



# Dispersion of the second harmonic generation from CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se) defect chalcopyrite: DFT calculations



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## ARTICLE INFO

### Article history:

Received 9 December 2013

Received in revised form 30 December 2013

Accepted 31 December 2013

Available online 10 January 2014

### Keywords:

Defect chalcopyrites

Birefringence

Nonlinear optical susceptibilities

## ABSTRACT

All electron full potential linear augmented plane wave method was used for calculating the nonlinear optical susceptibilities of CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se) within the framework of density functional theory. The exchange correlation potential was solved by recently developed modified Becke and Johnson (mBJ) approximation. The crystal structure of CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub> reveals a large uniaxial dielectric anisotropy ensuing the birefringence of –0.036 and –0.066 which make it suitable for second harmonic generation. The second order susceptibility  $|\chi_{ijk}^{(2)}(\omega)|$  and microscopic first hyperpolarizability  $\beta_{ijk}(\omega)$  were calculated. The calculated  $|\chi_{123}^{(2)}(\omega)|$  and  $|\chi_{312}^{(2)}(\omega)|$  static values for the dominant components found to be 18.36 pm/V and 22.23 pm/V for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub>. Both values shifted to be 60.12 pm/V and 108.86 pm/V at  $\lambda = 1064$  nm. The calculated values of  $\beta_{123}(\omega)$  is  $6.47 \times 10^{-30}$  esu at static limit and  $12.42 \times 10^{-30}$  esu at  $\lambda = 1064$  nm for CdGa<sub>2</sub>S<sub>4</sub>, whereas it is  $8.82 \times 10^{-30}$  esu at static limit and  $20.51 \times 10^{-30}$  esu at  $\lambda = 1064$  nm for CdGa<sub>2</sub>Se<sub>4</sub>. The evaluation of second order susceptibilities and first hyperpolarizabilities suggest that CdGa<sub>2</sub>X<sub>4</sub> possess huge second harmonic generation.

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## 1. Introduction

Several investigations have been carried out to understand the perspective phenomenology existing in the study of nonlinear optical properties (NLO) of semiconductors [1]. Novel materials exhibit appropriate traits like phase matching for appliance in laser technology or else in devices based on optical parametric oscillators are explored. The most important class among them are recently studied family of defect chalcopyrite (DC) [2,3]. Their nature is diamond like broad band gap semiconductors suitable for optoelectronic appliances in ultraviolet region [4,5]. Such class of semiconductors illustrate a substantial curiosity for a variety of technological applications similar to infrared-transmitting windows materials, laser and nonlinear optics (NLO) technologies [6,7]. Specific features of thiophene polymer derivatives is crucial dependence on the dipole–dipole interactions [8], which play crucial role during the photocarrier transfer. The latter also will play principal role in the efficiency of the photovoltaic (PV) devices.

In the CdGa<sub>2</sub>S<sub>4</sub> material the local states extensive spectrum is because of the complex chemical composition with two cations which consequences in elevated photosensitivity and incredible luminescence, X-ray luminescence and cathodoluminescence in

CdGa<sub>2</sub>S<sub>4</sub> [9,10]. Such assets illustrate the optical isotropic issue, birefringence and stimulated radiation with its utmost at 2.1 eV ( $T = 80$  K) give clues that the compound is potential nominee for the development of narrow-band tuned optical filters, electro-optical modulators and lasers on its basis [10,11]. CdGa<sub>2</sub>S<sub>4</sub> has furthermore some other intriguing properties like pessimistic resistance, elevated photo-conductivity result, charge storage and electro-optical memory [12]. The CdGa<sub>2</sub>Se<sub>4</sub> material is a blemish chalcopyrite-type well known semiconductor, usually exploited in NLO influence high photosensitivity and strapping luminescence in the visible range [13,14]. Electro-photographic layer derived from it display a high-quality photographic distinction and high resolution [15].

CdGa<sub>2</sub>Se<sub>4</sub> is in fact an capable substance utilized in a variety of nonlinear optical apparatus as gyrotropic media, narrow-band optical filter [16], solar units, detectors and temperature sensors [17]. Several theoretical and experimental research has been executed utilizing distinct methods for investigation of electronic band structure, charge density, optical activity such as photo luminescence, florescence, birefringence of CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se) [3,18–20]. On this material CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se), Fuentes-Cabrera [21] also executed the ab initio calculation within the framework of DFT, using the ultrasoft Vanderbilt-type pseudopotentials technique. In which he calculated the energy band gap as 2.19 and 1.36 eV for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub>.

