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Impurity induced cross luminescence in KMgCl_3 : An ab-initio study

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Abstract. Density functional theory calculations have been carried out to calculate the electronic structure and optical properties of host and Cs doped KMgCl_3 . All the calculations were performed by using the Tran and Blaha modified Becke-Johnson potential (TB-mBJ) in order to accurately predict the band gap and the optical spectra. The investigated compound is found to be an insulator with direct band gap of 4.7, 6.9 eV using Generalized Gradient Approximation (GGA), and TB-mBJ functionals respectively. The calculated refractive index shows the optical isotropy of this compound in the low energy region, though the structure is anisotropic. From our theoretical calculations we predict KMgCl_3 doped with Cs to be a better cross luminescence material compared to host compound, where additional Cs states are present below the valence band of the compound. Detailed discussion is presented in the manuscript.

Keywords: Cross luminescence, Electronic structure, Optical properties, Scintillators

1. Introduction

Research in the field of scintillators has been evolving since 1930's, emphasising the demand for the study of scintillators experimentally and theoretically to find an ideal scintillator and also to improve the existing scintillators. Scintillator is said to be ideal, if it follows some of the characteristics like, high light yield, less decay time, high density, high energy resolution [1]. Short wavelength and fast decay emission of BaF_2 crystal increased its attention towards the fast scintillators [2–5]. The mechanism involved in the fast emission is the recombination of holes of upper core valence band with the electrons from the valence band, and this type of intrinsic emission is called core valence luminescence (CVL) or cross luminescence or Auger free luminescence [1,2,5–16]. The compound which exhibit cross luminescence not only show less decay time, high light yield but also high thermal stability. The general criteria to observe the cross luminescence is that the energy difference between the valence band and upper core valence band should be less than the band gap of the compound. In order to observe CVL, it is also needed that the incident energy should be sufficient enough to excite the upper core level electrons to the conduction band, leaving a hole in upper core valence band which plays an important role in cross luminescence [1].

Cross luminescence is mostly observed in the case of alkali, and alkaline-earth halides (AX , ABX_3 type, where A, B, X are single, divalent cations, and halides respectively). Some of the cross luminescence materials are CsF [2], CsCl [2,3], KF [5], RbF [4,5], CsBr [8], RbCaF_3 , CsCaCl_3 , CsSrCl_3 [11], CsMgCl_3 [12,13], CsMgF_3 [13], KMgF_3 , KCaF_3 [17] etc., and RbCl , KCl , RbCaCl_3 , KCaCl_3 [18] are few of the compounds where cross luminescence is not observed. It is to be noted that on moving from AX to ABX_3 type, the distance between the nearest neighbor ions i.e. A^+ , and X^- increases resulting in the decrease in the CVL transition probability in ABX_3 type compound with increase in decay time and light output [7]. Recently CVL is also observed in ASnF_3 ($\text{A}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$) compounds studied from density functional theory calculations [19]. The wide band gap halide crystals can also exhibit impurity induced core valence luminescence by doping with CVL active ions (Ba^+ , Rb^+ , Cs^+ , K^+) because of the fact that the additional impurity states are present below the valence band resulting in reducing the energy difference between the valence band and upper core valence band. Impurity induced CVL is observed in RbCaCl_3 , KCaCl_3 , RbBr ($\text{Rb}_{1-x}\text{Cs}_x\text{Br}$ ($x < 0.2$)) with the addition of Cs [3,18,20]. In the present manuscript, our focus is mainly towards the study of materials possessing impurity induced CVL.

The present studied compound KMgCl_3 crystallizes in orthorhombic crystal structure [21]. Until now there are only few experimental studies available on the enthalpy calculations [22,23], and structural phase transitions of KMgCl_3 [24,25]. To the best of our knowledge there are no theoretical studies available on the the host compound, and we have predicted the electronic structure, optical properties of host compound as well as Cs doped KMgCl_3 together with the type of transition involved in host and Cs doped KMgCl_3 .

2. Computational details

Ab-initio calculations are carried out by using the Full potential linearized augmented plane wave method (FP-LAPW) implemented in WIEN2k package [26,27]. For all the calculations we have used the experimental lattice parameters with the optimized lattice positions [21]. FP-LAPW is one of the accurate methods for calculating the electronic structure and optical properties of the solids. In this method the core electrons are treated fully relativistically and the valence electrons are treated semi-relativistically. The basis functions are expanded up to $R_{mt} \times K_{max} = 9$, where R_{mt} is the smallest muffin tin sphere radii and K_{max} is the plane wave cut-off. We have used tetrahedron method for the k-point integration over the Brillouin zone [28]. The compound of the present study is an insulator, and as we know that the local density approximation (LDA) and generalized gradient approximation (GGA) [29] underestimate the band gap, we have used the Tran and Blaha modified Becke-Johnson potential (TB-mBJ) [30–34], which give the band gap values comparable to the experimental values. We have used $14 \times 9 \times 14$ k-mesh with 320 k-points in irreducible Brillouin Zone (IBZ) for electronic structure calculation and $19 \times 13 \times 19$ k-mesh with 700 k-points in IBZ for the optical properties calculations of the host compound. In order to perform doping calculations we have created $2 \times 2 \times 1$ super cell and replaced 2 of the K atoms with Cs atom, out of eight leading to 25% doping (due to the constraint on computational resources). We have used $17 \times 8 \times 6$ k-mesh for electronic structure, and $30 \times 15 \times 10$ k-mesh for optical properties calculations of $\text{KMgCl}_3:\text{Cs}$.

