Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information for

Exploring Novel Anti-Perovskites X_4A_2O (X = K, Rb, Cs; A = Cl, Br, I) with Excellent Photoelectric Performance towards Photovoltaic Applications

Yuqi Zhang,[a] Kai Li,[a] Min Zhang *[ab] and Lei Li *[ab]

[a] *College of Physics and Electronic Information, Inner Mongolia Normal University, Hohhot 010022, China.*

[b] *Inner Mongolia Key Laboratory of Applied Condensed Matter Physics, Hohhot 010022, China.*

E-mail: zhangm@imnu.edu.cn; lilei@imnu.edu.cn

CALCULATION METHOD

In the calculation of carrier transport characteristics, we employed the deformation potential (DP) method,[1] wherein a strain ranging from -2% to 2% was applied to the material in order to determine its elastic modulus C and deformation potential constant E_1. The formula for calculating the carrier mobility of the material is as follows:

$$\mu = \frac{(8\pi)^{1/2}\hbar^4 eC}{3(m^*)^{5/2}(k_B T)^{3/2}E_1^2} \tag{S1}$$

In the equation, $\hbar$, e, C, m^*, k_B, T and E_1 respectively denote the reduced Planck constant, elementary charge, elastic modulus, effective mass of charge carriers, Boltzmann constant, Kelvin temperature and deformation potential constant.

The macroscopic optical properties of materials are usually represented by the complex dielectric function:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \tag{S2}$$

In this equation, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ represent the real and imaginary components of the complex dielectric function respectively, with ω denoting the frequency of photons. The dielectric function demonstrates a linear response to electromagnetic interactions and is closely associated with the band gap value E_g. The determination of $\varepsilon_2(\omega)$ can be achieved through momentum matrix elements as expressed below:

$$\varepsilon_2(\omega)=\frac{4\pi^2\mathrm{e}^2}{\Omega}\lim_{q\to 0}\frac{1}{q^2}\sum_{c,v,k}2\omega_k\delta\left(\varepsilon_{ck}-\varepsilon_{vk}-\omega\right)\times\left\langle u_{ck+e_{\alpha}q}\middle|u_{ck}\right\rangle\left\langle u_{ck+e_{\beta}q}\middle|u_{vk}\right\rangle^{*} \tag{S3}$$

The equation includes e_α and e_β, which represent unit vectors along the α and β directions, q representing the wave number of incident electromagnetic waves, Ω representing the volume of a crystal cell, and c and v respectively representing conduction band and valence band. The imaginary part $\varepsilon_2(\omega)$ of the complex dielectric function is obtained through integration of momentum matrix elements between unoccupied and occupied wave functions in the Brillouin zone, representing the energy required for the formation of an electric dipole moment. This quantity is directly proportional to the absorption spectrum and reflects optical transitions from valence band maximum (VBM) to conduction band minimum (CBM) at the threshold energy level. The peak value corresponds to the number of electrons undergoing transition. The larger the imaginary components of the complex dielectric function, the greater the extent of electronic excitation and the poorer the insulation performance of the system. In this case, there is a higher possibility for electrons to absorb photons, resulting in a larger number of electrons in an excited state and a higher probability of transition occurring. The real part $\varepsilon_1(\omega)$ of the dielectric function is derived from the imaginary part using the Kramers-Kronig transformation[2]:

$$\varepsilon_1(\omega)=1+\frac{2}{\pi}P\int_0^{\infty}\frac{\omega'\varepsilon_2(\omega')}{\omega'^2-\omega^2}\mathrm{d}\omega' \tag{S4}$$

In the equation, P represents the Cauchy principal value of the integral. The polarization behavior of materials can be comprehended through $\varepsilon_1(\omega)$, which is commonly employed to indicate the magnitude of charge polarization in response to an external electric field and reflects the material's intrinsic energy storage capability. A higher dielectric constant signifies a more pronounced affinity for charges. If the influence of lattice vibrations is neglected, the value at zero frequency or zero energy limit is the static dielectric constant $\varepsilon(0)$. The presence of a higher static dielectric constant can enhance the occurrence of low-level charge defects, thereby reducing radiation recombination and exciton binding energy. Additionally, it signifies a decrease in long-range Coulomb attraction due to the screening effect on charged defects and impurities, resulting in reduced carrier recombination, scattering, and trapping.[3]

The absorption coefficient α is a crucial parameter for assessing the light-absorbing capability of materials, and its relationship with frequency ω within a specific range of photon energy can be determined using the subsequent formula:

$$\alpha(\omega)=\sqrt{2}\omega\left[\sqrt{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)}-\varepsilon_1(\omega)\right]^{1/2} \tag{S5}$$

In principle, the maximum efficiency of a solar cell is determined by the universally recognized and classical Shockley-Queisser (SQ) limit.[4] The mathematical formulation is as follows:

$$\eta=\frac{p_m}{p_{in}} \tag{S6}$$

The variables P_m and P_{in} respectively denote the peak power density and the total incident power density of the solar energy spectrum in the given equation. Due to the reliance solely on the electronic band gap value of the material, estimation of maximum efficiency in this method is approximate. Building upon this, Liping Yu and Zunger developed the Spectroscopic Limited Maximum Efficiency (SLME) method for solar cells.[5,6] The calculation of power density P can be obtained by multiplying current density J with voltage V, as depicted in the following equation.