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Using WIEN2k code, Lavrentyev et al. [22] also calculated the band-structure for CdGa<sub>2</sub>Se<sub>4</sub> compound, employing the APW + LO technique; they obtained the energy band gap 1.35 eV.

Ma et al. [23] used VASP code within GGA to calculate the structural, elastic, electronic and optical properties of CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se). Their calculation were not precise due to the energy gap's underestimation. In our recent work [24] we calculated electronic structure and linear optical properties of the reported compounds which give close agreement to the experimental results but there was deficiency of nonlinear optical (NLO) properties. The present work focused on NLO using all electron full potential linear augmented plane wave (FP-LAPW) method which confirmed to be one of the most accurate method in DFT for calculation of electronic structure and optical properties of materials [25,26].

## 2. Crystal structure and computational details

The crystal structure of CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se) are defect chalcopyrite (DC) tetragonal having space group  $I\bar{4}$  (No. 82) as shown in Fig. 1a and b. The lattice parameter and atomic positions of CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se) are taken from Ref. [23]. We have employed the FP-LAPW within WIEN2K package [27]. The exchange correlation potential was solved by recently developed modified Becke and Johnson (mBJ-GGA) format [28]. The energy cutoff was taken to be  $K_{\max} = 7.0/R_{MT}$  in order to expand the wave function of plane wave in the interstitial region. The  $R_{MT}$  represent muffin-tin (MT) sphere radius and  $K_{\max}$  represent the magnitude of largest  $K$  vector in plane wave expansion. The chosen muffin-tin (MT) sphere radii for Cd, Ga, S and Se are 2.0 atomic units (a.u.) in CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se). The wave function inside the sphere was expanded up to  $l_{\max} = 10$  where as the Fourier expansion of the charge density was reduced up to  $G_{\max} = 12(\text{a.u.})^{-1}$ . The self consistent calculations were believed to be converged when the difference in total energy of the crystal did not exceed  $10^{-5}$  Ryd for subsequent steps. The self consistent calculations were obtained by 657  $k$  points and 1221  $k$  points for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub>, respectively in irreducible Brillouin zone (IBZ).

## 3. Results and discussions

### 3.1. Some salient features

The calculated band structure participate noteworthy role for exploration of the material. Most of the physical properties of many compounds which are directly interrelated to the electronic band structure of the material, while the basis of the band structure can be related to the density of state [29]. High symmetry points of the Brillouin zone (BZ) have been selected for calculating

the electronic band structure of CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se) using the recently modified MBJ schemes. The calculated merged band structure in Fig. 2 shows that the valence band maximum and conduction band minimum are positioned at centre of BZ ensuing direct band gap ( $\Gamma \rightarrow \Gamma$ ) of 3.39 eV and 2.50 eV for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub> respectively, which shows close agreement with experimental band gap (3.4 eV and 2.54 eV).

We calculated the birefringence  $\Delta n(\omega)$  using the result of our previous work [24] for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub> as shown in Fig. 3. The relation  $\Delta n = n_e - n_o$  is used for calculating the birefringence. The terms  $n_e$  and  $n_o$  represents the refractive indices classified in extraordinary and ordinary ray of polarized light.  $\Delta n(\omega)$  is essential in the non-absorbing region below the gap [30]. The static values of  $\Delta n(\omega)$  is calculated for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub> (−0.036 and −0.66) (see Fig. 3).

### 3.2. Non linear optical susceptibilities

The expressions for complex second-order nonlinear optical susceptibility tensor  $\chi_{ijk}^{(2)}(-2\omega; \omega; \omega)$  are commonly written as [31–34]:

$$\chi_{inter}^{ijk}(-2\omega; \omega; \omega) = \frac{e^3}{\hbar^2} \sum_{nml} \int \frac{d\vec{k}}{4\pi^3} \frac{\vec{r}_{nm}^i \{\vec{r}_{ml}^j \vec{r}_{ln}^k\}}{(\omega_{ln} - \omega)} \times \left\{ \frac{2f_{nm}}{(\omega_{mn} - 2\omega)} + \frac{f_{ml}}{(\omega_{ml} - \omega)} + \frac{f_{ln}}{(\omega_{ln} - \omega)} \right\} \quad (1)$$

