tuned over a significant range using both chemical substitutions and structural modifications [1, 5]. For instance, compositional control in these quaternary semiconductors offers the possibility to tune the energy band gap and hence the opto-electrical properties of these materials. This ability to change the band gap through compositional variation is highly beneficial for their application in solar cells. Bearing this in mind, the precise control and accurate determination of the elemental composition of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ is essential. On top of this, the crystallography of the NCs, such as phase, strain, defects, etc, will also affect the properties of the final films and ought to be studied in tandem with the compositional evaluation.

In this paper, we present the use of electron probe microanalysis (EPMA) for the precise determination of the stoichiometry and the use of x-ray Raman spectroscopy to determine the crystallographic information. Accuracy in EPMA comes from better probe current control coupled with calibration standards. This analysis is conventionally more commonly used for the quantification of bulk samples due to the large x-ray interaction volume (a few hundred nm to μm). It is possible to extend this technique to thin film and/or nanoparticle investigations because of the possibility of accurately determining the film thickness or the nanoparticle size using other methods and hence of offsetting the larger interaction volume. $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs with a range of Ga to In ratios were prepared using the hot injection method.

Stoichiometric CuInSe_2 exists in various crystal structures and it commonly crystallizes as chalcopyrite, which is the stable phase at room temperature [1]. This phase is body centered tetragonal (space group $I\bar{4}2d$, $c \approx 2a$) with Cu at 0, 0, 0, In at 0, 0, 0.5 and Se at 0.227,

0.25, 0.125. When Ga is introduced into $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$, it shares the same lattice site as In i.e. 0, 0, 0.5. Each Se is coordinated by two Cu and two In/Ga atoms and each Cu and In/Ga is coordinated by four Se atoms. Random distribution of the cations leads to the formation of sphalerite (space group $F\bar{4}3m$) [6] with ...ABCABC... stacking and wurtzite (space group $P6_3mc$) [7], with ...ABABAB... close-packed stacking (figure 1) both of which are thermodynamically unstable at room temperature. Nanocrystals synthesized via the solution route may exhibit mixed structures due to the numerous inherent metastable processes involved, which can have profound effects on the properties. As the major Bragg peaks of chalcopyrite and sphalerite occur at similar scattering angles (2θ), x-ray diffraction (XRD) alone is insufficient to determine the existence of mixed phases. Shirakata et al [8] reported using Raman spectroscopy as a complementary characterization tool for phase determination and the observed Raman active modes of CuInSe_2 at 182 cm^{-1} coexisting with 175 cm^{-1} are attributed to sphalerite with disordered cation atoms and chalcopyrite structures respectively.

Despite many studies of this material, systematic knowledge of the crystal structure and micro-strain induced in the lattice in NCs is still limited. These structural variations and the crystal lattice distortion can alter the properties of the materials and hence a systematic characterization accompanied with optical studies of the NCs is very important. Herein we report a detailed investigation of the composition and crystal structure of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs synthesized using the hot coordinating solvent method over the entire composition range ($0 \leq x \leq 1$) by XRD, Raman scattering, EPMA, transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), UV–visible spectroscopy and cyclic voltammetry (CV) and discuss the effects of structural variations on the optoelectronic properties.

2. Experimental details

2.1. Synthesis of wide stoichiometry $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs

Quaternary $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs ($0 \leq x \leq 1$) were synthesized by reacting metal-hexadecylamine (HDA) complexes with a Se-HDA suspension. A typical synthesis of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ NCs has been described in detail in our previous work [9]. A typical synthesis procedure for synthesis of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ NCs start with heating a stoichiometric mixture of 0.2 mmol CuCl (Sigma-Aldrich, 99.995%), 0.1 mmol InCl_3 (Sigma-Aldrich, 99.999%) and 0.1 mmol gallium (III) acetylacetonate ($\text{Ga}(\text{acac})_3$, Sigma-Aldrich, anhydrous $\geq 99.999\%$) and 6.5g of n-Hexadecylamine (HDA, Sigma-Aldrich, 95%) in a 50 mL three-neck flask in an oxygen free environment to 80°C and degassed for 1h. The complete dissolution of cation precursors at around 130°C was confirmed by a change in the color of the solution from blue to yellow. A suspension of 0.4 mmol selenium powder (Se, Kanto Chemical Co. Inc., 99.0%) in 4g of HDA was heated to 50°C and injected into the reaction flask at 130°C under constant stirring and nitrogen flow. The mixture was further heated to 240°C and held for an hour. After the reaction was completed, the mixture was cooled down to 60°C . Toluene and methanol were added to the solution and sonicated for 10 mins to remove residual ligands and also the unreacted precursors. The solution was then centrifuged at 9000 rpm for 20 min, followed by 7000 rpm for 10 min. The supernatant was discarded for each centrifugation and the NCs were redispersed in toluene before the next centrifugation.

