

Linear and Nonlinear Optical Susceptibilities of Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ Compounds

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Abstract— The complex density functional theory (DFT) calculations of linear and nonlinear optical susceptibilities for the Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds have been reported, using the full potential linearized augmented plane wave (FP-LAPW) method. We have employed the local density approximation (LDA), generalized gradient approximation (GGA-PBE). In addition the Engel– Vosko generalized gradient approximation (EVGGA) formalism, which optimizes the corresponding potential for the spectral features of the linear and nonlinear optical susceptibilities, was employed. We have calculated the frequency-dependent complex $\epsilon(\omega)$, its zero-frequency limit $\epsilon_1(\omega)$, refractive index $n(\omega)$, the reflectivity $R(\omega)$ and electron energy loss function $L(\omega)$. Calculations are also reported for the frequency-dependent complex second-order nonlinear optical susceptibilities. We find opposite signs of the contributions of the $2(\omega)$ and $1(\omega)$ inter/intra-band to the imaginary part for the dominant component through the optical frequency range.

Keywords— linear optical susceptibilities; nonlinear optical susceptibilities; DFT

I. INTRODUCTION

Numerous investigations have been conducted to know the standpoint philosophy presently existing in the analyses of nonlinear optical properties (NLO) of semiconductors. With the aim to get better production in the industrial area. It is accomplished that a substantial correlation subsist between the electro-negativity and the band gap in semiconductors [1]. Therefore it is remarkable to exploit the influence of physical and chemical trends for instance the electro-negativity on the NLO in semiconductors [1]. Innovative compounds having appropriate features such as phase matching for applications in the area of laser or in devices based on optical parametric oscillators (OPO) are investigated [1]. When the electro-negativity of the materials increases or decreases it influences the second harmonic generation. Many efforts has been made to get the relations between band gaps, single bond energy, atomic numbers, electro-negativities and refractive indices [2,3]. The thiophosphates (transition metal) configured a broad and attractive class of compounds that have been the area of studies due to their different structural chemistries [4] and their physical properties. Only the AuPS_4 [5] is the ternary thiophosphate of gold, a number of compounds appropriating to the ternary Ag-P-S and Cu-P-S system have been described

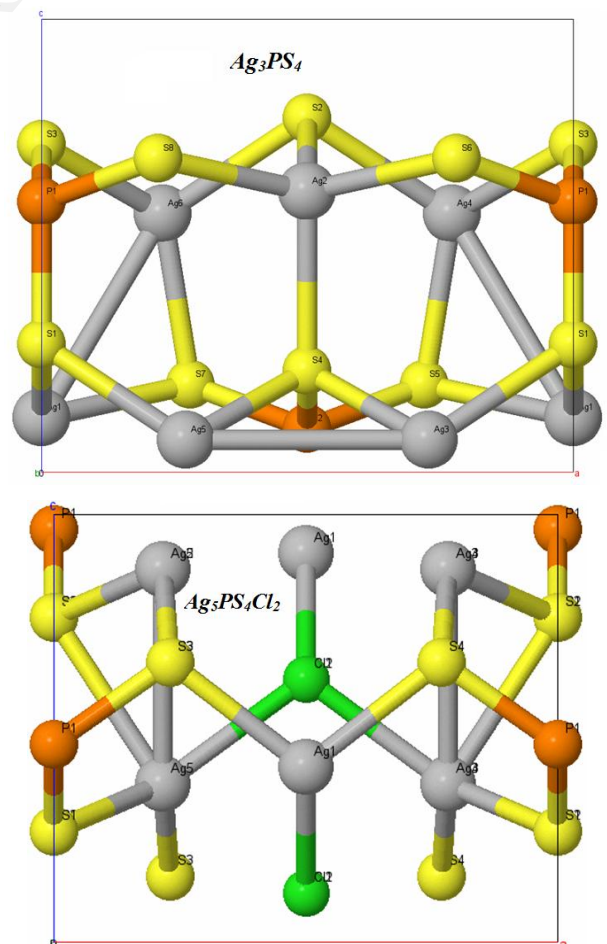
in the texts, e.g. $\text{Ag}_4\text{P}_2\text{S}_6$ [6], $\text{Ag}_4\text{P}_2\text{S}_7$ [7], $\text{Ag}_7\text{P}_3\text{S}_{11}$ [8,9], Cu_3PS_4 [10] and CuPS_2 [11].

In this manuscript we have computed the linear and nonlinear optical properties of Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds.

II. COMPUTATIONAL METHODOLOGY

The Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ crystal structure has been exposed in Fig. 1. Both has the orthorhombic structure with space group # 31 ($P m n 2_1$) and # 38 ($A m m 2$). The lattice constants for the $\text{Ag}_3\text{PS}_4/\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds are $a = 7.647(3)/7.409(1)$ Å, $b = 6.858(2)/11.143(2)$ Å, $c = 6.506(1)/6.258(1)$ Å, [12].