The optical response of the system can be well described by the dielectric function $\epsilon(\omega)$ at all photon energies. The dielectric function consists of real ($\epsilon_1(\omega)$) and imaginary ($\epsilon_2(\omega)$) parts of dielectric functions. The imaginary part of dielectric function is related to the electronic band structure of solid and is given by the following equation [35,36]

$$\epsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{i,j} \int_k \langle i/M/j \rangle^2 f_i(1 - f_j) \delta(E_{j,k} - E_{i,k} - \omega) d^3k \quad (1)$$

where i, j are the initial and final states of transition respectively, and M is the dipole matrix. f_i, E_i indicate the i^{th} state Fermi distribution function, energy of an electron respectively with wave vector k . The real part of dielectric function can be calculated from the imaginary part of dielectric function by using the Kramers-Kronig relation [37,38] as given below

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{(\omega')^2 - \omega^2} d\omega' \quad (2)$$

where P indicate the principle value of integration. From real and imaginary parts of dielectric functions we can calculate the refractive index, extinction coefficient, energy loss function ($L(\omega)$) with the following relations [12,35,36]

$$n(\omega) = \left[\frac{\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} + \epsilon_1(\omega)}{2} \right]^{\frac{1}{2}} \quad (3)$$

$$k(\omega) = \left[\frac{\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega)}{2} \right]^{\frac{1}{2}} \quad (4)$$

$$L(\omega) = \text{Im} \left[-\frac{1}{\epsilon(\omega)} \right] \quad (5)$$

From the calculated refractive index, extinction coefficient values one can calculated the absorption coefficient ($\alpha(\omega)$), reflectivity ($R(\omega)$) by the following relations [36]

$$\alpha(\omega) = \frac{2\omega k(\omega)}{c} \quad (6)$$

$$R(\omega) = \frac{(n(\omega) - 1)^2 + k(\omega)^2}{(n(\omega) + 1)^2 + k(\omega)^2} \quad (7)$$

3. Results and discussion

3.1. Electronic properties

Crystal structure of KMgCl_3 (Fig. 1) shows the formation of octahedra between Mg, and Cl atoms, where Mg atom occupy center of the octahedra, while the Cl atoms occupy the vertices of the octahedra. The electronic band structure of KMgCl_3 obtained using the TB-mBJ functional along with the high symmetry lines of the first Brillouin zone is shown in Fig. 2(a). From the band structure plot we observed that KMgCl_3 is a direct band gap insulator with valence band maximum and conduction band minimum at Γ point. The band gap is found to be 4.7 eV, 6.9 eV with GGA, TB-mBJ functionals respectively (shown in Table 1). In order to know the predominant states near valence and conduction bands we have plotted the density of states using TB-mBJ functional as shown in Fig. 3(a). From the figure it is clearly seen that the valence band is dominated by Cl-p states with lesser hybridization of Mg-s,p states, and spread around the energy region around 0 to -3.7 eV. The upper most core valence band which play an important role in the cross luminescence is situated around the energy range -10.91 eV to -11.0 eV and these states are mainly due to K-p states. Conduction band states are dominated by Mg-s,p, K-d, Cl-d states. Schematic energy band diagram (energy versus wave vector (K)) for the host compound is shown in Fig. 4, where E_g stands for energy gap of the compound. E_{VC} , δE_V stands for the energy difference between top of the valence band and top of the upper core valence band, width of the valence band respectively. In order to have cross luminescence active material, it is necessary that the energy difference

between valence band and the upper core valence band be lesser than the band gap of the compound, and in the present investigated host compound, we observed (from figure 4) this criteria not to be satisfied indicating that CVL is not active in KMgCl_3 compound.

We still want to analyse whether impurity induced CVL would be present in this compound. In order to check the impurity induced CVL, we have doped with Cs by replacing 25% of K with Cs. The plotted band structure and density of states of Cs doped KMgCl_3 is shown in Fig. 2(b), Fig. 3(b) respectively, and calculated band gaps are given in Table 1 by using TB-mBJ functional. Interestingly, we observed that the additional doped states are below the valence band and are dominated by Cs-p states (around -4.8 eV to -5.1 eV). It is to be noted that similar results were observed in RbCaCl_3 , KCaCl_3 [18] resulting in the reduction of the energy difference between the valence band and upper most core valence band. Schematic diagram of energy versus K for the Cs doped KMgCl_3 compound is shown in Fig. 4, where we can see E_{VC} is reduced compared to host compound which clearly shows that it is satisfying the criteria of cross luminescence and Cs doped KMgCl_3 compound act as cross luminescence material.

Depending on the type of transition involved, scintillators are characterized into three types, A-type, L-type, AL-type. In the case of A-type the energy difference between top of the valence band and top of the upper core valence band (E_{VC}) should be more than the band gap (E_g) of the compounds (figure 4), where as in L-type of compounds $E_{VC} < E_g$ (figure 4). In case of AL-type compound $E_{VC} - \delta E_V < E_g$, where δE_V is the width of the valence band. In L-type of compound cross luminescence can be observed. The present investigated compound KMgCl_3 is found to be of A-type where Auger luminescence is dominated with no possibility of cross luminescence. But with the addition of Cs to the host compound, we observed a change from A-type to L-type giving rise to the auger free luminescence with the possibility of cross luminescence. This clearly indicate the KMgCl_3 doped with Cs is CVL active material.