By varying the precursor ratio, $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs of the required compositions were synthesized using the same route described for $x = 0.5$.

2.2. Materials Characterization

The compositions of the as-prepared $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs were quantitatively determined using energy probe microanalysis (EPMA) equipped with five wavelength dispersive

spectrometers (WDS). Drop cast samples were deposited on a Si substrate followed by carbon coating. The analysis was carried out at 12 keV with a beam current of 20 nA employing Cu metal, InSb, GaAs and Bi₂Se₃ as the standards for Cu, In, Ga and Se respectively. The ratio of the x-ray intensities collected from the sample and those from the standard at the same accelerating voltage (k-ratio) was calculated. This was used to calculate the weight percentage of the various components using the Bastin and Packwood correction for thin films [10], given a known nanoparticle size. For each composition the average of a few areas of drop cast samples was taken. The phase and crystallographic structure of the NCs were characterized using grazing incidence x-ray diffraction (GIXRD) performed using a Bruker D8 Advance with a fixed θ of 0.5°, scanning rate of 0.2° min⁻¹, step size of 0.02° and 2 θ range from 10 to 80°, using CuK α radiation ($\lambda_{\text{ave}}=1.54\text{\AA}$) at 40 kV and 40 mA. The starting Rietveld refinement model used CIF files of CuInSe₂ [11], CuGaSe₂ [12] and CuIn_{0.52}Ga_{0.48}Se₂ [13]. The fundamental parameters peak-shape profile was used; a five-coefficient Chebychev polynomial and 1/ x background, zero error, scale factors, unit cell parameters and crystal size were sequentially refined using the TOPAS V4 program [14]. The weight percentage of each phase was calculated based on quantitative phase analysis using the Rietveld method [15]:

$$W_a = \frac{S_a(ZMV)_a}{\sum_i S_i(ZMV)_i} \quad (1)$$

where W_a is the weight fraction of phase a , S is the Rietveld scale factor, Z is the number of formula units in a unit cell, M is the molecular mass for a formula unit and V is the unit cell volume. The micro-Raman spectra were recorded from 50 to 600 cm⁻¹ by using an XY Dilor–Jobin Yvon–Spex spectrometer attached to an Olympus microscope, equipped with a double monochromator and a multi-channel detection system. The 632.8 nm He–Ne laser line was used as an irradiator source with a power density of 20 mW and an Olympus $\times 100$ objective.

Spot size was estimated to be around 413 nm. Laser power density was controlled by a neutral variable density filter incorporated before the microscope optics. The size and morphology of the NCs was characterized using transmission electron microscopy (TEM). Samples for TEM were prepared by dropping NCs dispersed in toluene onto lacey carbon-coated copper grids. TEM studies were carried out using a JEOL 2100F microscope at an acceleration voltage of 200kV. To identify the oxidation state of the samples, electron energy loss spectra (EELS) were collected with a Gatan imaging filter (GIF) on a Philips CM 300 TEM. For optical characterization, the NCs were dispersed in toluene. The ultraviolet-visible/near infra-red (UV-Vis/NIR) absorption spectrum of the NCs was obtained using a UV-VIS/NIR PerkinElmer Lambda 900 spectrophotometer at room temperature and under ambient conditions with wavelengths ranging from 300 to 1300 nm (step size of 0.5 nm).