Fig. 1: Unit cell structure



Self-consistent FP-LAPW [13] calculations on Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds has been conducted using the WIEN2k package [14]. The unit cell structure for both compounds has been shown in Fig.1. An adequate trade-off between accuracy and cost was achieved by taking a number of basic functions up to $\text{RMT_Kmax}=9$, whereas the RMT is the minimum radius of the muffin-tin spheres and Kmax provides the scale of the largest K vector in the plane wave basis. The muffin-tin radii R_{MT} were chosen for Ag_3PS_4 compound as following; $R_{\text{MT}}(\text{Ag})=2.37$ a.u. and $R_{\text{MT}}(\text{S and P})=1.82$ a.u., whereas for $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compound as; $R_{\text{MT}}(\text{Ag})=2.39$ a.u., $R_{\text{MT}}(\text{S and P})=1.84$ a.u. and $R_{\text{MT}}(\text{Cl})=2.16$ a.u.

Furthermore, inside muffin-tin spheres, the valence wave functions are extended up to $l_{\text{max}}=10$. The exchange and correlation effects are treated by the local density approximation (LDA), generalized gradient approximation (GGA-PBE) and EVGGA functional [15-18]. The energy dependence on \mathbf{k} points in the irreducible wedge of the Brillouin zone (IBZ) has been checked, and the mesh size has been set to $10 \times 10 \times 10$ points.

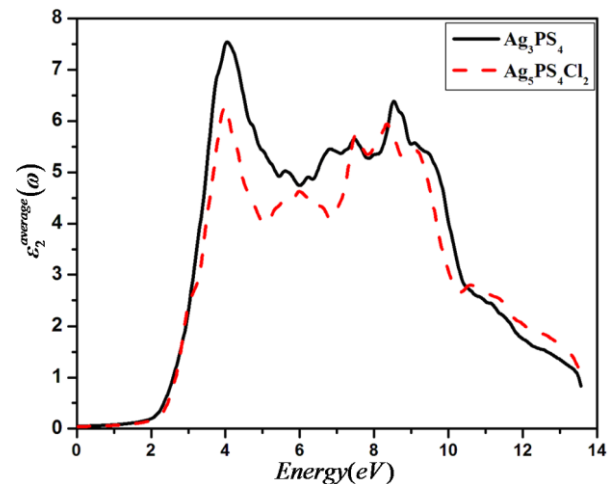
III. RESULTS AND DISCUSSION

A. Linear optical properties

In this section we will talk about the dielectric function (complex quantity) $\epsilon(\omega)$ of Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds. These properties are resolved by the dielectric function $\epsilon(\omega)$ as specified by the following expression $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The dielectric function absorptive part, $\epsilon_2(\omega)$ contingents on the momentum matrix elements and the joint density of states. The optical properties can be illustrated through the transverse dielectric function $\epsilon(\omega)$. For $\epsilon(\omega)$, there exist two impacts i.e. the intraband and interband transitions. The contribution of first one is only vital for metals. While the former one, can be torn apart in to direct and indirect transitions. Here in this article we overleap the indirect interband transitions, that implicate the scattering of phonons assuming a small contribution to the frequency dependent dielectric functions. For calculating the direct interband contribution to the absorptive part, so this is obligatory to summarize all conceivable transitions from valence band to the conduction band taking the suitable transition dipole matrix elements into description.

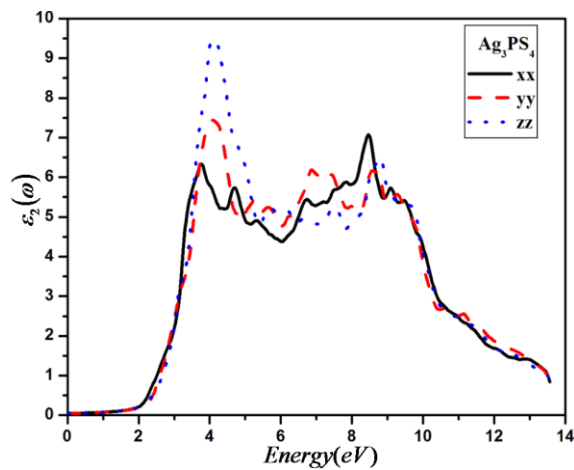
The spectra of the optical properties have been evaluated for an energy range 0–14 eV, this spectra of both compounds enclose numerous peaks which communicate to electronic transitions from the occupied band to unoccupied band. We firstly calculated the average dielectric function of both compounds as shown in Fig. 2.