$$\chi_{intra}^{ijk}(-2\omega; \omega; \omega) = \frac{e^3}{\hbar^2} \int \frac{d\vec{k}}{4\pi^3} \left[ \sum_{nm} \omega_{nm} \vec{r}_{nm}^i \{\vec{r}_{ml}^j \vec{r}_{ln}^k\} \left\{ \frac{f_{nl}}{\omega_{ln}^2 (\omega_{ln} - \omega)} - \frac{f_{lm}}{\omega_{ml}^2 (\omega_{ml} - \omega)} \right\} - 8i \sum_{nm} \frac{f_{nm} \vec{r}_{nm}^i \{\Delta_{mn}^j \vec{r}_{nm}^k\}}{\omega_{mn}^2 (\omega_{mn} - 2\omega)} + 2 \sum_{nm} \frac{f_{nm} \vec{r}_{nm}^i \{\vec{r}_{ml}^j \vec{r}_{ln}^k\} (\omega_{ml} - \omega_{ln})}{\omega_{mn}^2 (\omega_{mn} - 2\omega)} \right] \quad (2)$$

$$\chi_{mod}^{ijk}(-2\omega; \omega; \omega) = \frac{e^3}{2\hbar^2} \int \frac{d\vec{k}}{4\pi^3} \left[ \sum_{nml} \frac{f_{nm}}{\omega_{mn}^2 (\omega_{mn} - \omega)} \{\omega_{nl} \vec{r}_{lm}^i \{\vec{r}_{mn}^j \vec{r}_{nl}^k\}\} - \omega_{lm} \vec{r}_{nl}^i \{\vec{r}_{lm}^j \vec{r}_{mn}^k\}\} - i \sum_{nm} \frac{f_{nm} \vec{r}_{nm}^i \{\vec{r}_{mn}^j \Delta_{mn}^k\}}{\omega_{mn}^2 (\omega_{mn} - \omega)} \right] \quad (3)$$

By mean of these formulae one can perceive that  $\chi_{ijk}^{(2)}(-2\omega; \omega; \omega)$  show three foremost contributions: the intra-band transitions  $\chi_{intra}^{ijk}(-2\omega; \omega; \omega)$ , the inter-band transitions  $\chi_{inter}^{ijk}(-2\omega; \omega; \omega)$ , and the modulation of inter-band terms by intra-band terms  $\chi_{mod}^{ijk}(-2\omega; \omega; \omega)$ , where  $n \neq m \neq l$ . Here  $n$  represents the valence states,  $m$  the conduction states and  $l$  symbolize all states ( $l \neq m, n$ ) and  $i, j$  and  $k$  correspond to Cartesian indices. Two type of transitions can occur,  $vcc'$  and  $v'vc$ . The first expression contains one valence band and two conduction bands, and

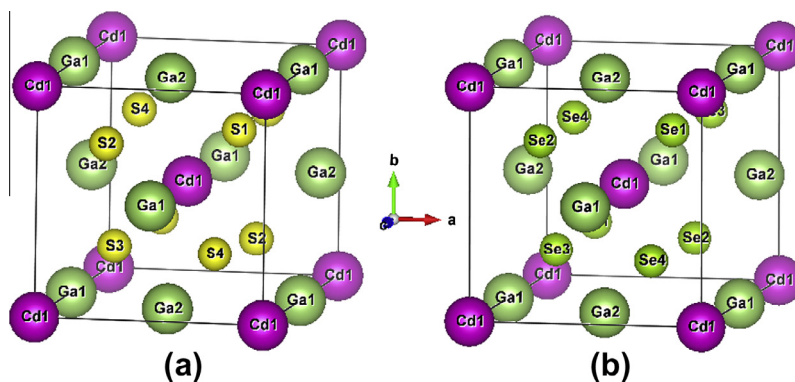


Fig. 1. Crystal structure (a) CdGa<sub>2</sub>S<sub>4</sub> and (b) CdGa<sub>2</sub>Se<sub>4</sub>.