Cyclic voltammetry (CV) measurements were performed on an Autolab PG302N electrochemical workstation. Carbon and gold electrodes were used as working and counter electrodes respectively. The reference electrode was a Ag/AgCl electrode with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in acetonitrile as the supporting electrolyte. The ferrocene/ferrocenium couple was utilized as an internal standard [16]. A few drops of diluted NC suspension in chloroform were deposited onto the surface of the working electrode to form an NC film. The scan rate was set at 100 mV/s and during all the measurements, the electrolyte solution was deoxygenated by bubbling N₂ gas through it for 10 min. In this measurement, a treatment with hydrazine was used to remove the ligands by soaking the working electrode (coated with CuIn_xGa_{1-x}Se₂ NCs) in 0.1 M solution of hydrazine in acetonitrile for 30 s leading to an improvement in the electrochemical measurements.

3. Results and discussion

3.1. Morphological and compositional study of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ nanocrystals

Table 1 shows a comparison of the measured values of x in $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ using EPMA with the nominal values (according to the stoichiometry of the starting reaction). A value for the thickness comparable to the interaction volume of the NCs was used in calculating the composition from EPMA. The Cu:Se ratio was found to be within 1 standard deviation of the molar ratio, 1:2, while the Ga:(In+Ga) ratio deviates from the starting precursor ratio. This indicates that the NC stoichiometry is controlled well using this synthesis method. The morphologies of the synthesized $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs were investigated using TEM. As shown in Figure 2 across the whole composition range, the NC size distribution is relatively narrow with a nearly spherical morphology. TEM images suggest that the average particle size for all the $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs synthesized using this hot coordination route was around 20 nm and the change in composition did not change the size of the NCs. This indicates that even though the decomposition temperature and reactivity of the In and Ga precursors are different [17], the presence of HDA in the precursors makes the reactivity comparable as the creation of precursor complexes allows the reaction to occur at lower temperature [18]. This helps achieve a narrow size and shape distribution with a range of compositions. Identical reaction parameters were used throughout the whole series, which makes composition control in the hot coordination method simple compared to other synthesis methods.

EELS (Figure S1, supporting information) of the $\text{CuIn}_{0.49}\text{Ga}_{0.51}\text{Se}_2$ compound confirmed that all the four elements are present with their expected oxidation states (Cu^+ , In^{3+} , Ga^{3+} , Se^{2-}). From the In EELS in Figure S1, the edge at around 532 eV is indicative of the presence of oxygen, for which there are many possible sources. Since there are no distinct crystalline

oxides present as seen from the x-ray diffraction pattern, the oxygen could be present in the $\text{CuIn}_{0.49}\text{Ga}_{0.51}\text{Se}_2$ compound in other forms, e.g. substituting for Se as a surface oxide in the form of Cu-O or In-O (most probably amorphous). This was compared with reported EELS of In_2O_3 nanowires and it was found to be very similar [19]. From a comparison of CuO and Cu_2O EELS [20] with the Cu edge in as synthesized Cu_2Se and $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ NCs (Figure 3), it can be concluded that the presence of oxygen in these NCs did not have a major effect on the shape of the Cu edge. Therefore, there might be only some traces of amorphous In_2O_3 in the sample as it was not observed in the XRD pattern.

3.2. Microstructural study of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ nanocrystals using Raman spectroscopy and x-ray diffraction analysis

The major Bragg peaks in the XRD patterns of both chalcopyrite and sphalerite CuInSe_2 occur at similar 2θ values. Hence to detect the presence of the chalcopyrite phase, the weak 211 and 301 reflections must be present. However, it is nearly impossible to de-convolute these two phases if they coexist in the samples. In addition, the presence of micro-strain and preferred orientations of the NCs often perturbs the relative intensity of the XRD patterns, complicating any attempt to distinguish the structures.

Previous studies have shown that through the use of Raman spectroscopy, structural variations (sphalerite and chalcopyrite) in CuInSe_2 thin films can be detected when XRD fails to do so [8]. Raman spectroscopy also provides information on the crystalline quality, strain and compositional variation in semiconducting materials which will in turn affect the opto-electrical properties. In the present work, Raman spectroscopy was carried out to determine the crystal structures present in CIGSe NCs. This study was conducted for the first time on $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs with a range of compositions.