Fig. 2: Average imaginary part dielectric function of both compounds

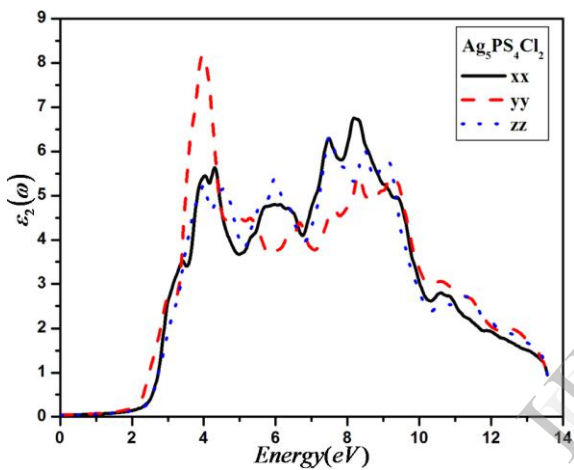


As it is clear from the (average) spectra of both compounds that, as we move from Ag_3PS_4 compound to $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compound, though there is a small shift in the structure towards the higher energy and also the magnitude of the peaks decreases.

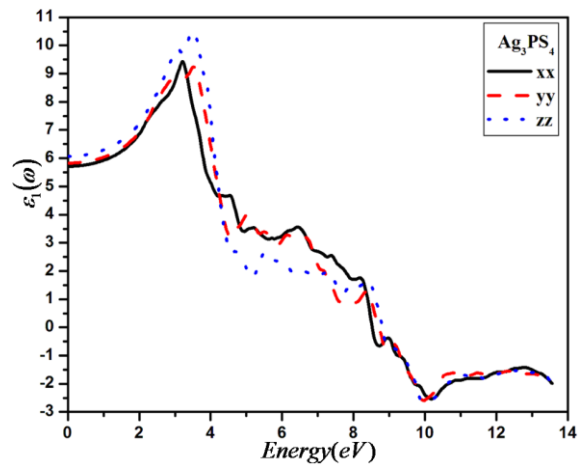
As our investigated compounds has the orthorhombic symmetry, hence the dielectric functions are resolved into three components $\epsilon^{xx}(\omega)$, $\epsilon^{yy}(\omega)$ and $\epsilon^{zz}(\omega)$. The investigated spectra of the imaginary part $\epsilon_2^{xx}(\omega)$, $\epsilon_2^{yy}(\omega)$ and $\epsilon_2^{zz}(\omega)$ of the frequency dependent dielectric function are shown in Fig. 3 (a and b) for both compounds. We can explain the different structures, we divide the optical spectra into two major groups, the first from 2.0 to 6.0 eV and the second from 6.0 eV and above. The first group is subjugated by S-p and P-s/p transitions, the first interband transition arises between the valence band maximum (VBM) and conduction band minimum (CBM), and the first peaks of $\epsilon_2^{xx}(\omega)$, $\epsilon_2^{yy}(\omega)$ and $\epsilon_2^{zz}(\omega)$ for Ag_3PS_4 ($\text{Ag}_5\text{PS}_4\text{Cl}_2$) compounds are at 3.72, 4.05 and 4.09 eV (4.04, 3.98 and 4.01 eV). The next group of the peaks is construed from the transitions from either S-p or P-p states to Ag-s or Ag-p states for Ag_3PS_4 compounds while in $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compound these peaks can be deduced from either S-p or P-p states to Ag-s or Ag-p or Cl-s states, where the main peaks of $\epsilon_2^{xx}(\omega)$, $\epsilon_2^{yy}(\omega)$ and $\epsilon_2^{zz}(\omega)$ for Ag_3PS_4 ($\text{Ag}_5\text{PS}_4\text{Cl}_2$) compounds are located at 8.47, 6.87 and 8.77 eV (8.20, 8.31 and 7.49 eV).

Fig. 3: Calculated imaginary $\varepsilon_2(\omega)$ 

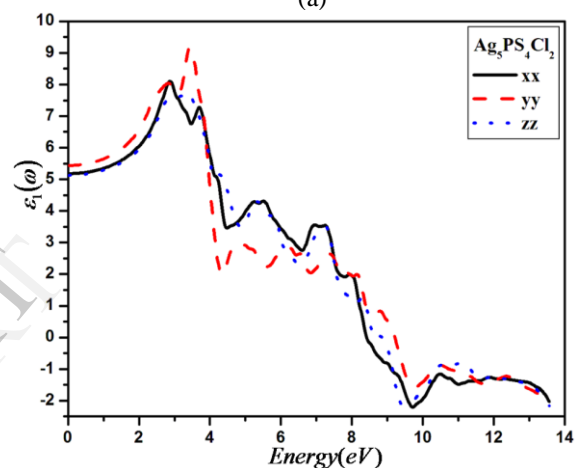
(a)