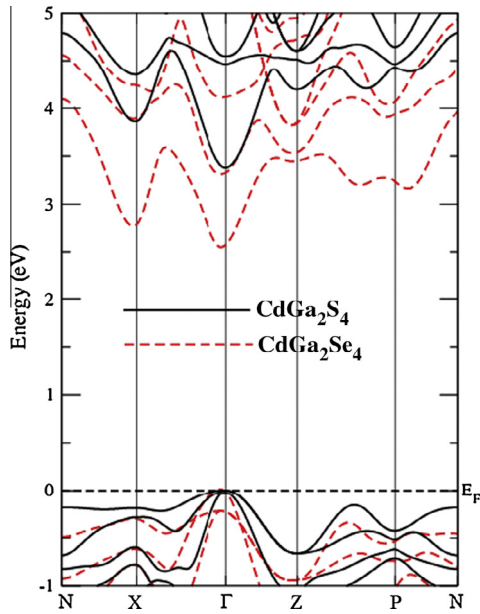


Fig. 2. Merged electronic band structure of CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se).

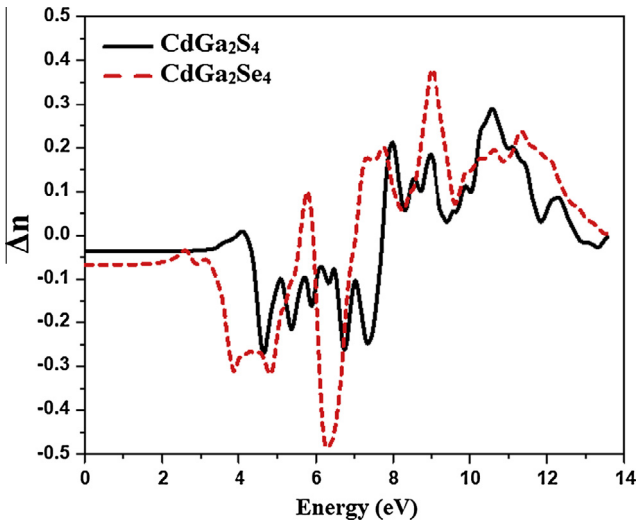


Fig. 3. Calculated birefringence of CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se).

the second transition involves two valence bands and one conduction band. The symbols can be defined as  $\Delta_{nm}^i(\vec{k}) = v_{nm}^i(\vec{k}) - v_{nm}^i(\vec{k})$  with  $v_{nm}^i$  being the  $i$  component of the electron velocity given as

$$v_{nm}^i(\vec{k}) = i\omega_{nm}(\vec{k})r_{nm}^i(\vec{k}) \text{ and } \{r_{nm}^i(\vec{k})r_{ml}^j(\vec{k})\} \\ = \frac{1}{2}(r_{nm}^i(\vec{k})r_{ml}^j(\vec{k}) + r_{nm}^j(\vec{k})r_{ml}^i(\vec{k})) \quad (4)$$

The momentum matrix element  $P_{nm}^i$  was used to calculate the position matrix elements between band states  $n$  and  $m$ ,  $r_{nm}^i(\vec{k})$ , using the relation [35]: where  $r_{nm}^i(\vec{k}) = \frac{P_{nm}^i(\vec{k})}{i\hbar\omega_{nm}(\vec{k})}$ , with the energy difference between the states  $n$  and  $m$  given by  $\hbar\omega_{nm} = \hbar(\omega_n - \omega_m)$  and  $f_{nm} = f_n - f_m$  represent difference of the Fermi distribution functions [36]. The one-electron virtual transitions (transitions between one valence band state and two conduction band states,  $vcc'$ ) give a momentous contribution to the second-order tensor. The virtual-hole contribution (transitions between two valence band states and one conduction band state,  $vv'c$ ) is ignored since

