



# CsMgCl<sub>3</sub>: A promising cross luminescence material



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## ABSTRACT

Full-potential linearized augmented plane wave method has been used to study the cross luminescence of halide scintillators. The electronic structure and optical properties of alkali halides such as CsMgCl<sub>3</sub>, CsCaCl<sub>3</sub>, and CsSrCl<sub>3</sub> are presented. One of the major criteria for the cross luminescence to happen is the energy difference between valence band and next deeper core valence band being lesser when compared to energy gap of the compound, so that radiative electronic transition may occur between core valence band and valence band which might lead to fast scintillation. We found this criterion to be satisfied in these compounds leading to cross luminescence. The presence of high energy peaks in the absorption spectra indicates the creation of holes in the core valence band, which is an essential criterion for the occurrence of cross luminescence. The electronic structure, and optical properties studies clearly indicate CsMgCl<sub>3</sub>, CsCaCl<sub>3</sub>, and CsSrCl<sub>3</sub> to be cross luminescence materials comparable to CsCl which is one of the well known fast scintillators. In addition, CsMgCl<sub>3</sub> is found to be better among the studied compounds with optical isotropy though the compound is structurally anisotropic.

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## 1. Introduction

Cross luminescence is one of the important criteria for fast scintillation. The compounds which exhibit cross luminescence or core valence luminescence (CVL) are very interesting because of their fast decay and high thermal stability. In the past few decades there were continued experimental and theoretical search progressing in various directions searching for scintillators with desired properties, but there is no unique scintillator available, with high efficiency, high yield, fast scintillation, good energy resolution, which provoke further research in exploring fast scintillators which are having very less decay time. Cross luminescence is one of the phenomena for fast scintillation with less decay time of the order of nanoseconds (ns) or less, where radiative transition is observed between halogen derived valence band and upper most cation core valence band resulting in Auger free luminescence. With the incident radiation, electrons from core valence band will be excited to conduction band leaving a hole in the core valence band, and these holes combine radiatively with electrons from the valence band, while the hole created in the valence band might combine with electrons from the conduction band. The main participant of this process is the core holes. The

radiative transition of electrons from valence band to core valence band will lead to the cross luminescence (also called Auger free luminescence) with short wavelength [1–12]. The general requirement for CVL is that energy difference between top of the valence band and top of core valence band ( $E_{VC}$ ) should be less than the band gap ( $E_g$ ) of the compound. If  $E_{VC} > E_g$ , then Auger transitions are dominated because of their higher probability. The incident energy should be such a way that it will excite the core level electrons, leaving a hole in core valence band. The decay time of CVL compounds is very small with the emission in the short wavelength region. The fast scintillation observed in BaF<sub>2</sub> opened up the origin for CVL in scintillators [5,13], which is also observed in AX (A=alkali, X=halide), and ABX<sub>3</sub> (A=alkali, B=alkali-earth, and X=halide) [2] compounds. Moving from AB to ABX<sub>3</sub> type of compounds, decay time and light output are reported to increase because of the increase in the distance between A–X, thereby reducing the overlap of wave functions which may result in smaller probability of CVL [2]. Though the decay time may be higher in ABX<sub>3</sub>, it might be advantageous to get a better light yield which further provokes us to explore this series. Here we are mainly interested in studying the cross luminescence in ABX<sub>3</sub> (A=alkali, B=alkali-earth, and X=halide) type, CsMgCl<sub>3</sub>, CsCaCl<sub>3</sub>, and CsSrCl<sub>3</sub>, compounds and would like to explore the type of transition involved through computed electronic structure and optical properties calculations. These are preferred over well known binary compound CsCl because of higher yield of cross

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luminescence reported experimentally [2,8]. Cross luminescence is observed in some of the  $ABX_3$  type compounds such as  $RbCaF_3$ ,  $CsCaCl_3$ ,  $CsSrCl_3$ ,  $CsMgCl_3$ ,  $CsMgF_3$  [8,9,14–17], barium based fluorides [18], and  $KF$ ,  $KMgF_3$ , and  $KCaF_3$  [19]. Cross luminescence is also observed in impure systems like  $Rb_{1-x}Cs_xBr$  ( $x < 0.2$ ) [2], and  $A_{1-x}Cs_x CaCl_3$  ( $A=K, Rb$ ) crystals [20,21] (where addition of  $Cs$  leads to CVL in these compounds) implying the importance of  $Cs$  in the context of cross luminescence.