Raman spectra from the $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ compositions used here are shown in Figure 4 and illustrate the various phonon modes of the $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ chalcopyrite structure. The most intense peak occurs in between 175 cm^{-1} and 188 cm^{-1} for all $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$, compositions and this corresponds to the A_1 optical phonon mode of the symmetric vibration of Se atoms in the c -plane, which is in agreement with previous studies [21].

The A_1 mode Raman peak from the $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ chalcopyrite structure [11] was reported to be at $174\text{--}175\text{ cm}^{-1}$ for $x = 1$ [8], and its Raman shift increases according to the equation: Raman shift (cm^{-1}) = $-13x + 188$ [22]. Another Raman peak observed at 183.4 cm^{-1} for $x = 1$ is not related to the chalcopyrite active mode but to a phonon mode related to the sphalerite lattice with disordered cations [8]. This cation disordering of the Cu^+ , In^{3+} and Ga^{3+} ions at the $4a$ Wyckoff site (0, 0, 0) in $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ causes anti-site defects, creating both donors and acceptors.

The majority of the peaks in the Raman spectra match those for chalcopyrite. In addition, only the spectrum for CuInSe_2 shows a clear and sharp S peak, while for the rest of the samples, the presence of S is indicated by a shoulder, and from the increasing A_1 area compared to S area, it is possible to deduce that the chalcopyrite phase has increased as the Ga content increases. This shows that the crystal structure is mainly chalcopyrite although some parts of the cations are disordered (i.e sphalerite). To the best of our knowledge, there is no report of Raman spectra from single-phase sphalerite since this is the high temperature phase and thermodynamically the chalcopyrite phase is favored at room temperature. Figure 5 illustrates the gradual shift of the A_1 and S peaks from CuInSe_2 to CuGaSe_2 as the Ga content increases. The increase of the A_1 mode frequency as the Ga content increases is

postulated to be due to mass reduction in the system since the mass of Ga is 61% of that in In [21]. With increasing In content (x), the fitted linear equations are:

$$\text{Raman shift (cm}^{-1}\text{)} = -9.598x + 183.5 \text{ (R}^2 = 0.899\text{) for the A}_1 \text{ mode} \quad (2)$$

$$\text{Raman shift (cm}^{-1}\text{)} = -8.251x + 190.9 \text{ (R}^2 = 0.957\text{) for the S mode} \quad (3)$$

Table 2 shows that the ratio of the area under the curve for the A₁ and S modes decreases with increasing x , which is proportional to the atomic ratio of chalcopyrite to sphalerite, with the CuGaSe₂ showing pure chalcopyrite phase. The fitted quadratic equation is:

$$\frac{\text{Area}_{A_1}}{\text{Area}_S} = 7.239x^2 - 14.73x + 9.663 \text{ (R}^2 = 0.993\text{)} \quad (4)$$

Hence, for the characterization of the cation disordering in CuIn _{x} Ga_{1- x} Se₂ NCs the Raman measurements are superior to powder XRD.

This study also confirmed that it is possible to monitor the stoichiometric changes since the Raman peaks shift away from the CuInSe₂ peak position to the CuGaSe₂ position when Ga replaces In by making use of the linear relationship between the A₁ peak position and intensity (Figure 5).

Besides the A₁ peak, multiple peaks between 212 and 273 cm⁻¹ correspond to either the B₂ or E mode or a combination of the two [22, 23]. Peak broadening can be attributed to disorder in the NC structure [8]. Previous studies of thin film CuIn _{x} Ga_{1- x} Se₂ reported that the peak at 260 cm⁻¹ is attributed to the Cu rich phase [8, 24]. The peaks between 212 and 273 cm⁻¹ were labeled for CuInSe₂ NC in Figure S2. In the present study, this peak is attributed to the B₂+E mode of CuIn _{x} Ga_{1- x} Se₂ NCs and also systematically shifts with the composition, similarly to observations in earlier reports [22, 23]. The Raman spectra from CuIn_{0.49}Ga_{0.51}Se₂ NCs in