$$P=JV=\left\{J_{\mathrm{sc}}-J_0\left[\exp\left(\frac{eV}{k_BT}\right)-1\right]\right\}V \tag{S7}$$

In the equation, J_{sc} and J_0 represent short circuit current density and reverse saturation current density, respectively. The calculation of J_{sc} and J_0 can be derived if the absorption coefficient $\alpha(E)$, AM1.5G solar spectrum I_{sun}, and blackbody spectrum $I_{\mathrm{bb}}(E,T)$ are known. The corresponding formula is as follows:

$$J_{\mathrm{SC}}=\mathrm{e}\int_0^{\infty}\alpha(E)I_{\mathrm{sun}}(E)\mathrm{d}E \tag{S8}$$

$$J_0=\frac{J_0^{\mathrm{r}}}{f_{\mathrm{r}}}=\frac{\mathrm{e}\pi}{f_{\mathrm{r}}}\int_0^{\infty}\alpha(E)I_{\mathrm{bb}}(E,T)\mathrm{d}E \tag{S9}$$

In the equation, J_0^{r} and f_{r} respectively denote the radiation composite current density and radiation composite current fraction.

The open circuit voltage is the maximum output voltage of a solar cell under zero current (open circuit) conditions. The calculation formula is as follows:

$$\mathrm{V_{OC}} = \frac{k_B T}{e} \ln\left(1 + \frac{J_{\mathrm{SC}}}{J_0}\right) \tag{S10}$$

The fill factor (FF) reflects the ratio of the actual output power of the solar cell to the ideal power, and is an important parameter to characterize the performance of the solar cell. The greater the value, the higher the photoelectric conversion efficiency of the battery. The formula is as follows:

$$FF = \frac{V_m \times J_m}{V_{\mathrm{OC}} \times J_{\mathrm{SC}}} \tag{S11}$$

In the equation, V_m and J_m represent the voltage and current density at the maximum power point (MPP), respectively.

Table S1 Lattice constant and angle of anti-perovskites X_4A_2O (X = K, Rb, Cs; A = Cl, Br, I)

Materials	a (Å)	b (Å)	c (Å)	$\alpha = \beta = \gamma$
K_4Cl_2O	5.172	5.172	16.055	90°
K_4Br_2O	5.237	5.237	16.789	90°
K_4I_2O	5.344	5.344	17.717	90°
Rb_4Cl_2O	5.466	5.466	16.819	90°
Rb_4Br_2O	5.528	5.528	17.515	90°
Rb_4I_2O	5.639	5.639	18.240	90°
Cs_4Cl_2O	5.785	5.785	17.591	90°
Cs_4Br_2O	5.838	5.838	18.246	90°
Cs_4I_2O	5.923	5.923	19.079	90°

Table S2 Elasticity modulus C (GPa) and deformation potential constant E_1 (eV) of X_4A_2O in in-plane (x/y) and out-of-plane (z) directions

Materials	$C_{x/y}$	C_z	$E_{1\text{e-}x/y}$	$E_{1\text{e-}z}$	$E_{1\text{h-}x/y}$	$E_{1\text{h-}z}$
K_4Cl_2O	51.24	32.87	6.16	0.80	6.67	1.35
K_4Br_2O	43.25	28.08	5.37	0.86	5.87	1.91
K_4I_2O	45.47	23.90	7.01	1.41	7.37	2.74
Rb_4Cl_2O	42.99	27.19	6.41	1.20	8.19	1.90
Rb_4Br_2O	37.89	23.89	7.31	2.47	9.02	3.64
Rb_4I_2O	39.05	21.94	5.08	0.56	6.27	0.80
Cs_4Cl_2O	19.93	20.96	9.94	1.98	13.82	3.22
Cs_4Br_2O	16.87	19.32	9.22	2.43	13.17	4.05
Cs_4I_2O	14.37	18.05	7.57	0.55	10.41	2.29