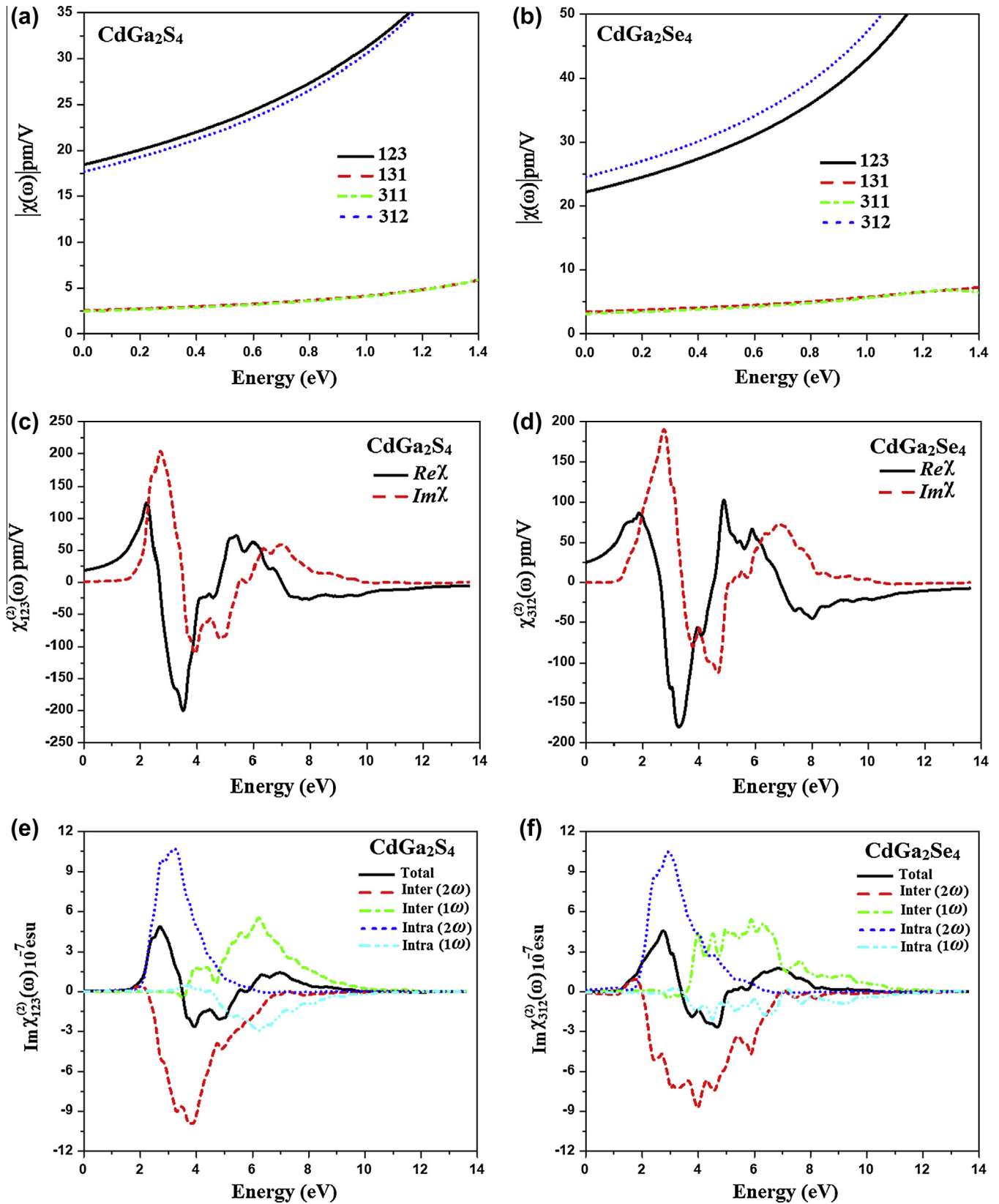
it was initiated to be negative and minor than the virtual-electron contribution. For simplicity we symbolize  $\chi_{ijk}^{(2)}(-2\omega; \omega; \omega)$  by  $\chi_{ijk}^{(2)}(\omega)$ . The subscripts  $i, j$ , and  $k$  represent the Cartesian indices.

The current calculations exposed that the independent dominant tensor components are  $\chi_{123}^{(2)}(-2\omega; \omega; \omega)$  and  $\chi_{123}^{(2)}(-2\omega; \omega; \omega)$  for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub>, respectively. The three polarization directions of the tensor components along  $x, y$  and  $z$  are represented in the subscript. Since the nonlinear optical (NLO) properties are very sensitive to the band gap of the material as compared to linear optical properties therefore, the results of the mBJ format were selected. This scheme have noticeably manipulate the second order nonlinear optical dispersion because it calculate better band gap as compared to experiment, however it is still underestimate the energy band gap by around 1% and 4% for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub>, respectively. In order to eliminate this negative aspect the quasiparticle the self-energy corrections was performed at the level of scissors operators in which the energy bands are rigidly transfer to bring the calculated energy gap equivalent to the experimental gap.