3.2. Chemical bonding

Chemical bonding can be well understood from the charge density calculations. We have plotted the charge density difference plot for the KMgCl_3 host compound as shown in Fig. 5. The large electronegativity difference between K(Mg), and Cl denote the charge transfer from K(Mg) to Cl atoms indicating the ionic nature of the compound. From the figure we can clearly see that the charge present between Mg and Cl atoms are mutually sharing indicating the slight covalent nature of Mg-Cl bond. The isolated K with no sharing of charges between K-Cl indicate the ionic nature of bonding between K-Cl. That is there exists ionic bonding with slight covalent nature of bonding in this compound and similar behaviour is also seen for other alkali halide compounds [12, 16]. Cs doped KMgCl_3 also shows the similar bonding nature as that of the host compound. In order to know the charge transfer among the constituent elements quantitatively

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we have calculated the bader charge [39, 40]. The calculated bader charges are 0.866e, 1.718e, and -2.584 for K, Mg and Cl (for 3 Cl atoms) respectively. From these values we can notice 0.866e charge transfer from K to Cl, 1.718e charge transfer from Mg to Cl (we can see more red region near Mg), and Cl is obtaining electron from K, Mg by -2.584e.

3.3. Optical properties

The analysis of the optical properties of the materials leads to the better understanding of the electronic structure and vice versa. We have calculated optical properties using the higher “k” points by using the TB-mBJ functional to arrive at the accurate optical properties. In order to understand the response of the system to the electromagnetic radiation, we have calculated the complex dielectric function, absorption coefficient, refractive index, electron energy loss function, reflectivity of the host compound. The imaginary part of complex dielectric function is calculated from the momentum matrix element between the filled and unfilled states. The real part of dielectric function is calculated from imaginary part of dielectric function by using the Kramers-Kronig relation. The other important optical parameters such as refractive index, absorption coefficient, conductivity, electron energy loss function, reflectivity are calculated from the real and imaginary part of dielectric functions. The calculated dielectric function is shown in Fig. 6 (a) with real and imaginary parts as a function of photon energy. The imaginary part of dielectric function start from 7 eV, which is due to the transition of electrons from valence band to conduction band that is from Cl-p to Mg-s. A peak around 12 eV shows the transition of electrons from Cl-p states to K-d, Cl-d states. The spectra also shows the broad peaks around 18 eV and 22 eV which is due to the transition of electrons from K-p, Cl-s states to conduction band respectively. The real part of dielectric function shows that KMgCl_3 is optically isotropic compound in the low energy region. Other important parameter that can be observed from the real part of dielectric function is the zero frequency limit of dielectric function also called static dielectric function and is found to be 2.5. The real part of dielectric function initially is found to increase with the energy reach a maximum value, after which it decreases. At some specific values of energy it goes to negative values, and for this region of energy, the system may possess metallic nature [36].

The refractive index ‘n’ and extinction coefficient ‘k’ plots as function of photon energy is shown in Fig. 7 (a). Refractive index plot shows optical isotropy of the compound though KMgCl_3 is structurally anisotropic, and this particular feature of the compound find its application as ceramic scintillator. $n(\omega)$ also gives the information about the speed of the light in the compound which is an important parameter for the optoelectronic devise applications. The static refractive index values of the host compound is found to be 1.574, 1.576, 1.575 along x, y, z directions respectively. These values shows the clear isotropy in the host compound as the difference between these values are very

small. The calculated extinction coefficient ($k(\omega)$) shows the loss of photon energy in the medium. $k(\omega)$ also projects a similar trend of imaginary part of dielectric function because of the fact that photon energy loss in the medium leads to the transition of electrons from valence band to conduction band. We have also calculated the other important optical property i.e. frequency dependent absorption coefficient which describes the absorption of photon energy in the material and is shown in Fig. 8 (a). Based on the absorption coefficient value, materials are divided into transparent, opaque, and translucent. For the present studied compound there is no absorption below 7 eV which shows KMgCl_3 to be a transparent material below 7 eV. The absorption spectra shows the transition of electron from occupied states to unoccupied states, and it is mostly observed in the ultraviolet region around 7 to 30 eV.

Electron energy loss function also calculated from the dielectric function as shown in Fig. 9, (a) it represent the energy loss per unit length of a fast moving electron across the medium. The significant peaks of the function are called the plasma peaks, and they indicate the electronic charge oscillations in the system and the corresponding frequencies are called plasma frequencies. The plasma peaks are observed around the energy of 11.4, 15.9, 18.7 (large), 21.8, 22.7, 25.1 (large), 26.07, 27.2, 27.8, 30.1 eV for the KMgCl_3 compound. We have noticed that at these values of plasma peak energies, real part of dielectric function cross the zero value and becomes negative. The reflectivity plot of KMgCl_3 is shown in Fig. 10 (a), and the value of reflectivity at zero frequency (zero frequency limit of reflectivity) is found to be 0.05. High reflectivity peaks are observed for the energy region from 10 to 20 eV. Unfortunately there are no experimental studies available for comparison.