(b)

Fig.4: Real part $\varepsilon_1(\omega)$ of dielectric tensor (d and e)

(a)



(b)

We have investigated the real part of the dielectric function $\varepsilon_1(\omega)$, using the Kramers–Kronig relations [19]. The investigated spectra of $\varepsilon_1(\omega)$ for both compounds are exposed in Fig. 4 (a and b). The zero frequency limit $\varepsilon_1(0)$ is the mainly imperative quantity, known as the electronic part of the static dielectric constant which is greatly influenced by the band gap. The static values $\varepsilon_1^{xx}(0)$, $\varepsilon_1^{yy}(0)$ and $\varepsilon_1^{zz}(0)$ for Ag_3PS_4 ($\text{Ag}_5\text{PS}_4\text{Cl}_2$) compounds are 5.71 (5.17), 5.82 (5.43) and 6.06 (5.12). We note that a smaller energy gap (E_g) acquiesces a larger $\varepsilon_1(0)$ value [20–24]. This could be cleared through Penn model [25]. This model is based on this formula $\varepsilon(0) = 1 + (\hbar\omega_p / E_g)^2$. From this expression it is apparent that $\varepsilon(0)$ is inversely proportional to E_g . The value of the E_g can be find out from this expression by using the values of both $\varepsilon_1(0)$ and $\hbar\omega_p$ (plasma energy).

The absorption coefficient can be evaluated from the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. The $I^{xx}(\omega)$, $I^{yy}(\omega)$ and $I^{zz}(\omega)$ spectra has been shown in Fig. 5 (a and b), at 2.0 (2.5) eV the first absorption peak is originated for the Ag_3PS_4 ($\text{Ag}_5\text{PS}_4\text{Cl}_2$) compounds. The absorption coefficient of the band at 3.6 (4.3) eV are anticipated by our computing to be 45.0 (70.0) $\times 10^4 \text{cm}^{-1}$ for Ag_3PS_4 ($\text{Ag}_5\text{PS}_4\text{Cl}_2$) compounds. Seeing as that the absorption coefficient in the fundamental region is exalted almost $200 \times 10^4 \text{cm}^{-1}$ Ag_3PS_4 compound and more than $200 \times 10^4 \text{cm}^{-1}$ for $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compound at high energy.

The reflectivity spectra $R^{xx}(\omega)$, $R^{yy}(\omega)$ and $R^{zz}(\omega)$ for Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds has been shown in Fig. 5 (c and d). It shows a weak anisotropy between the three components but this anisotropy increases a little when we move from Ag_3PS_4 compound to $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds. The energy loss function ($L^{xx}(\omega)$, $L^{yy}(\omega)$ and $L^{zz}(\omega)$) (see Fig. 5(e and f) shows the main peak in the energy loss function, which defines the screened plasma frequency ω_p [26], are located at 8.70 eV. This main peak corresponds to the abrupt reduction of the reflectivity spectrum ($R^{xx}(\omega)$, $R^{yy}(\omega)$ and $R^{zz}(\omega)$) and to the zero crossing of $\varepsilon_1(\omega)$ (Fig. 4(a and b)). From the reflectivity spectrum, one can say that these compounds show small reflectivity at low energies then a rapid increase in the reflectivity occurs at intermediate and high energies. The reflectivity maxima take

place from inter-band transitions. They occurred between the energy range 10.0–14.0 eV for both compounds, which is in the ultraviolet. i.e. both compounds can be therefore serve as a possible shield for ultraviolet radiation.

The calculated refractive indices $n^{xx}(\omega)$, $n^{yy}(\omega)$ and $n^{zz}(\omega)$ for Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds are shown in Fig. 5 (g and h). The peaks that appears in the refractive index spectra are narrated to the peaks emerged in the imaginary part of the dielectric function. At low energies, the refractive index for both compounds assorted between 2.0 and 2.5. But a rapid decreasing occurs at high energies, in the refractive indices of both compounds.

This phenomena is significant physical parameter linked to the microscopic atomic interactions. Through theoretical stance, there exist two different approaches in screening this subject: the refractive index is associated to the density and the local polarizability of these individuals are related to the energy gap E_g of the material [27,28].