The second-order nonlinear optical effect can be expressed by tensor  $\chi_{ijk}^{(2)}(\omega)$  which is third rank tensor in the electric dipole approximation (EDA) contains non vanishing elements for noncentrosymmetric crystalline arrangement. The third order NLO effects are illustrated by the tensors  $\chi_{ijkl}^{(3)}(\omega)$  and  $\gamma_{ijkl}$  and no symmetry requirements are compulsory for occurrence of these effects [37]. Since the crystal structure of both CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub> are tetragonal having space group  $I\bar{4}$  (No. 82) which contains two crystallographic symmetry elements, results several parameters equal to zero and only four nonzero components namely, 123, 131, 311 and 312 are exists. Fig. 4a and b represents the calculated  $|\chi_{ijk}^{(2)}(\omega)|$  for four tensor components which elucidate highest value of  $|\chi_{123}^{(2)}(\omega)|$  for CdGa<sub>2</sub>S<sub>4</sub> at static limit 18.36 pm/V and 60.12 pm/V at  $\lambda = 1064$  nm, as compared to the other components. While for CdGa<sub>2</sub>Se<sub>4</sub>  $|\chi_{312}^{(2)}(\omega)|$  is prevailing with values of 22.23 pm/V and 108.86 pm/V at static limit and at  $\lambda = 1064$  nm. The static values of dielectric tensor components of optical susceptibilities are very important because it used for calculation of relative frequency of SHG efficiency [38]. We have selected the dominant components (123, 312) of  $|\chi_{ijk}^{(2)}(\omega)|$  for further explanation of NLO.

Fig. 4c and d represents the dispersion of real and imaginary part of second order optical susceptibilities  $\chi_{123}^{(2)}$  and  $\chi_{312}^{(2)}$  of both CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub>, respectively. The maximum value of Re  $\chi_{123}^{(2)}$  and Im  $\chi_{123}^{(2)}$  of CdGa<sub>2</sub>S<sub>4</sub> are located at 2.3 eV and 2.9 eV with maximum value of 125 pm/V and 208 pm/V. For CdGa<sub>2</sub>Se<sub>4</sub> both peaks shift to 4.9 eV and 2.85 eV with decreasing peaks (105 pm/V and 187 pm/eV) for both Re  $\chi_{312}^{(2)}$  and Im  $\chi_{312}^{(2)}$ .

Fig. 4e and f corresponds to the intra- and inter-contribution of  $\omega$  and  $2\omega$  resonance for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub>, respectively. The complex second-order nonlinear optical susceptibility is almost zero below half of the band gap ( $E_g/2$ ). The  $2\omega$  resonance give response to energy above half of the band gap while  $\omega$  term come into action for energy greater than band gap value ( $E_g$ ). The clear vision of  $\omega$  and  $2\omega$  resonance can be seen in Fig. 4g and h. One can notice that  $2\omega$  resonance is greater than  $1\omega$  resonance in both cases. The highest peaks of inter- and intra-term of  $2\omega$  resonance in CdGa<sub>2</sub>S<sub>4</sub> are located at 3.3 eV and 3.8 eV which elucidates value of  $10.6 \times 10^{-7}$  esu and  $-10.0 \times 10^{-7}$  esu. When S is replaced by Se in the reported compound the peaks shifted to 3.0 eV and 4.0 eV with maximum value of  $10.5 \times 10^{-7}$  esu and  $-8.2 \times 10^{-7}$  esu for inter- and intra-term of  $2\omega$  respectively. Both inter- and intra-contribution of  $1\omega$  for CdGa<sub>2</sub>S<sub>4</sub> are positioned at 6.3 eV with the value of  $5.5 \times 10^{-7}$  esu and  $-3.0 \times 10^{-7}$  esu. As one move from CdGa<sub>2</sub>S<sub>4</sub> to CdGa<sub>2</sub>Se<sub>4</sub> the inter-contribution shift to 5.9 eV with same value