Figure 4 also show that there are peaks between 100 cm^{-1} and 160 cm^{-1} which are labeled in Figure S3. Some of these peaks, such as the one at 124 cm^{-1} , are attributed to the B_1 mode of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ [23] while others are still unidentified. Since these peaks may not correspond to the $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ Raman phonon modes, based on previous studies, it was suggested that these peaks indicate the presence of ordered vacancy compounds (OVC), which are mainly related to Cu vacancies[21, 24, 25]. A previous study indicated that the peak at 155 cm^{-1} corresponds to the vibrational mode of the localized phonon due to a defective structure of the chalcopyrite phase with Cu-poor OVC [24, 26], in $\text{Cu}(\text{In, Ga})_3\text{Se}_5$ single crystal which was not detected by EPMA. The OVC peak is more prominent in $\text{CuIn}_{0.49}\text{Ga}_{0.51}\text{Se}_2$ NCs. Lastly, a strong vibrational peak was discovered in the Raman spectra of CuGaSe_2 near 274 cm^{-1} (B_2 mode of this composition) and the second order of this mode can be seen at 540 cm^{-1} [21]. The peak at 263 cm^{-1} matches the Cu_{2-x}Se impurity present in this compound (Figure 4). In principal, sphalerite is a high temperature meta stable phase of bulk CIGS. However, it was shown that NCs of the meta stable sphalerite phase of CIS can be synthesized via hot injection [7, 27]. It was demonstrated that adding the Se precursors at low temperature and increasing the temperature slowly to prevent high supersaturation will allow the atoms to organize into the thermodynamically preferred chalcopyrite phase [27] as we have observed in our work. Therefore, a metastable sphalerite phase in CIS cannot be induced by the localized heating induced by the micro-Raman measurement. However, we acknowledge that proper local power study needs to be conducted in the future as the Raman shift is commonly observed with different power.

XRD patterns from $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs with $(0 \leq x \leq 1)$ are shown in Figure 6 and all diffraction peaks show a systematic shift to higher 2θ angles with increasing Ga content. The shift can be attributed to the substitution of smaller Ga ions into larger In lattice sites (the

ionic radii of tetrahedrally coordinated In^{3+} and Ga^{3+} are 0.62 and 0.47 Å, respectively [28]). The unit cell parameters and reliability factors from Rietveld refinement of the diffraction patterns for $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs of the diffraction compositions are tabulated in Table S1. As mentioned in the introduction, it was difficult to model both chalcopyrite and sphalerite structures so only the former phase of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ was used and the accuracy of the results was confirmed by the good refinement fits as indicated in Table S1. The lattice parameters for the chalcopyrite phase derived from XRD patterns together with the idealized lattice parameters assuming a solid solution using Vegard's law are plotted in Figure 7. Although the volume of the unit cell follows Vegard's law very closely the unit cell parameter, c , deviates from that predicted using Vegard's law. The unit cell parameter, a , was expected to be smaller than that predicted to compensate for c . For $x = 0.25$ and 0.77 , the $c/2a$ ratio is close to unity, which metrically corresponds to cubic sphalerite. However from Raman spectroscopy, the clear peaks at 182.3 for $x = 0.25$ and 176.4 for $x = 0.77$, cannot be unambiguously assigned to the chalcopyrite A1 mode suggesting that although they are metrically cubic, the cations have an orderly arrangement leading to the doubling of c . More studies are required to understand and determine the structure properly. In CuGaSe_2 , approximately 4 wt.% of Cu_{2-x}Se impurity was observed (Figure S4) and this is consistent with the Raman peaks observed at 263 cm^{-1} .

3.3. Energy levels of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ nanocrystals (optical and electrochemical studies)

Figure 8 shows the optical absorption spectra of synthesized $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs as a function of the stoichiometric parameter, x . It can be observed that the absorption edge is in the visible region and there is a long absorption tail in the infrared region. Also, this tail is shorter when Ga is present. This observation is in line with the absorption spectra of bulk $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ [29]. The absorption onset for $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs is blue-shifted with increasing Ga content.