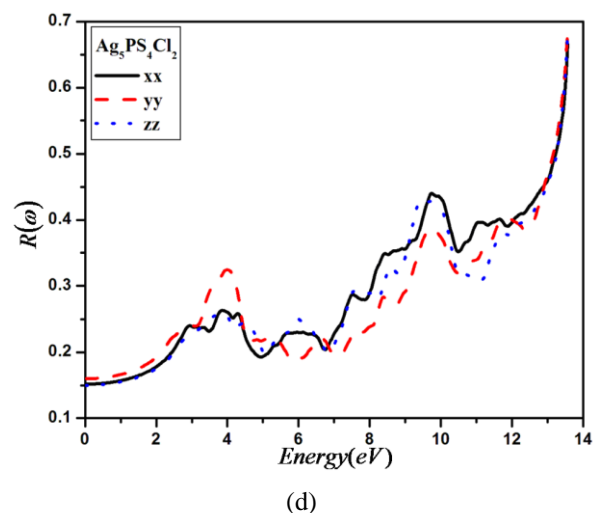
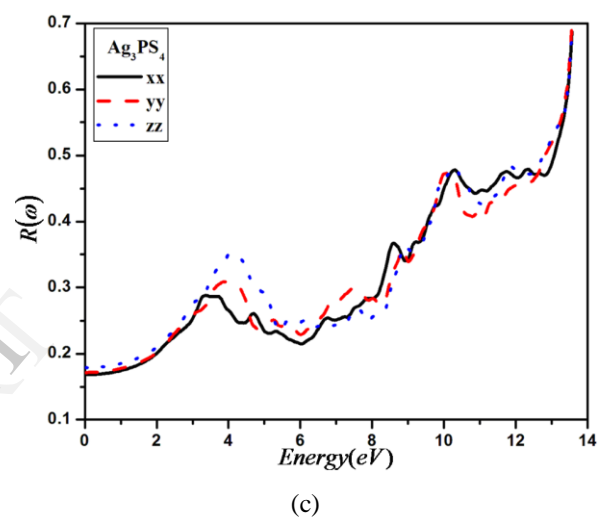
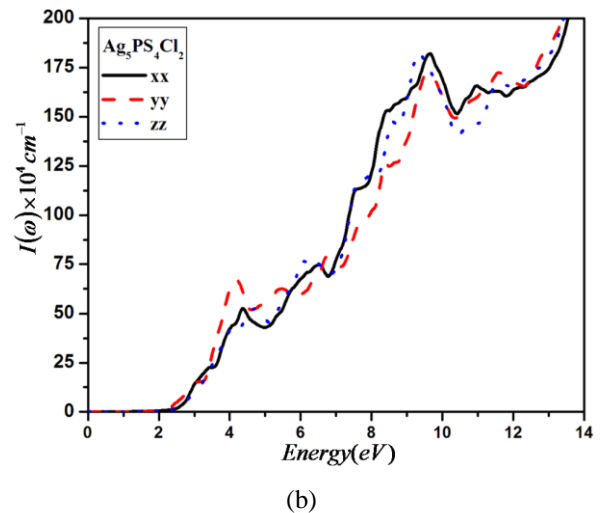
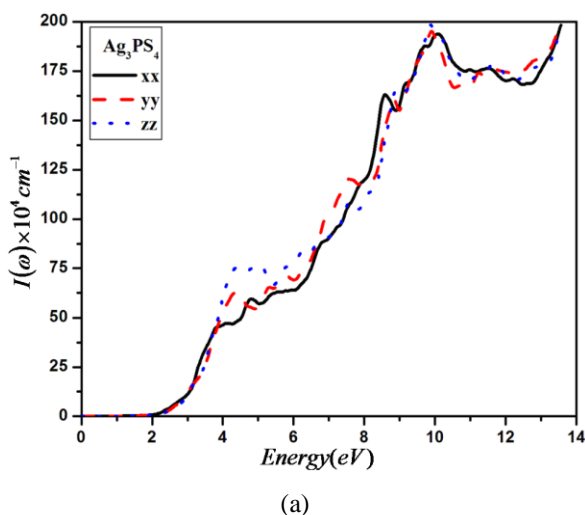
Hervé and Vandamme proposed an empirical formula, in order to be motivated by simple physics of light refraction and dispersion, as follows [28]:

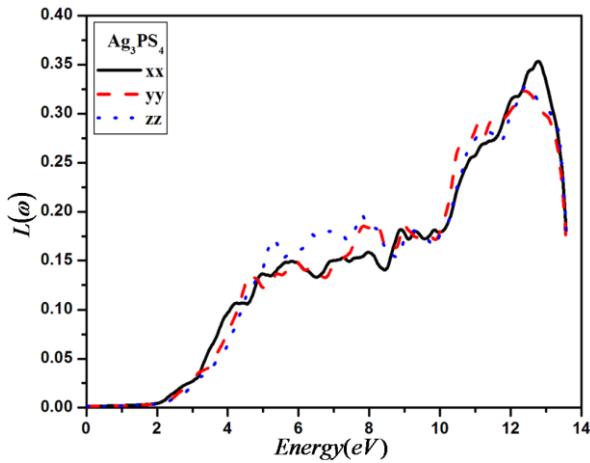
$$n = \sqrt{1 + \left(\frac{A}{E_g + B} \right)}$$

where $A=13.6\text{eV}$ and $B=3.4\text{ eV}$ and E_g is the band gap. The calculated refractive indices of our investigated compounds are 2.79 and 2.73 for Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds. This is confirmed by the computation of the optical dielectric constant ϵ_∞ , which depends on the n .