In order to visualize the effect of Cs addition on the KMgCl_3 compound, we have also calculated the optical properties of Cs doped KMgCl_3 . The dielectric spectra of the host and Cs doped KMgCl_3 as shown in Fig. 6(a), (b) are almost similar with the same threshold energy value, as the additional states are present below the valence band without changing the band gap of the compound. The major difference observed between both the compounds is the peak around 14.26 eV in the Cs doped compound, which is absent in the host compound, and is due to the presence of additional Cs-p state in the $\text{KMgCl}_3:\text{Cs}$. This peak indicates that there are transition of electrons from Cs-p (upper core valence band) to conduction band creating the hole in upper core valence band, which plays an important role in the cross luminescence. This hole in the upper core valence band recombine radiatively with the electrons from the valence band resulting in $\text{KMgCl}_3:\text{Cs}$ acting as CVL active material. Real part of dielectric function of Cs doped KMgCl_3 shown in figure 6(b) indicate the static zero frequency limit of dielectric function for doped system to be around 2.5 and this value is not changed compared to host compound. Form the refractive index plot (Fig. 7 (b)) we have observed the optical isotropy of the Cs doped KMgCl_3 compound. The static refractive index values are found to be 1.770, 1.768, 1.770 along x, y, z directions. Similar to dielectric spectra,

additional peak is also observed in absorption spectra (Fig. 8 (b)). Electron energy loss function for Cs doped compound is shown in Fig. 9 (b), and the significant peaks called plasma peaks are observed around the same energy range of the host compound. The zero reflectivity (Fig. 10 (b)) limit (i.e reflectivity value at zero frequency) for the Cs doped compound is increased to 0.054 when compared to the host compound (0.05). No significant difference is observed from the host to Cs doped compound except for an increase in the reflectivity value (for the highest peak).

4. Conclusions

Detailed ab-initio calculations were performed to study the electronic structure and optical properties of KMgCl_3 host as well as with Cs doping based on the FP-LAPW method using TB-mBJ functional. From our calculations we have predicted that the impurity induced cross luminescence can be observed in KMgCl_3 with Cs doping, though the host compound is not a CVL active material i.e. with an addition of Cs, KMgCl_3 is changing from A to L-type. The main reason for the impurity induced cross luminescence is that the additional Cs states are observed below the valence band of the host compound. This may result in reduction of the energy difference between valence band to upper core valence which satisfies the condition of CVL i.e. energy difference between valence band and upper core valence band should be less than the band gap of the compound. We have also observed the host compound to be optically isotropic.

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Table 1. Calculated band gaps, in eV, of KMgCl_3 , Cs doped KMgCl_3 compounds using GGA and TB-mBJ functionals along with the available theoretical values.

Method	KMgCl_3 (other theory [41])	$\text{KMgCl}_3:\text{Cs}$
GGA	4.67(4.71)	4.70
TB-mBJ	6.99(6.44)	6.97

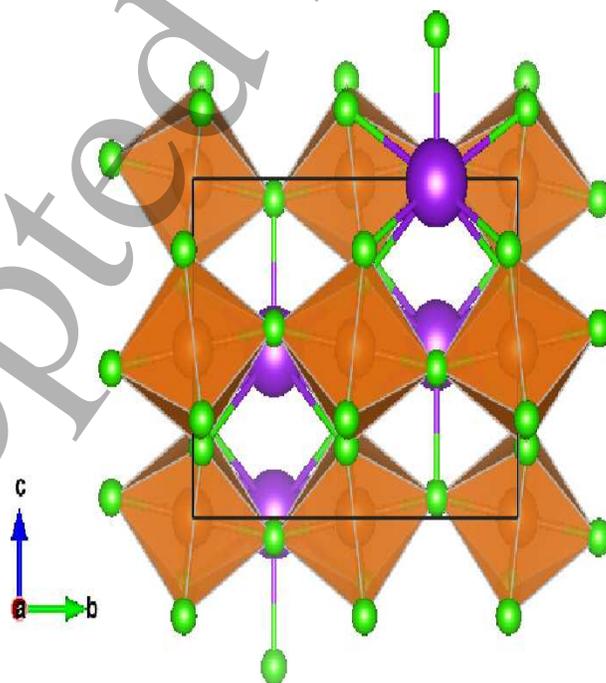
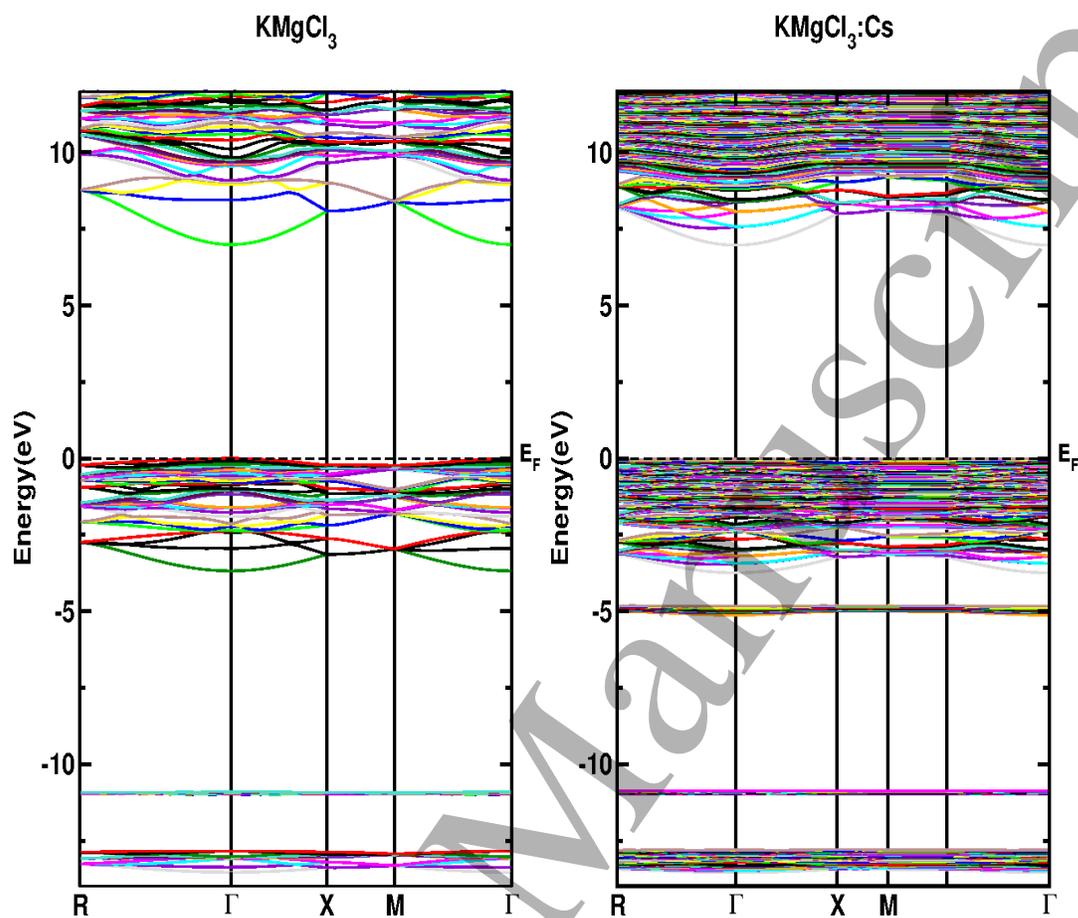