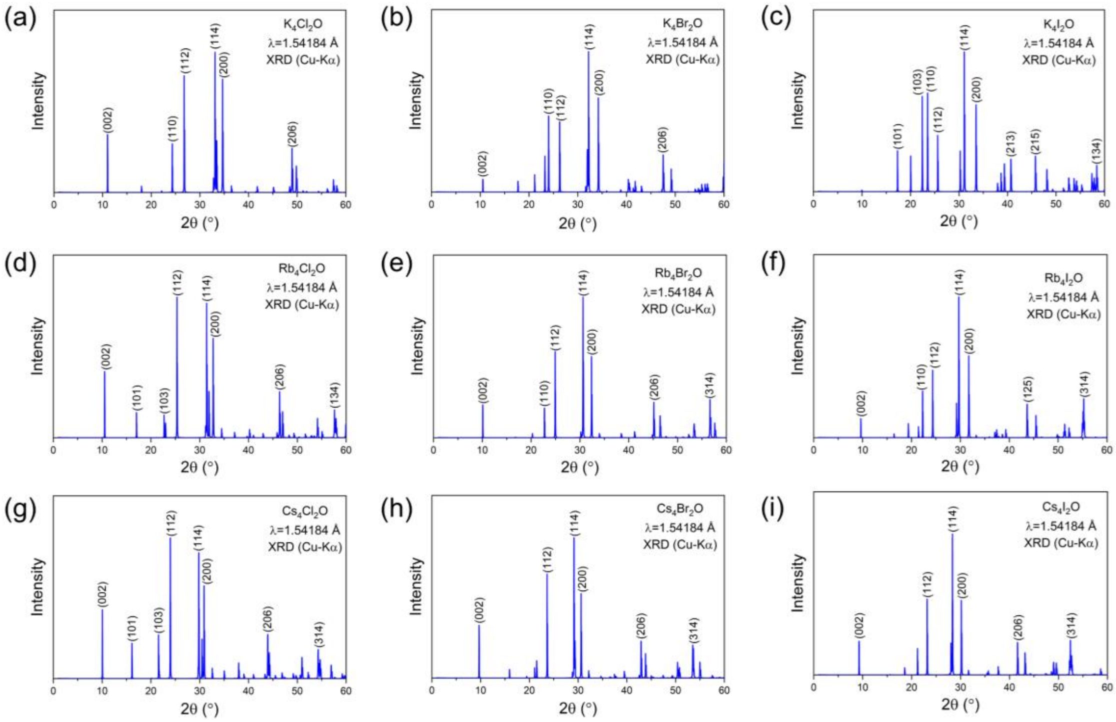

Fig.S1 X-ray diffraction (XRD) patterns of X_4A_2O

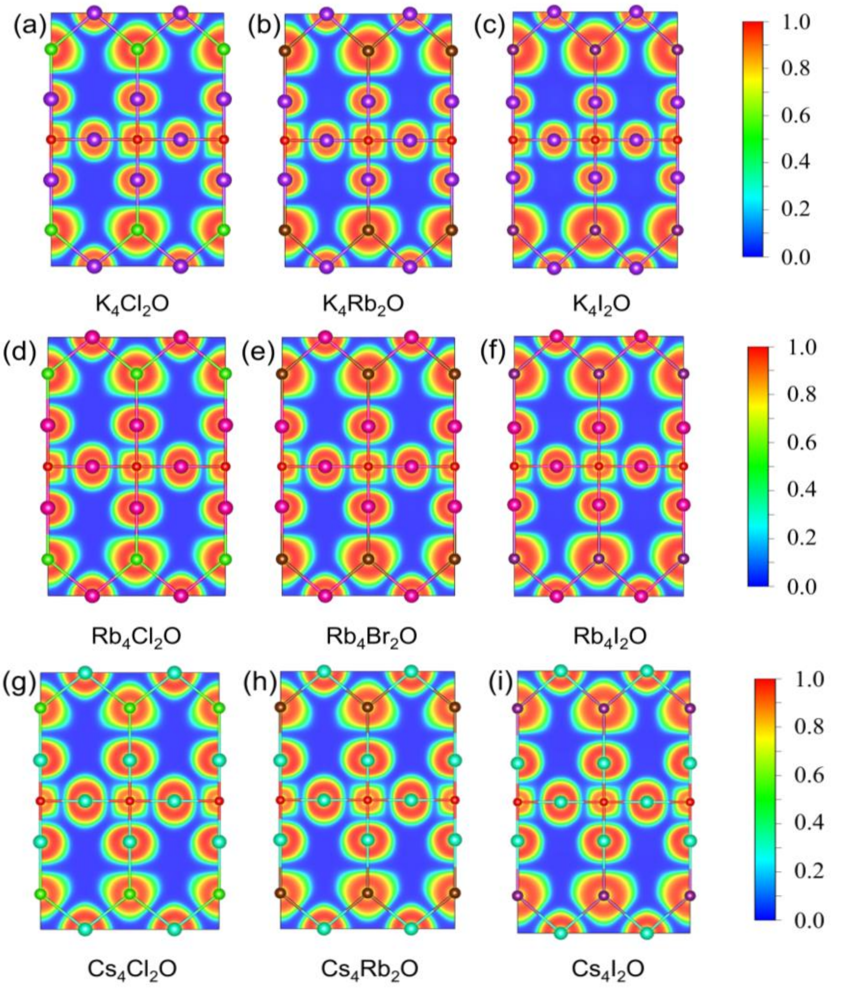

Fig.S2 Electron localization functions (ELF) in the direction (100) of X_4A_2O