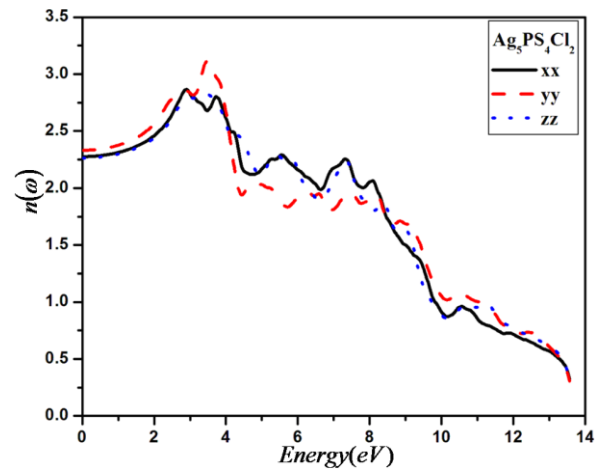
The refractive index spectra $n^{xx}(0)$, $n^{yy}(0)$ and $n^{zz}(0)$ for the investigated compounds, shows a difference in the anisotropy as one goes from Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compound. We may conclude, frankly, that the static value of $n(0)$ decreases as the band gap increases. The static values $n^{xx}(0)$, $n^{yy}(0)$ and $n^{zz}(0)$ for Ag_3PS_4 ($\text{Ag}_5\text{PS}_4\text{Cl}_2$) compounds are 2.30 (2.27), 2.41 (2.33) and 2.46 (2.26).

Fig. 5: Calculated absorption co-efficient (a and b), reflectivity (c and d), energy-loss spectrum (e and f) and the refractive index (g and h)

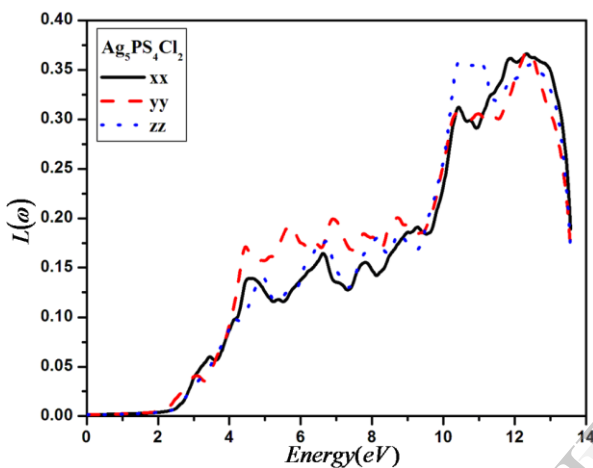




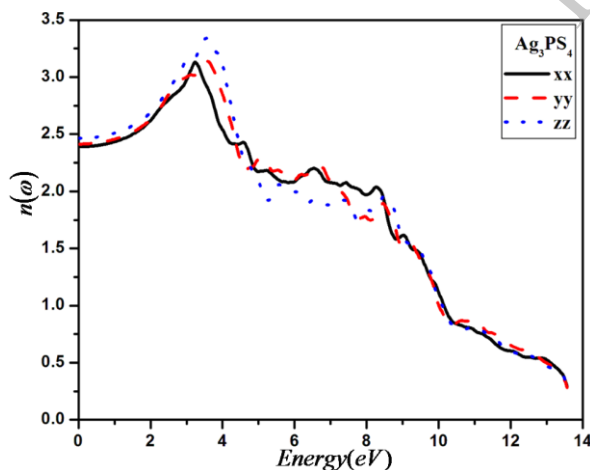
(e)



(h)



(f)



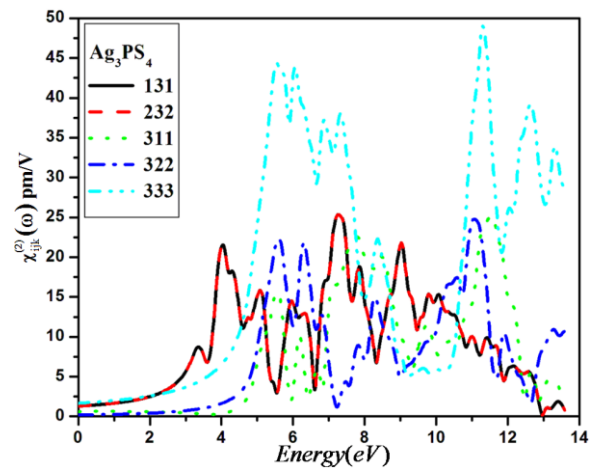
(g)