Recently, theoretical studies have been carried out on  $CsCaCl_3$  in which the authors reported the elastic constants, and optical properties of these compound [22]. The scintillation properties of doped  $CsCaCl_3$  and  $CsCaI_3$  are investigated experimentally as well as theoretically. The temperature dependence of photo-luminescence excitation, emission, and decay time was measured (experimentally), the band structure and the efficiency of the cross luminescence of these materials are also explained (theoretically) [23]. The structural, elastic, chemical bonding and optoelectronic properties of  $CsSrM_3$  ( $M=F, Cl$ ) are studied through the density functional calculations [24]. Our main focus in the present work is to address the cross luminescence of these compounds, the type of transition involved, and also to compare the scintillation characteristics of these three scintillators through the calculated electronic structure, and optical property calculations. The organization of the paper is as follows, in Section 2 we describe the computational details of our calculations, in Section 3 we discuss the results and discussion part followed by conclusions.

## 2. Computational details

Full potential linearized augmented plane wave method (FP-LAPW) has been used to perform the first principles total energy calculations as implemented in wien2K code [25,26]. FP-LAPW is an accurate method for calculating the electronic structure and optical properties of the compounds. The wave function is expanded in spherical harmonics within the atomic sphere, while outside the sphere it is expanded using plane-wave basis. The potential is given by

$$V(r) = \begin{cases} \sum_{lm} V_{lm}(r) Y_{lm}(\hat{r}) & \text{inside sphere} \\ \sum_K V_K e^{iK \cdot r} & \text{outside sphere} \end{cases} \quad (1)$$

The exchange-correlation potential is calculated within the generalized gradient approximation (GGA) [27], and Tran and Blaha modified Becke–Johnson potential (TB-mBJ) [28,29]. The separation between the core states and valence states is set to  $-6.0$  Ry. The wave functions in the interstitial region were expanded using plane waves with a cutoff of  $R_{MT}K_{max} = 9$  in order to achieve energy eigenvalue convergence, where  $K_{max}$  is the plane wave cut-off, and  $R_{MT}$  is the smallest muffin tin sphere radii. Convergence tests were carried out using higher  $R_{MT}K_{max}$  values, giving no significant changes in the calculated properties. The compounds of present study are insulators, and as local density approximation (LDA) and generalized gradient approximation underestimate the band gap, we have used the Tran and Blaha modified Becke–Johnson potential (TB-mBJ), which gives the band gap values close to the experiments. Throughout our study we have computed the electronic structure, optical properties using the TB-mBJ functional at the experimental lattice parameters with optimized atomic position. We have used  $10 \times 10 \times 10$   $k$ -mesh with 84  $k$ -points in IBZ (irreducible Brillouine zone) for  $k$ -space integration for the electronic structure calculation and  $17 \times 17 \times 17$   $k$ -mesh for the optical property calculations. The optical properties of the materials can be well explained by using the dielectric function  $\epsilon(\omega)$  which consists of real and imaginary parts  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  respectively. The  $\epsilon_2(\omega)$  can be calculated from electronic band structure, and  $\epsilon_1(\omega)$  can be extracted from the  $\epsilon_2(\omega)$  by using

the Kramers–Kronig relation. From the  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  values one can calculate other optical parameters like refractive index and extinction coefficient [30]:

$$\epsilon_2(\omega) = \frac{\hbar^2 e^2}{\pi m^2 \omega^2} \sum_{c,v} \int d^3k \langle c_k | p^\alpha | v_k \rangle \langle v_k | p^\beta | c_k \rangle \times \delta(\epsilon_{c_k} - \epsilon_{v_k} - \omega) \quad (2)$$

where  $p$  is the momentum matrix element between  $\alpha$  and  $\beta$  states,  $c_k$  and  $v_k$  are the crystal wave functions corresponding to the conduction band and valence bands with crystal wave vector  $k$ .

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{(\omega')^2 - \omega^2} d\omega' \quad (3)$$

where  $P$  is the principle value of integration.