Figure 1. Crystal structure of KMgCl_3 compound showing the octahedral representation. Different colors denote different atoms, Purple-K, Orange-Mg, Green-Cl atoms.



34 **Figure 2.** Calculated band structure of KMgCl_3 , Cs doped KMgCl_3 using TB-mBJ
35 functional. KMgCl_3 to be a direct band gap insulator with valence band maximum
36 and conduction band minimum at Γ point.
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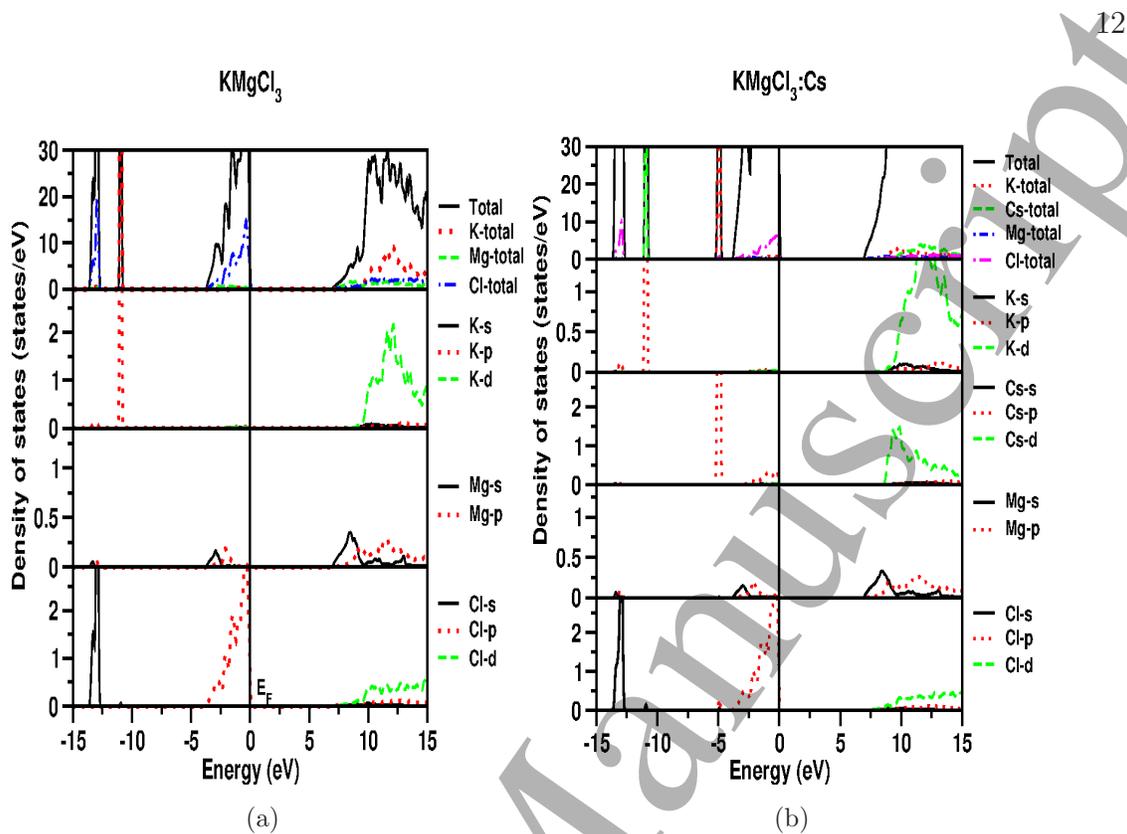


Figure 3. Calculated density of states of (a) host KMgCl_3 , (b) $\text{KMgCl}_3:\text{Cs}$ with TB-mBJ functional.