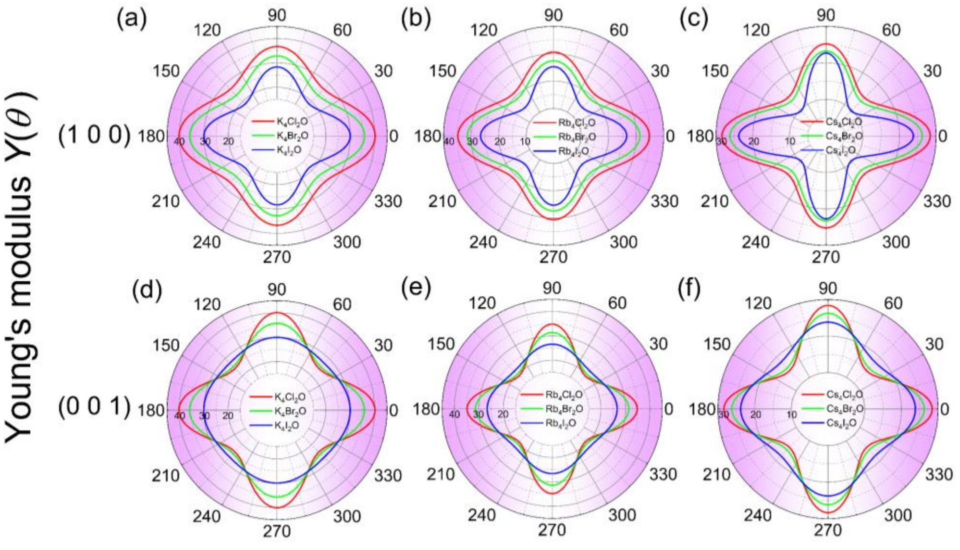

Fig.S3 The orientation-dependence of Young's modulus $Y(\theta)$ of X_4A_2O

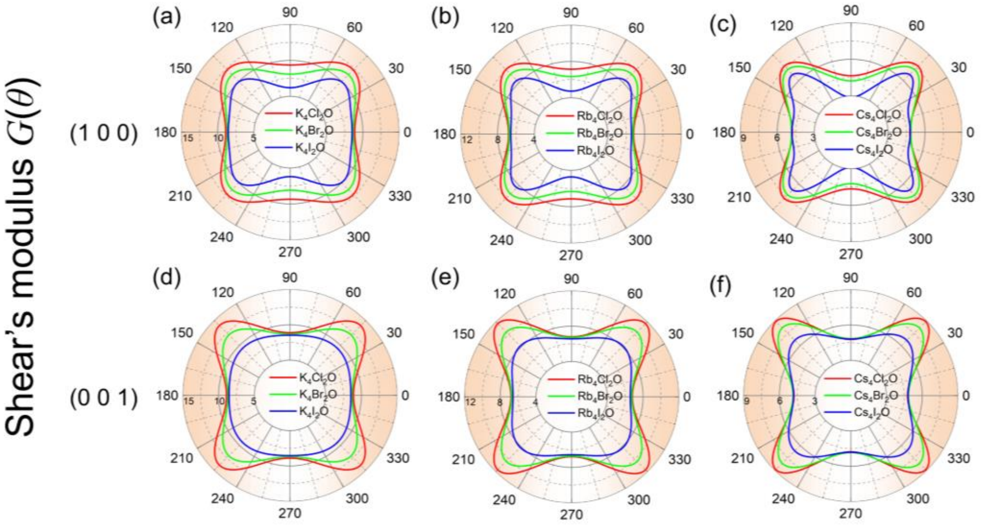

Fig.S4 The orientation-dependence of Shear's modulus $G(\theta)$ of X_4A_2O