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

$$k(\omega) = \left[ \frac{\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega)}{2} \right]^{1/2} \quad (5)$$

Moreover to the best of our knowledge, there are no theoretical calculations available on  $CsMgCl_3$ , though the other two compounds have some earlier theoretical calculations on optical properties [22–24]. In the present work, main emphasis is laid on studying the trends in the optical properties of  $ABX_3$  compounds. Among the studied compounds  $CsMgCl_3$  [31] crystallize in hexagonal crystal structure with space group  $P6_3/mmc$  with lattice parameters  $a=7.269$ ,  $b=6.187$  Å, with  $Cs$  atom at  $(1/3, 2/3, 0.75)$ ,  $Mg$  at  $(0, 0, 0)$  and  $Cl$  at  $(0.1556, -0.1556, 0.25)$ .  $CsCaCl_3$  and  $CsSrCl_3$  crystallize in the cubic perovskite structure with space group  $Pm-3m$  (space group number 221) with  $Cs$  atom located at  $(0, 0, 0)$ ,  $M$  ( $Ca, Sr$ ) at  $(0.5, 0.5, 0.5)$  and  $Cl$  at  $(0, 0.5, 0.5)$  with lattice parameters 5.390 and 5.615 Å for  $CsCaCl_3$  [22,32] and  $CsSrCl_3$  [24,33] respectively.

## 3. Results and discussions

### 3.1. Electronic properties

The computed energy band structure along the high symmetry points in the first Brillouine zone and total density of states of chloroperovskites are shown in Fig. 1 using the TB-mBJ functional along with  $CsCl$  band structure which is a well known cross luminescence material. These compounds are insulators with wide band gap because of large electro-negativity difference between halogen derived valence band and cation derived conduction band. From these band structure plots, we can clearly see that the energy difference between the top of the valence band and the top of the core valence band is less compared to energy gap ( $E_g$ ) of the compound, which is an essential criterion to observe cross luminescence. The width of valence band is more for  $CsMCl_3$  ( $M=Mg, Ca, Sr$ ), when compared with  $CsCl$  as seen from Fig. 1. But for a better cross luminescence, it is desirable that the width of the upper valence band (VB) and core valence band (CVB) are appreciably represented as  $A$  and  $B$  in the band structure plots respectively. But in  $ABX_3$  the VB width is more, while in  $CsCl$ , the CVB width is little more than that in  $CsMgCl_3$ . The higher value of CVB width compared to  $CsMCl_3$  ( $M=Mg, Ca, Sr$ ) might be one of the reasons for increased CVL probability in case of  $AB$  ( $CsCl$ ) compared to  $ABX_3$  which was discussed earlier. The calculated band gaps, width of the valence band ( $\delta E_V$ ), energy difference between top valence band and top core valence band ( $E_{VC}$ ), and  $E_{VC} - \delta E_V = E_{g_2}$  are given in Table 1, along with available experimental and theoretical values. The schematic diagram corresponding to these representations is shown in

**Fig. 1.** Band structure of CsCl, CsMgCl<sub>3</sub>, CsCaCl<sub>3</sub>, and CsSrCl<sub>3</sub> compounds, along with total density of states using the TB-mBJ functional, where *A* and *B* represent the width of the valence band and core valence band respectively. From the band structure plots it is clear that *A* increases from CsCl to CsMgCl<sub>3</sub> and decreases in CsSrCl<sub>3</sub>, and *B* decreases from CsCl to CsSrCl<sub>3</sub>.

Fig. 2(a), and the cross luminescence, which is the transition of electrons from valence band to core valence band, is depicted in Fig. 2(b). From Table 1, we can clearly see that  $E_{VC} < E_g$ ,  $\delta E_V > E_{g2}$  in case of CsMgCl<sub>3</sub> and,  $\delta E_V < E_{g2}$  for other compounds, and calculated band gap,  $\delta E_V$ ,  $E_{VC}$  and  $E_{g2}$  values are comparable to the available experimental and other theoretical values. We observed energy gap ( $E_g$ ) to decrease from CsMgCl<sub>3</sub> to CsCaCl<sub>3</sub> and then increase to CsSrCl<sub>3</sub>, and also the energy difference between the bottom of the valence band and the top of the core valence band ( $E_{g2}$ ) is found to increase from CsMgCl<sub>3</sub> to CsSrCl<sub>3</sub> because of the decrease in the width of the valence band. The direct  $\Gamma$ - $\Gamma$  band gap is predicted for CsMgCl<sub>3</sub>, whereas an indirect band gap along  $M$ - $\Gamma$  direction is observed for CsCaCl<sub>3</sub>, and CsSrCl<sub>3</sub> compounds. Scintillation phenomena can be observed in various ways depending on the type of transition involved, which are classified as A-type, L-type, and AL-type. In the case of A-type  $E_{VC} > E_g$ , where Auger luminescence is dominating, in the case of L-type  $E_{VC} < E_g$ , where Auger-free luminescence is observed between valence and core valence bands. AL-type of compounds are in between A-type and L-type. The compounds of present study are of L-type ( $E_{VC} < E_g$ ), where the cross luminescence can be observed between valence band and next deeper core valence band.