As $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ is a typical direct band gap semiconductor, the estimated optical energy band gap can be obtained from the absorption spectra by extrapolation as shown in Figure S5 and there is a gradual increase of E_g with x . The band gaps of CuInSe_2 and CuGaSe_2 obtained from Figure S5 were 1.05 eV and 1.62 eV respectively and these values are consistent with the reported bulk band gaps of 1.01 eV and 1.64 eV that can be derived from the following equation [30]:

$$E_g = 1.010 + 0.626(1-x) - 0.167x(1-x) = 1.636 - 0.793x + 0.167x^2 \quad (5)$$

A plot of the change in band gap with composition x can be seen in Figure 9. It is reported that the energy band gap of chalcopyrite crystals is lower than sphalerite as the different chemical nature of the Cu, In and Ga ions results in different bonding environments between each of these and their neighboring Se ions resulting in very different ionic character and bond lengths [1]. This bond length change reduces the band gap energy of the compound in the case of chalcopyrite structure compared to the sphalerite structure with identical chemical composition, because the latter has a disordered cation sub-lattice [1]. Therefore, the difference between the theoretical and experimental energy band gap in figure 9 may be attributed to this contribution from crystals with disordered cations (sphalerite phase). The energy band gap of quaternary chalcopyrite $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ compounds exhibits a quadratic dependence on the composition. The constant before x^2 is referred to as the bowing factor, which is understood to be a result of bond alteration in the lattice [31]. Our experiments showed that the variation is nonlinear for the band gap versus composition of the as synthesized NCs. The experimental optical energy band gap has a downward bowing with a value of 0.463 and this lies beyond the 0-0.25 range [1]. Bowing factors that are beyond this range may be an indication of the presence of disorder in the crystal structure as the theoretical bowing factor is calculated for an ordered chalcopyrite structure. The calculated energy band gap in Figure 9 is derived using the following equation:

$$E_g = 0.463x^2 - 1.059x + 1.632 \quad (6)$$

To further validate the energy band gap of the synthesized NCs, the electrochemical energy band gap is also calculated from the difference between the estimated oxidation and reduction potential of NCs as measured using cyclic voltammetry (CV). The oxidation process is related to the injection of a hole into the HOMO level of organic molecules or the valence band of inorganic semiconductors, and the reduction process is related to the injection of an electron into the LUMO level or conduction band. When ferrocene is used as the reference (a typical CV curve for ferrocene is shown in the supporting information, Figure S6), the valence and conduction bands of the inorganic semiconductors can be calculated using the following equation [16].

$$E_{HOMO/LUMO} = [(E_{ox/red} - E_{FC}) + 4.7] \text{eV} \quad (7)$$

CV curves for $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs are shown in Figure 10. There is a prominent oxidation peak and a relatively weak reduction peak, probably due to the difficulty of charge injection from the electrode to the p-type semiconductor NCs. The oxidation and reduction onsets are shown in Table S2. According to Shafarman and Stolt [32], the bulk band gap for CuInSe_2 is 1.02 eV with valence and conduction bands at *ca.* -5.6 and -4.6 eV respectively and for bulk $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ the energy band gap is 1.2 eV with valence and conduction bands at *ca.* -5.2 and -4.0 eV respectively. With increasing Ga ratio, the valence band maximum decreases slightly, while an increase in the conduction band is prominent [33]. Although the calculated electrochemical conduction and valence band of the NCs differs slightly from those reported, there is a systematic shift in the onset potentials of oxidation and reduction of the NCs as the Ga ratio increases (Table S2).

The optical and electrochemical energy band gaps calculated from the absorption edges and the CV measurements (Figure 9 and Table S2) were compared to those predicted by equation 5. Although both optically and electrochemically measured band gaps fall within the range of the theoretical band gaps of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ ranging from 1.01 eV to 1.64 eV, with increasing Ga content, there are slight discrepancies in the values. This could be due to the size of the synthesized NCs: as particle size decreases, the quantum confinement effect comes into play and this will increase the band gap. There is also the contribution from defects caused by micro-strain and crystal disordering.

The presence of local disorder causes defect bands at the valence and conduction bands and hence shifts the electronic bands [34]. Therefore the first oxidation onset seen in the CV curves which is very close to zero, can be attributed to these defects as well as the OVCs. The band gap of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs can be readily tuned by adjusting the ratio of Ga to In, resulting in band gaps ranging from 1.13 eV to 1.42 eV corresponding to compounds ranging from CuInSe_2 to $\text{CuIn}_{0.25}\text{Ga}_{0.75}\text{Se}_2$. There is a gradual increase in the band gap as the Ga content increases, which agrees with previous findings [1, 34].