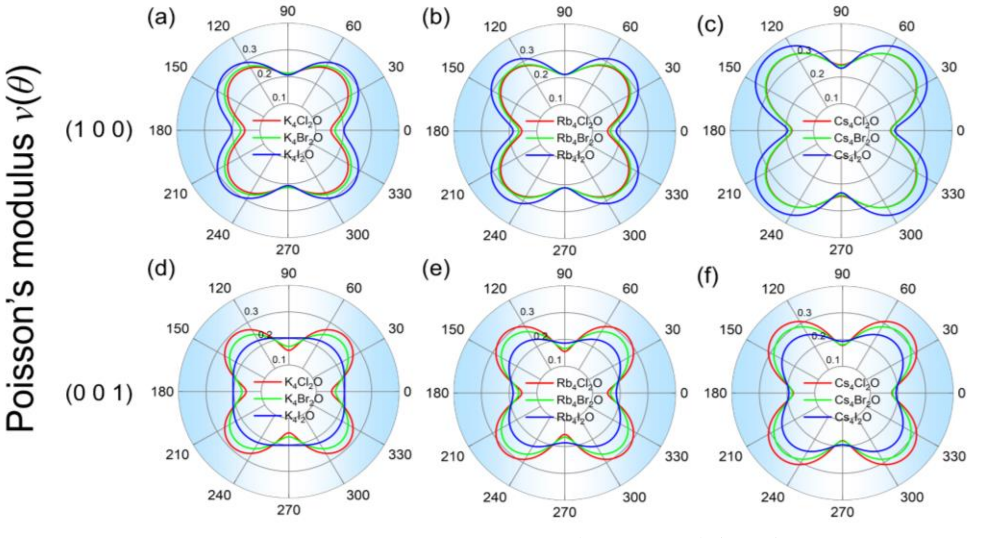

Fig.S5 The orientation-dependence of Poisson's modulus of X_4A_2O

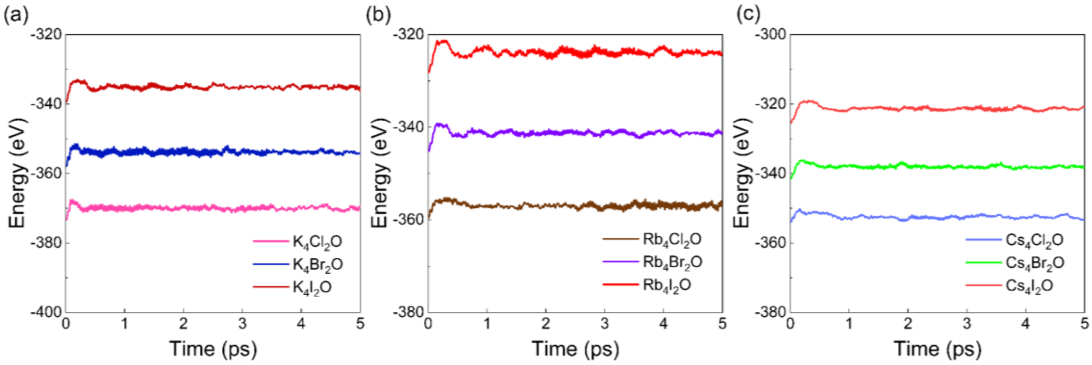

Fig.S6 *Ab initio* molecular dynamic (AIMD) simulation of X_4A_2O

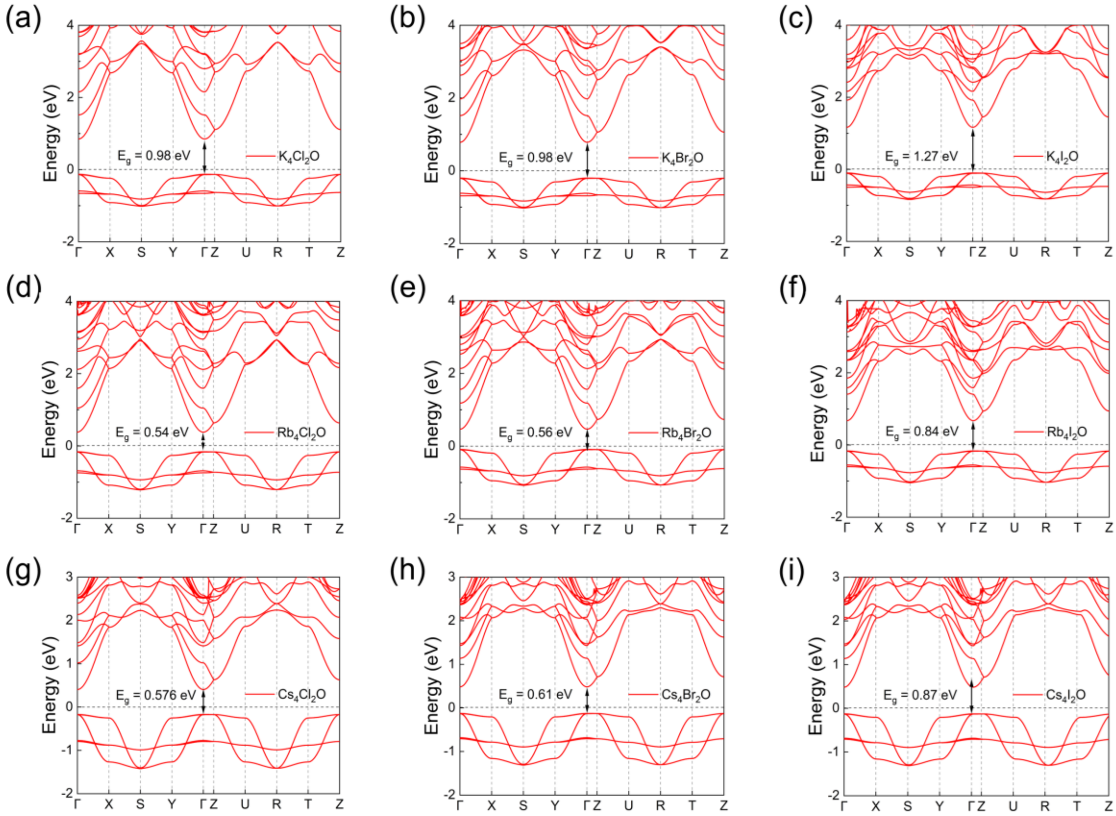