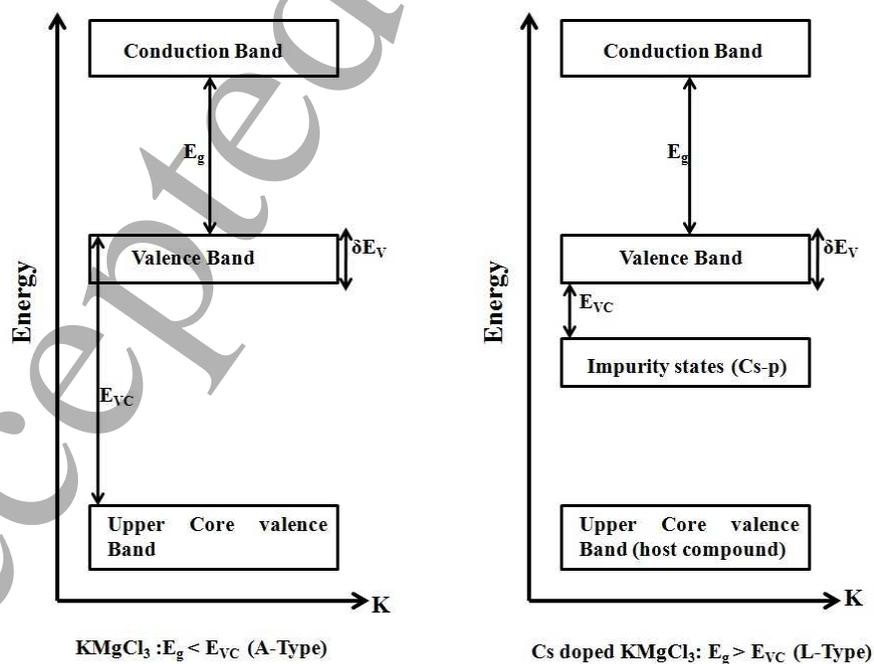


Figure 4. Schematic diagram of energy versus K plot of host and Cs doped KMgCl_3 representing A and L-type materials.

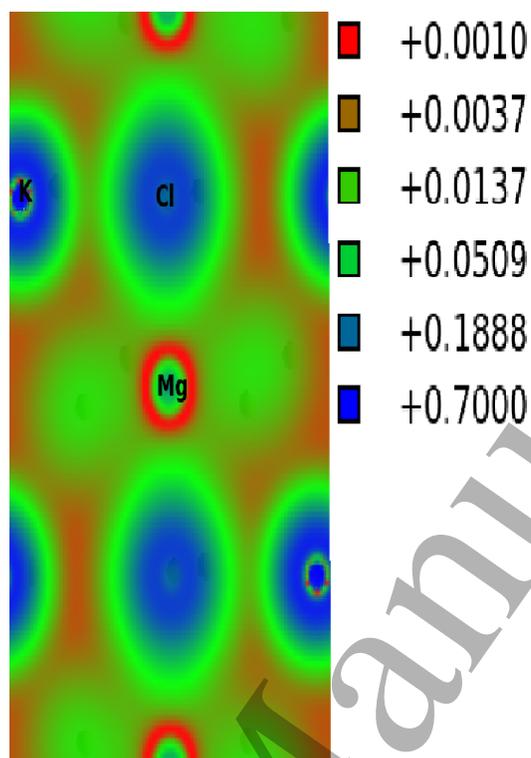


Figure 5. Difference charge density plots of KMgCl_3 along (100) plan.