**Fig. 4.** Calculated  $|\chi_{jk}^{(2)}(\omega)|$  of (a) CdGa<sub>2</sub>S<sub>4</sub> and (b) CdGa<sub>2</sub>Se<sub>4</sub>. Dispersion of calculated real and imaginary part of  $\chi_{123}^{(2)}(\omega)$  for CdGa<sub>2</sub>S<sub>4</sub>; (b) dispersion of calculated real and imaginary part of  $\chi_{312}^{(2)}(\omega)$  for CdGa<sub>2</sub>Se<sub>4</sub>; (c) calculated total  $Im\chi_{123}^{(2)}(-2\omega; \omega; \omega)$  along with inter ( $2\omega/\omega$ ) and intra ( $2\omega/\omega$ ) band contribution for CdGa<sub>2</sub>S<sub>4</sub>; (d) calculated total  $Im\chi_{312}^{(2)}(-2\omega; \omega; \omega)$  along with inter ( $2\omega/\omega$ ) and intra ( $2\omega/\omega$ ) band contribution for CdGa<sub>2</sub>Se<sub>4</sub>; (e) calculated  $|\chi_{123}^{(2)}(\omega)|$  along with  $\epsilon_2^{average}(\omega)$  and  $\epsilon_2^{average}(\omega/2)$  for CdGa<sub>2</sub>S<sub>4</sub>; and (f) calculated  $|\chi_{312}^{(2)}(\omega)|$  along with  $\epsilon_2^{average}(\omega)$  and  $\epsilon_2^{average}(\omega/2)$  for CdGa<sub>2</sub>Se<sub>4</sub>.



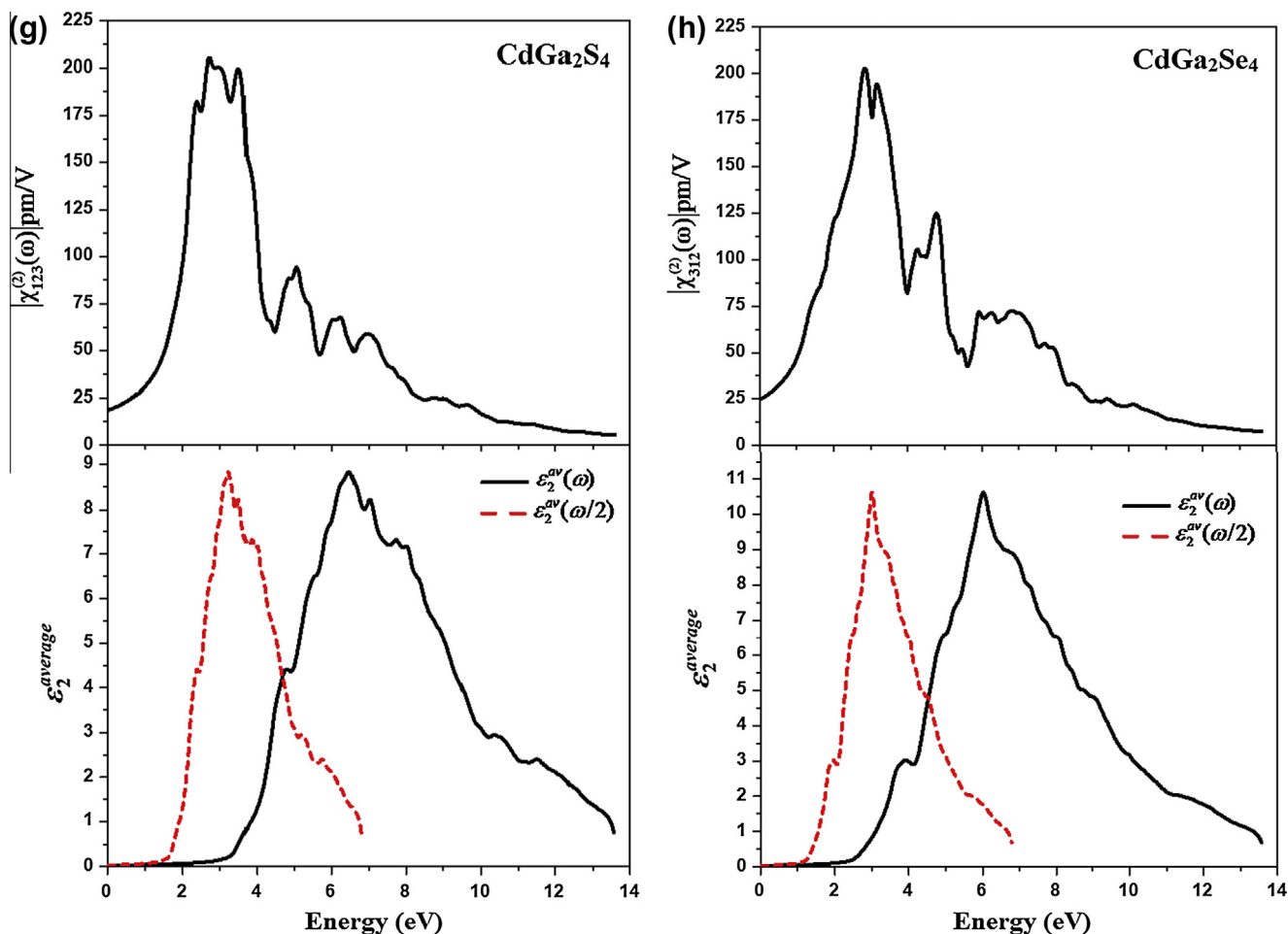


Fig. 4 (continued)

as that of CdGa<sub>2</sub>S<sub>4</sub>. The intra-contribution show maximum value of  $2.3 \times 10^{-7}$  esu around 4.5 eV.