Fig.S7 PBE band structure of X_4A_2O

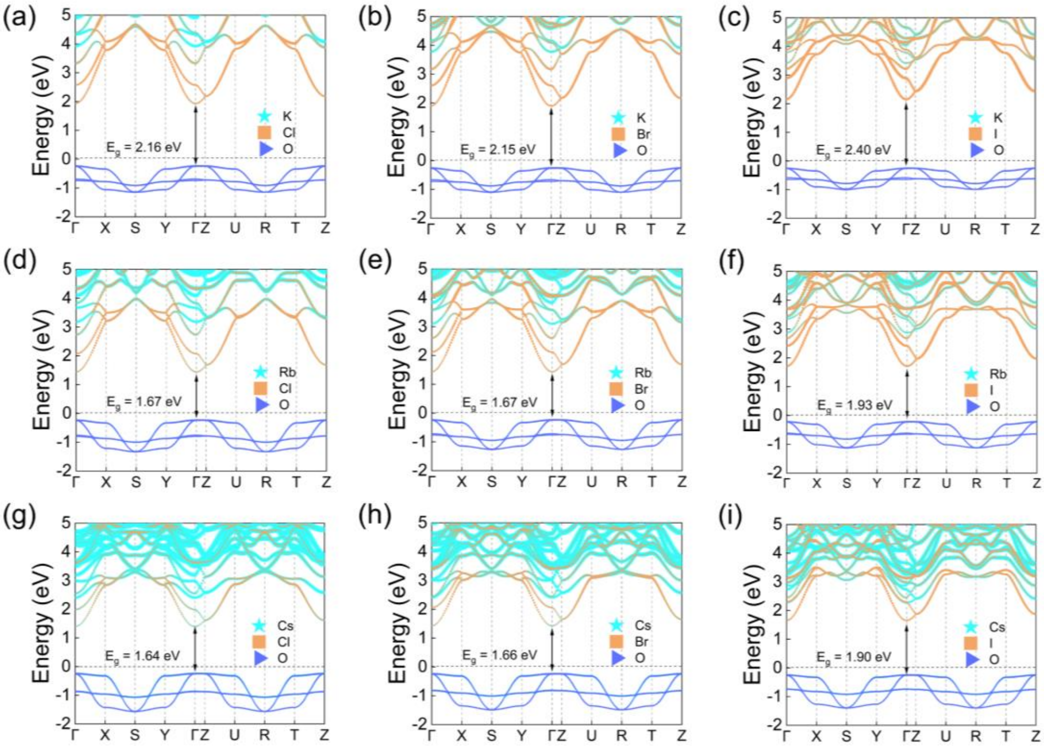

Fig.S8 HSE06 projected band structure of X_4A_2O

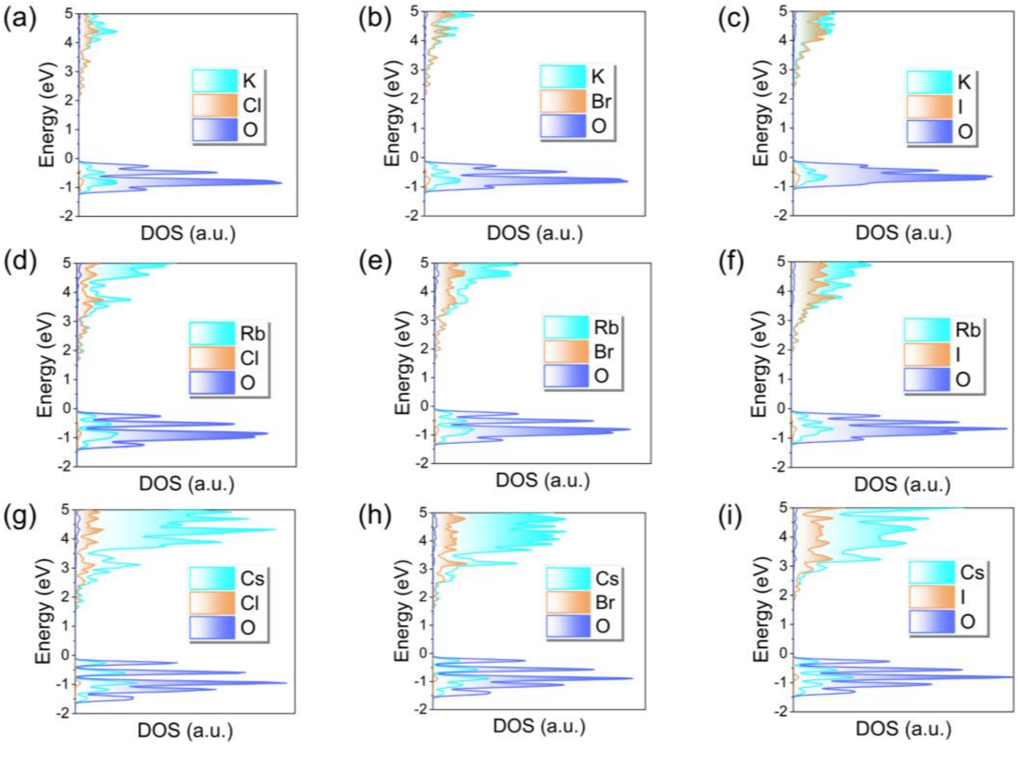

Fig.S9 Density of states of X_4A_2O