B. Nonlinear optical properties (NLO)

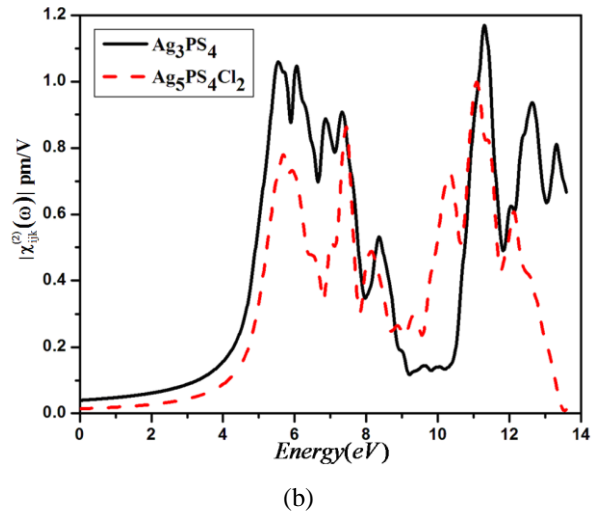
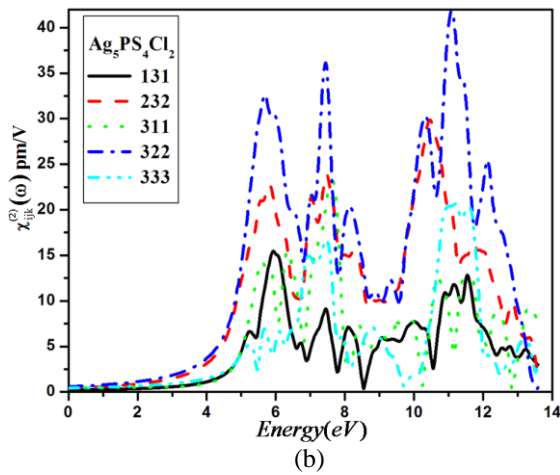
Since nonlinear optical properties are more sensitive to small changes in the band structure than the linear ones, and because of its mechanism itself, any anisotropy in the linear optical properties lead to improve the second harmonic generation effect (SHG).

This is apportioned to the actuality that the second harmonic response involves $2(\omega)$ resonance additionally to the customary ω resonance. Since Ag_3PS_4 and $Ag_5PS_4Cl_2$ compounds possess orthorhombic structure belongs to the space group # 31 ($P m n 2_1$) and # 38 ($A m m 2$). Thus these compounds having five independent non-zero tensor components; namely $\chi_{131}^{(2)}(\omega)$, $\chi_{232}^{(2)}(\omega)$, $\chi_{311}^{(2)}(\omega)$, $\chi_{322}^{(2)}(\omega)$ and $\chi_{333}^{(2)}(\omega)$. Here, the calculations predict that $\chi_{333}^{(2)}(\omega)$ is the dominant component for Ag_3PS_4 compound and $\chi_{322}^{(2)}(\omega)$ for $Ag_5PS_4Cl_2$ compound as shown in Fig. 6 (a and b).

Fig. 6: Calculated $\chi_{ijk}^{(2)}(\omega)$



(a)