Moreover Fig. 3e and f shows the calculated  $|\chi_{123}^{(2)}(\omega)|$  and  $|\chi_{312}^{(2)}(\omega)|$  the dominant tensor components (the upper panels) with average value of absorptive part of dielectric part  $\epsilon_2(\omega)$  as a function of  $\omega$  and  $\omega/2$  (lower panel). For CdGa<sub>2</sub>S<sub>4</sub> the  $2\omega$  resonance is responsible for spectral structure formation in the energy range between 1.70 eV and 3.40 eV. For CdGa<sub>2</sub>Se<sub>4</sub> the spectral structure shaped by  $2\omega$  resonance shifted to lower energy range between 1.27 eV and 2.54 eV. The succeeding structure in energy range (3.40–6.80) eV for CdGa<sub>2</sub>S<sub>4</sub> and (2.54–6.80) eV for CdGa<sub>2</sub>Se<sub>4</sub> are originated from joint effect of  $\omega$  and  $2\omega$  resonance. Rest of the structures are fashioned by only  $\omega$  resonance.

We have calculated the microscopic first hyperpolarizability,  $\beta_{ijk}$  in particularly their vector components along the dipole moment direction with respect to crystal axes, at the static limit and at  $\lambda = 1064$  nm, for the dominant component of  $|\chi_{ijk}^{(2)}(\omega)|$  for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub> respectively by using the expression [39,40];

$$\beta_{ijk} = \frac{\chi_{ijk}}{Nf^3} \quad (5)$$

where  $f$  represent local field factor which vary between 1.3 and 2.0.  $N$  symbolize number of molecules per cm<sup>3</sup>. In order to calculate  $\beta_{ijk}$  we used the dispersion spectra of  $|\chi_{123}^{(2)}(\omega)|$  and  $|\chi_{312}^{(2)}(\omega)|$  for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub>. The calculated values of  $\beta_{123}(\omega)$  is  $6.47 \times 10^{-30}$  esu at static limit and  $12.42 \times 10^{-30}$  esu at  $\lambda = 1064$  nm for CdGa<sub>2</sub>S<sub>4</sub>. As one replace S by Se in the reported compound the  $\beta_{312}$

increased to be  $8.82 \times 10^{-30}$  esu and  $20.51 \times 10^{-30}$  esu at static limit and at  $\lambda = 1064$  nm.

#### 4. Conclusions

We have calculated the nonlinear optical susceptibilities of CdGa<sub>2</sub>X<sub>4</sub> (X = S, Se) using all electron full potential linear augmented plane wave method based on DFT in Wien2k code. The recently developed modified Becke and Johnson (mBJ) scheme were used for solution of exchange correlation potential.

The calculated birefringence value (−0.036 and −0.66) show considerable anisotropy between the extra ordinary and ordinary components of the polarized light which show the appropriateness of CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub> for large second harmonic generations. We calculated dominant second order susceptibility tensor  $|\chi_{ijk}^{(2)}(\omega)|$ . The dominant 123 and 213 components of CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub> expose static value of 18.36 pm/V and 22.23 pm/V which shifts to 60.12 pm/V and 108.86 pm/V at  $\lambda = 1064$  nm. We also calculated the first hyperpolarizabilities  $\beta_{123}(\omega)$  and  $\beta_{312}(\omega)$  at static limit and at  $\lambda = 1064$  nm for CdGa<sub>2</sub>S<sub>4</sub> and CdGa<sub>2</sub>Se<sub>4</sub>.

#### Acknowledgment

The result was developed within the CENTEM project, reg. no. CZ.1.05/2.1.00/03.0088, co-funded by the ERDF as part of the Ministry of Education, Youth and Sports OP RDI programme. School of Material Engineering, Malaysia University of Perlis, Malaysia.

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