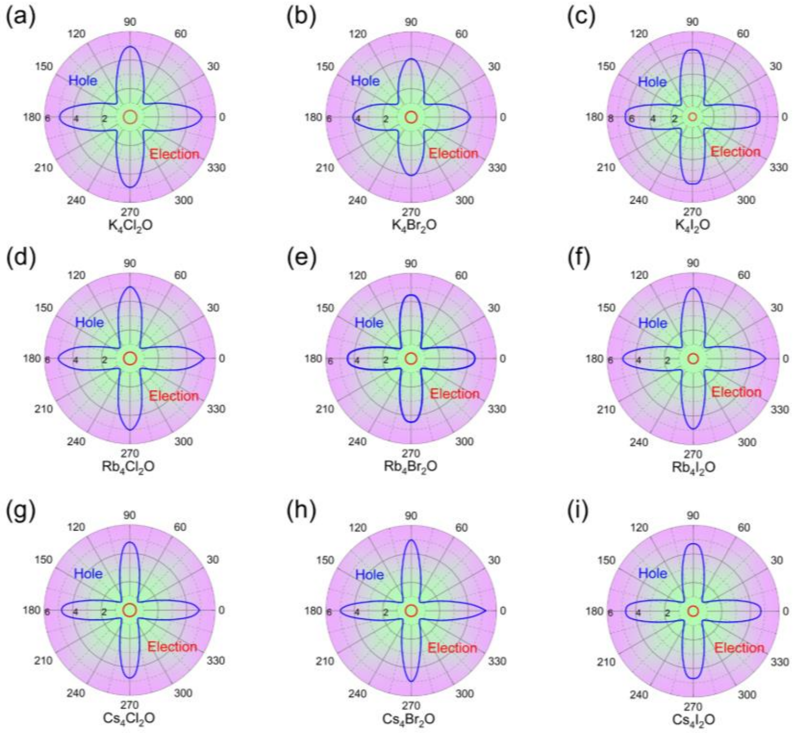

Fig.S10 Orientation-dependent carrier effective mass of X_4A_2O

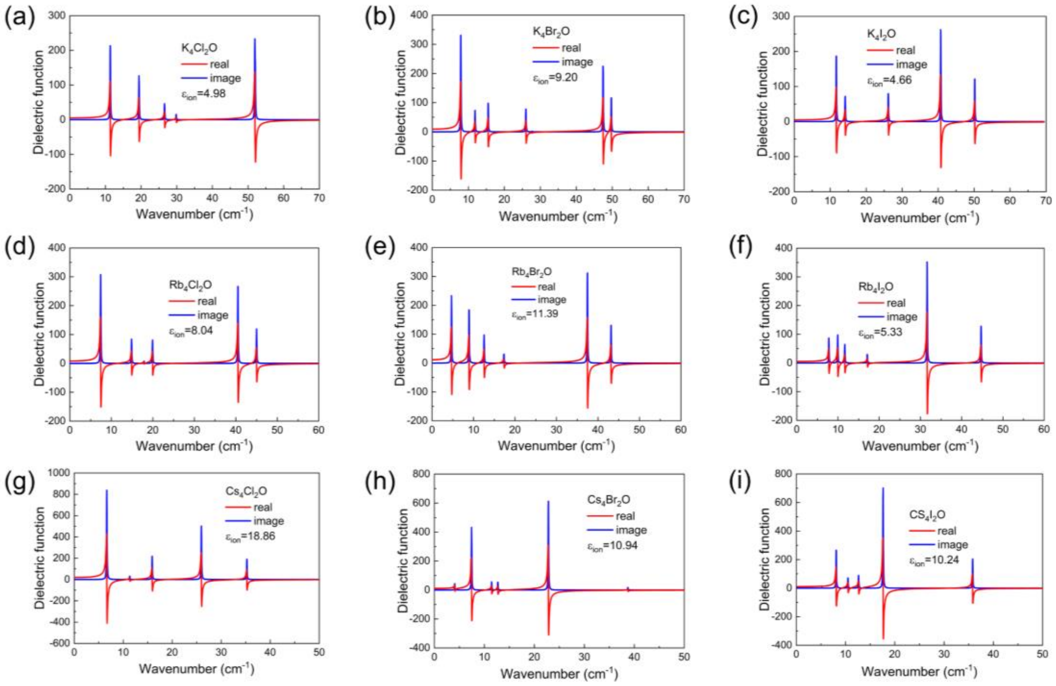

Fig.S11 Contributions of ions to the real and imaginary parts of dielectric functions of X_4A_2O