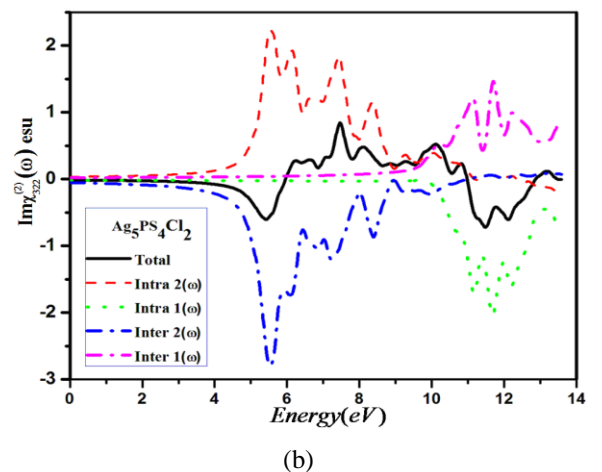
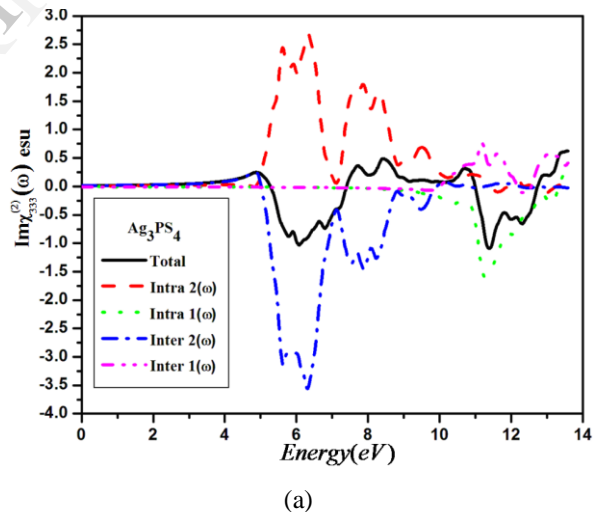
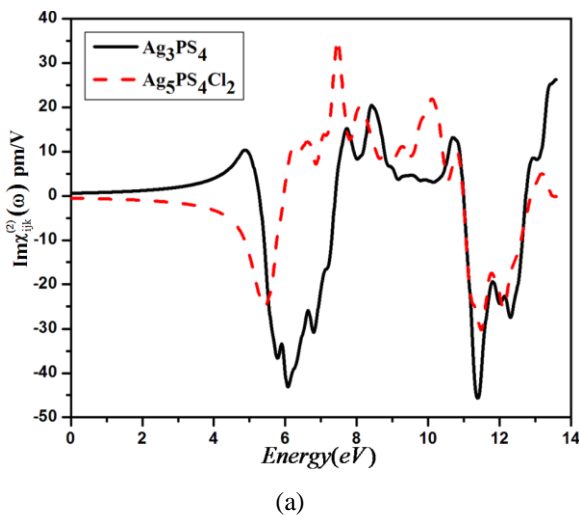


The calculated imaginary part of the second harmonic generation (SHG) is shown in Fig. 7a. It is clear that the imaginary part of the second harmonic generation is zero below half the band gap. The terms $2(\omega)$ start to conduce at energies $\sim 1/2E_g$ and the ω terms for energy values above E_g . Fig.7b shows the $|\chi_{322}^{(2)}(\omega)|$ and $|\chi_{333}^{(2)}(\omega)|$ of Ag_3PS_4 and $Ag_5PS_4Cl_2$ compounds. Following Fig.7b, we point out that moving from Ag_3PS_4 compound to $Ag_5PS_4Cl_2$ compound, guides to decrease the amplitude and shift all the structures of $\chi_{ijk}^{(2)}(\omega)$ towards higher energies. Following Fig. 7b, we found that the value of $|\chi_{333}^{(2)}(0)|$ is 0.05 pm/V for Ag_3PS_4 compound and the value of $|\chi_{322}^{(2)}(0)|$ for $Ag_5PS_4Cl_2$ compound is 0.02 pm/V.

Fig. 8 shows the 2ω and ω inter/intraband contributions to the imaginary parts of $\chi_{333}^{(2)}(\omega)$ for Ag_3PS_4 compound and $\chi_{322}^{(2)}(\omega)$ for $Ag_5PS_4Cl_2$ compound. Note the opposite signs of the two contributions throughout the frequency range. This fact may be useful for molecular engineering of the crystals in the desirable directions.

Fig. 7: (a) Calculated imaginary part of the second harmonic generation (SHG) and (b) Calculated $|\chi_{ijk}^{(2)}(\omega)|$ pm/V

Fig. 8: Calculated total $|\chi_{333}^{(2)}(-2\omega; \omega; \omega)|$ and $|\chi_{322}^{(2)}(-2\omega; \omega; \omega)|$ spectrum and on linear optical properties



IV. CONCLUSION

The full potential linearized augmented plane wave technique has been used for the theoretical investigation of the Ag_3PS_4 and $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compounds. We have calculated and analyzed their linear and nonlinear optical properties. We analyzed the real and imaginary part of the dielectric tensor with other related properties like reflectivity, refractive index, extension co-efficient and energy loss function of the linear optical properties. We concluded that the reflectivity maxima occur from inter-band transitions. They occurred between the energy range 10.0–14.0 eV for both compounds, which is in the ultraviolet. i.e. both compounds can be therefore serve as a possible shield for ultraviolet radiation.

Further to the linear properties we computed the second order nonlinear optical properties namely the SHG. We calculated the total complex susceptibility of all nonzero components of $\chi_{ijk}^{(2)}(\omega)$ and we found that that $\chi_{333}^{(2)}(\omega)$ is the dominant component for Ag_3PS_4 compound and $\chi_{322}^{(2)}(\omega)$ for $\text{Ag}_5\text{PS}_4\text{Cl}_2$ compound.

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