4. Conclusion

A detailed crystallo-chemical study of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs with a wide range of compositions synthesized using the hot injection method has been presented. In this study, quantitative analysis of the $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NC composition was performed using EPMA. Even though EPMA has rarely been used for measuring nanoparticle compositions, we have used this method for the first time for our compositional study of CIGS NCs and the results are close to the nominal values. In general, XRD is a good technique for lattice parameter determination and phase analysis. In this study, Raman spectroscopy was performed as a complementary characterization tool to determine the different phases in the synthesized NCs.

From the $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NC Raman spectra, we can observe the coexistence of the chalcopyrite A_1 mode and the sphalerite S mode with disordered cations. This analysis shows that the crystal structure is mainly chalcopyrite although some parts of the cations are disordered. Raman analysis complements XRD as cation disordering in $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs can be detected using the latter technique. With increasing substitution of In with Ga, the Raman peaks shift away from the CuInSe_2 peak position to the CuGaSe_2 position, which is an indication of a variation in the stoichiometry of the synthesized NCs. The broadening of the Raman modes can also be attributed to the strain in the sample due to the presence of the OVCs. The crystal lattice distortion was further confirmed by a systematic x-ray diffraction analysis of the crystal lattice parameters a , c , V and $c/2a$ compared to the idealized solid solution trend. $\text{CuIn}_{0.49}\text{Ga}_{0.51}\text{Se}_2$ NCs showed the maximum distortion amongst the range of compositions explored. UV-Visible spectroscopy and CV measurements indicate that while the energy band gap of NCs is within the range of the theoretical energy band gap for bulk $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$, there is a slight shift which can be attributed to the presence of defects caused by strain and the lattice distortion in the crystal structure of the NCs.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. M. Ahmadi and S.S. Pramana contributed equally to this work.

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Table Captions

Table 1: Composition of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs measured using EPMA. The lateral interaction volume is approximately 1-5 μm .

Table 2: Shift in the A_1 and S modes and the parameter (area of A_1 mode)/(area of S mode) representing the degree of disorder from the chalcopyrite structure as a function of the composition x in $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs.

Figure Captions

Figure 1: a) Chalcopyrite, b) sphalerite and c) wurtzite crystal structures of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ viewed along the close-packed direction.

Figure 2: TEM images of chalcopyrite $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs with x (a) 1, (b) 0.77, (c) 0.49, (d) 0.25 and (f) 0.

Figure 3: Background subtracted Cu L edge EEL spectra from $\text{CuIn}_{0.49}\text{Ga}_{0.51}\text{Se}_2$ NCs (solid line) and Cu_2Se (dotted line).

Figure 4: Raman spectra from $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs with a range of Ga/(Ga+In) ratios showing the shift in the A_1 mode of chalcopyrite $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ and also a deconvolution of the A_1 and the S mode. The peak marked * corresponds to the Cu_{2-x}Se impurity present in CuGaSe_2 .

Figure 5: Change in the A_1 and S Raman peak positions from $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs as a function of x .

Figure 6: XRD patterns from $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs with a range of Ga/(Ga+In) ratios. A systematic shift of the diffraction peaks to higher 2θ is due to the decreased lattice spacing as smaller Ga atoms are substituted for larger In atoms. Indices are shown on the CuInSe_2 NCs XRD pattern. The indices are similar for the other XRD patterns.

Figure 7: Unit cell parameters, (a) a , (b) c , and (c) unit cell volume. The dotted line represents Vegard's law. (d) Tetragonal distortion $\eta=c/2a$ as a function of x .

Figure 8: UV-Vis absorption spectra from $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs as a function of composition, x .

Figure 9: Comparison of the theoretical with the measured optical and electrochemical energy band gaps.

Figure 10: Cyclic voltammetry of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ NCs showing the oxidation and reduction onsets.

Table 1

Nominal x	Measured x
0.00	0.00
0.30	0.25(4)
0.50	0.49(6)
0.70	0.77(7)
1.00	1.00

Table 2

x	A ₁	S	Area of A ₁ mode/ area of S mode
0	183.6	191.7	~
0.25	182.3	188.5	6.5
0.49	176.6	186.1	4.0
0.77	176.4	184.3	2.8
1	174.4	183.4	2.1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10