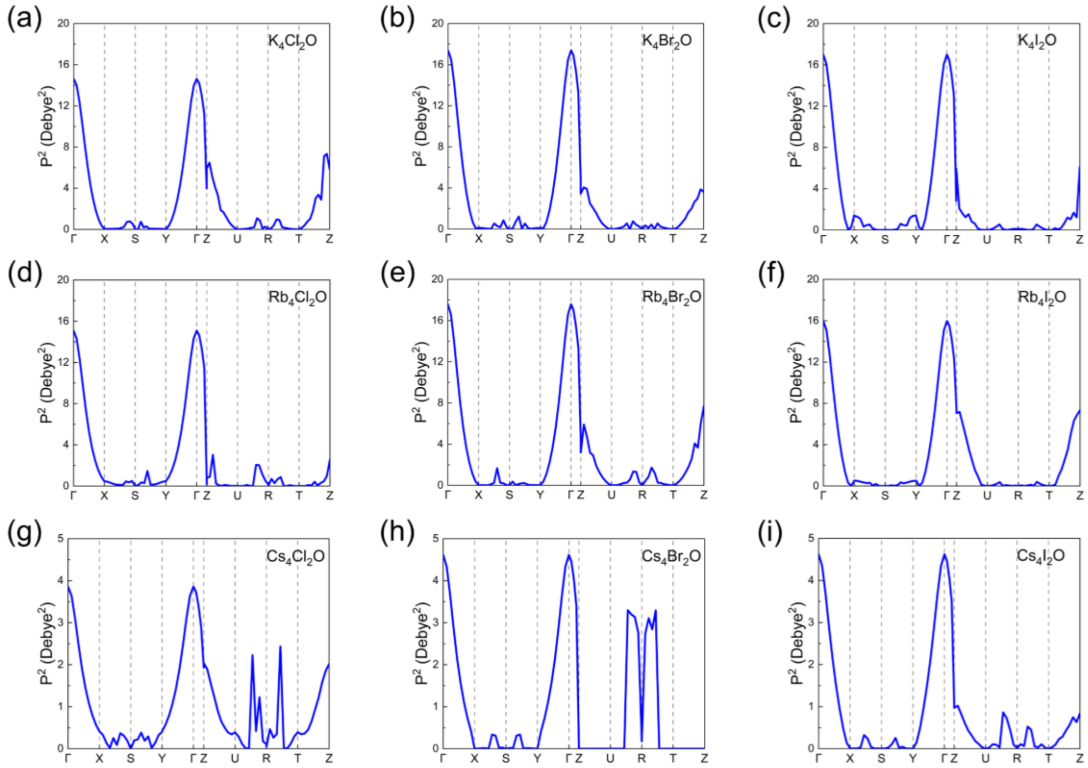

Fig.S12 Transition dipole moment of X_4A_2O

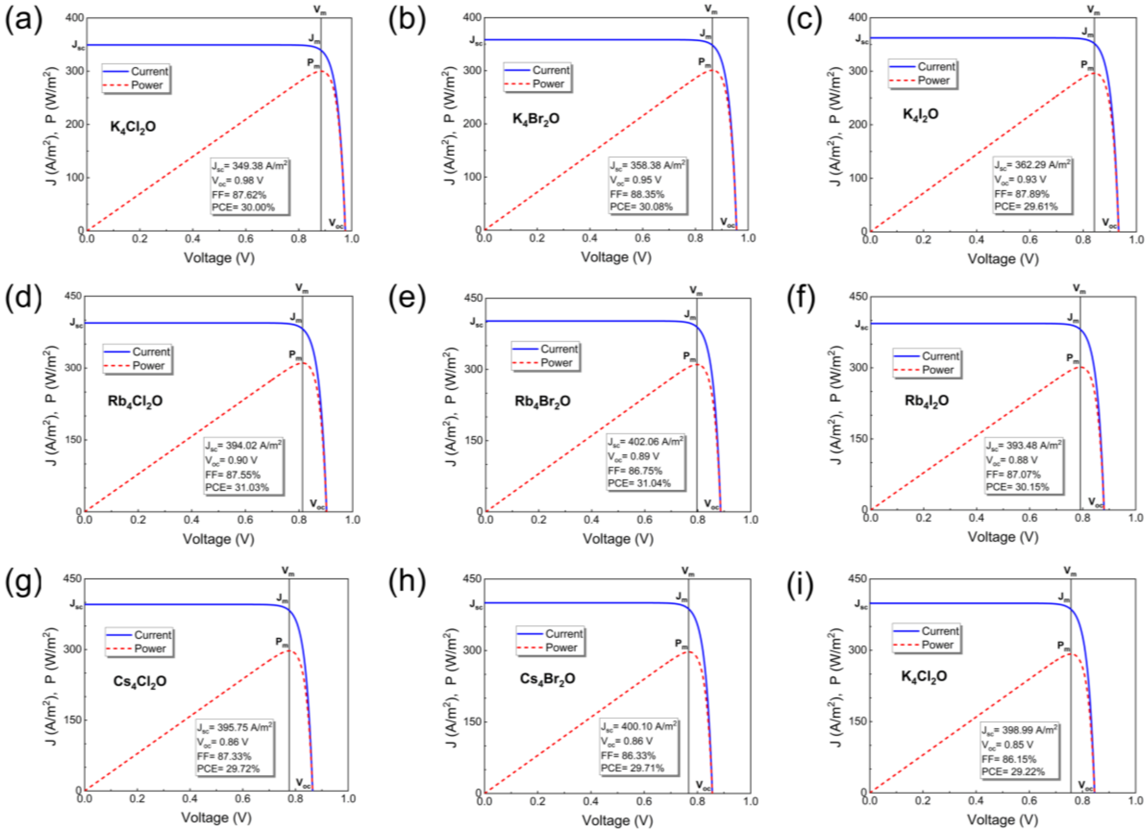

Fig.S13 The calculated *J-V* characteristic of X_4A_2O

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