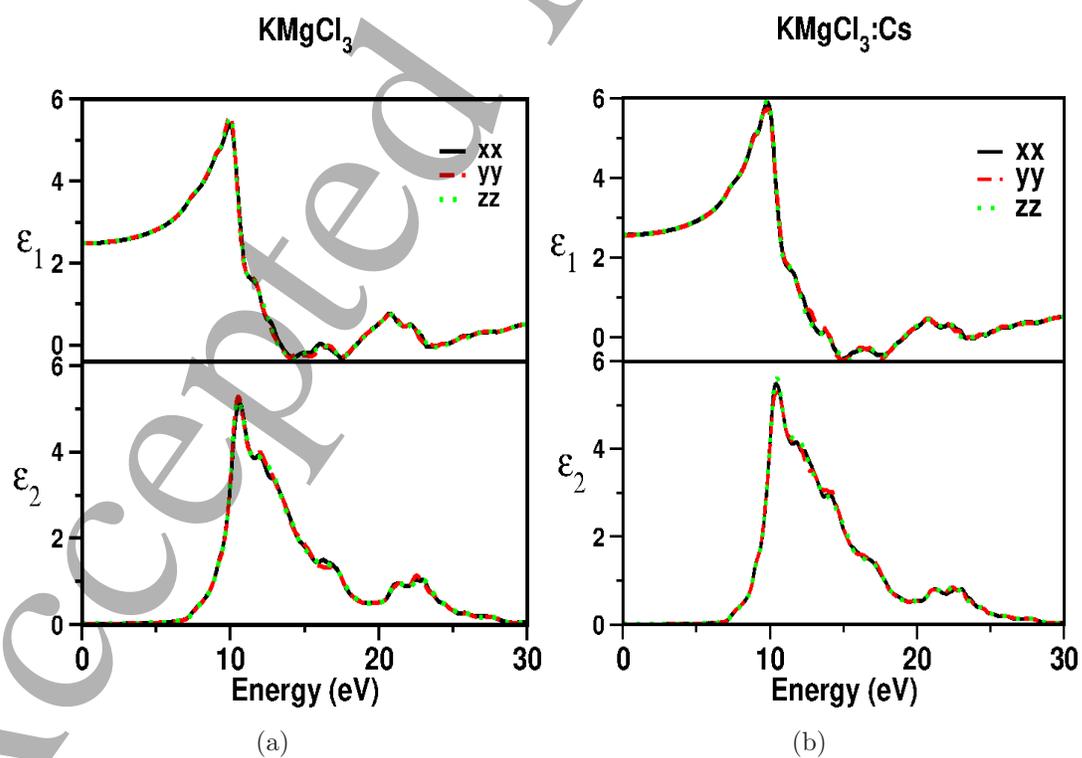
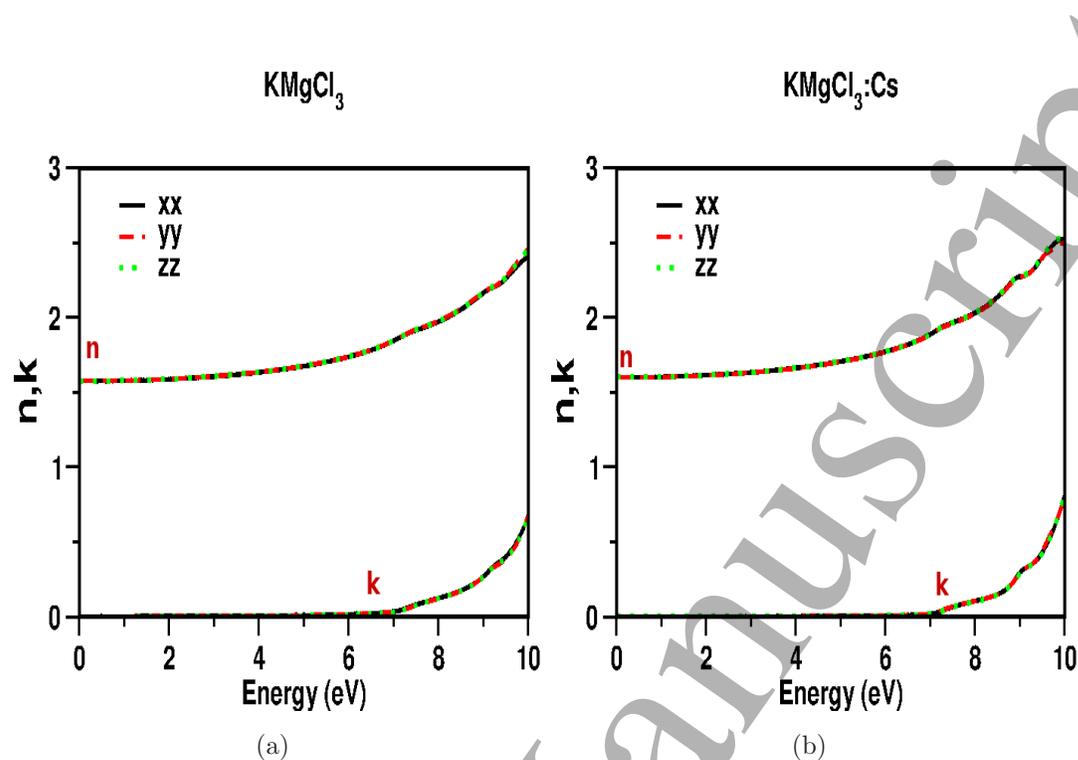
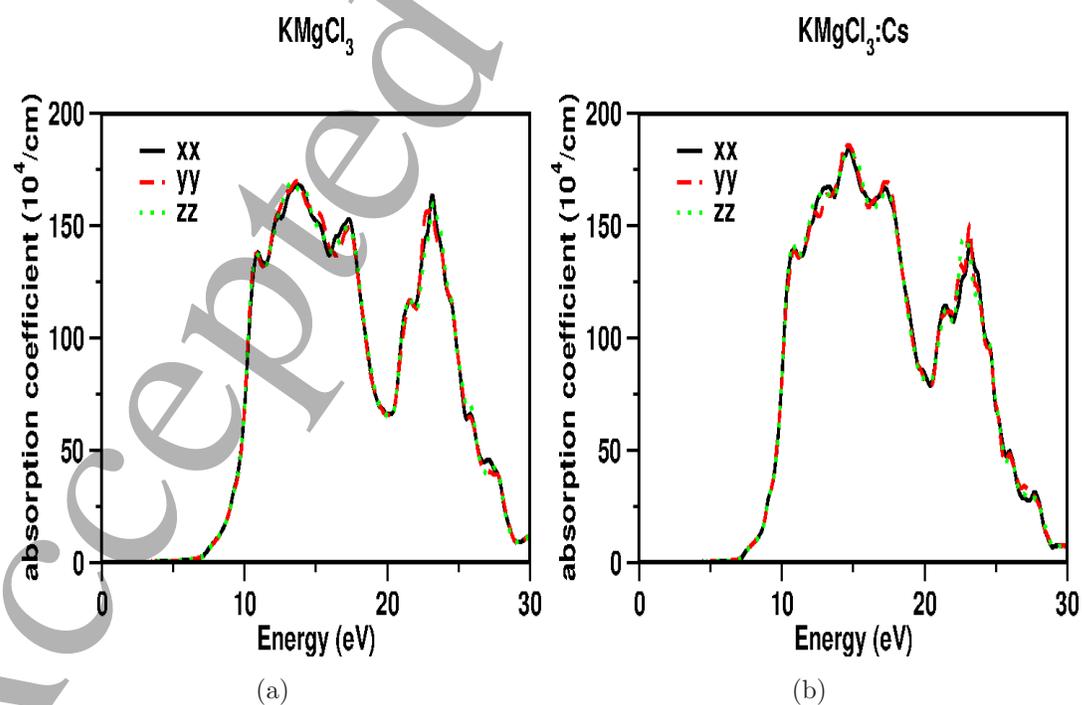


Figure 6. Real (upper panel) and imaginary (lower panel) parts of dielectric constants of (a) KMgCl_3 (b) $\text{KMgCl}_3:\text{Cs}$ using TB-mBJ functional.