Density of states of these compounds are studied for further understanding and the corresponding figures are shown in Fig. 3. Conduction band is due to Mg-s,p and Cs-d states in case of CsMgCl<sub>3</sub>, whereas these states are due to  $M$ -d ( $M$ =Ca, Sr) and Cs-d with minor contribution from Cl-d in case of CsCaCl<sub>3</sub> and CsSrCl<sub>3</sub>. The valence band is of Cl-p states hybridized with the Mg-s,p and Cs-p states in case of CsMgCl<sub>3</sub>, Ca-d,p and Cs-p states in the case of CsCaCl<sub>3</sub>, and Sr-d,p states in case of CsSrCl<sub>3</sub> compounds. Valence band spread around the energy

**Table 1**

Calculated band gaps, in eV, of CsMgCl<sub>3</sub>, CsCaCl<sub>3</sub>, and CsSrCl<sub>3</sub> compounds using GGA and TB-mBJ functionals along with the width of the valence band ( $\delta E_V$ ), the energy difference between the top of valence band and the top of core valence band ( $E_{VC}$ ), and  $E_{g2}(E_{VC} - \delta E_V)$  in eV, along with the available theoretical and experimental values.

Method	CsMgCl <sub>3</sub>	CsCaCl <sub>3</sub>	CsSrCl <sub>3</sub>
GGA	5.31	5.50 (5.35 <sup>a</sup> , 5.45 <sup>b</sup> )	5.16 (5.61 <sup>c</sup> )
TB-mBJ	7.76	6.89 (6.93 <sup>a</sup> )	7.52 (7.65 <sup>c</sup> )
Exp	8.5 <sup>d,e</sup>	8.5 <sup>d</sup> , 8.1 <sup>e</sup>	7.7 <sup>e</sup>
$\delta E_V$	2.88 (2.9 <sup>d,e</sup> )	2.24 (2.4 <sup>d</sup> , 2.8 <sup>e</sup> )	1.74 (2.5 <sup>e</sup> )
$E_{VC}$	5.48 (5.6 <sup>e</sup> ),	5.57 (5.9 <sup>e</sup> )	5.9 (5.8 <sup>e</sup> )
$E_{g2}$	2.6 (2.6 <sup>d</sup> , 2.7 <sup>e</sup> )	3.24 (3.1 <sup>d,e</sup> , 2.95 <sup>b</sup> )	4.16 (3.3 <sup>e</sup> )

<sup>a</sup> Ref. [22].

<sup>b</sup> Ref. [23].

<sup>c</sup> Ref. [24].

<sup>d</sup> Ref. [9].

<sup>e</sup> Ref. [17].

region 0 to  $-2.88$  eV for CsMgCl<sub>3</sub>, 0 to  $-2.24$  eV for CsCaCl<sub>3</sub>, and 0 to  $-1.74$  eV for CsSrCl<sub>3</sub> compounds. The width of the VB of CsMgCl<sub>3</sub> is little higher because of the presence of Mg-s,p states, and also Cs-p states, whereas these Cs-p states are relatively lesser in CsCaCl<sub>3</sub> and they are absent in case of CsSrCl<sub>3</sub>. VB width of CsCl is less compared to CsMgCl<sub>3</sub> because of missing states  $M$ -d or Mg-s,p states in the valence band. The VB width being more is an essential property and it is discussed in detail while explaining optical properties in the later section. The core valence band is situated around  $-5.48$  to  $-5.63$  eV for CsMgCl<sub>3</sub>,  $-5.57$  to  $-5.67$  in case of CsCaCl<sub>3</sub>, and  $-5.9$  to  $-5.95$  eV for CsSrCl<sub>3</sub>, and these states are mainly due to Cs-p states for all the