27 **Figure 7.** Refractive index, extinction coefficient plots of KMgCl_3 , and $\text{KMgCl}_3:\text{Cs}$
 28 using TB-mBJ functional showing the optical isotropy of the compounds.
 29



58 **Figure 8.** Calculated absorption coefficient of (a) KMgCl_3 and (b) Cs doped KMgCl_3
 59 along three directions using TB-mBJ functional.
 60

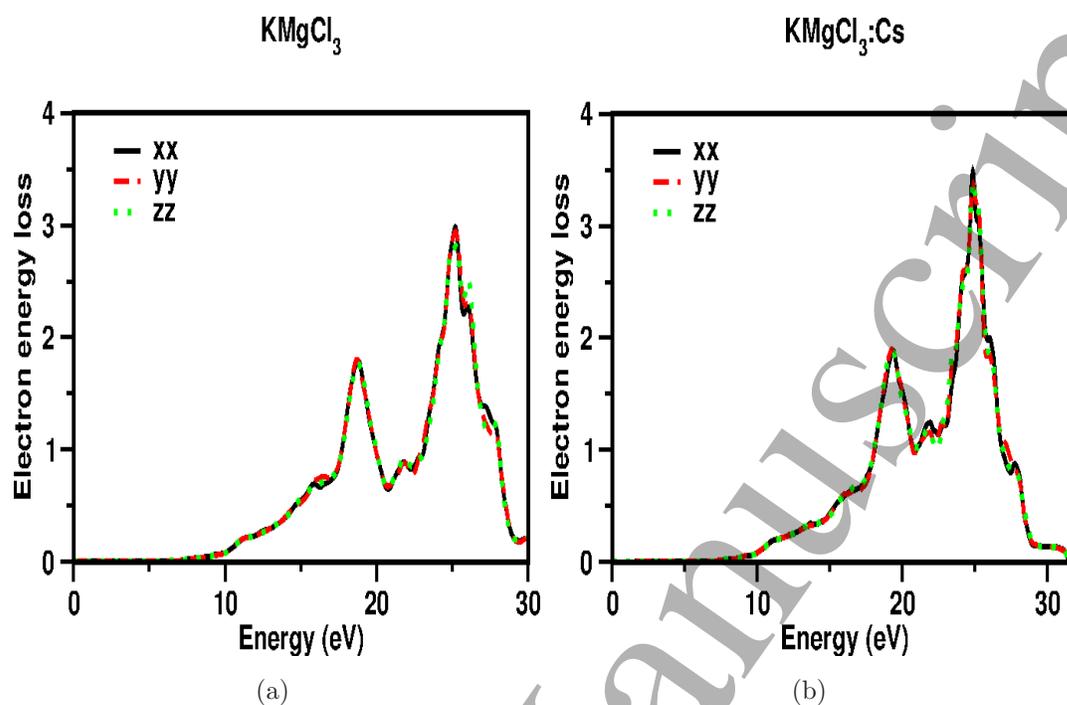


Figure 9. Calculated electron energy loss functions along the three crystallographic directions of host and Cs doped KMgCl_3 .

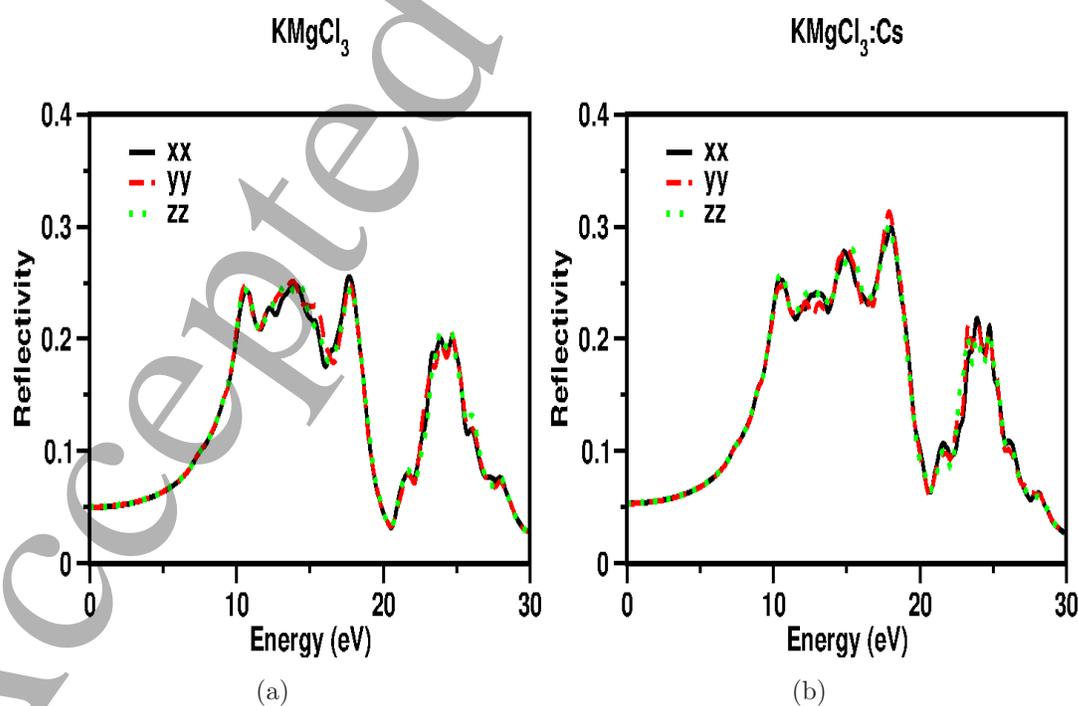


Figure 10. Reflectivity of KMgCl_3 and $\text{KMgCl}_3:\text{Cs}$ calculated using the TB-mBJ functional.