

FIRST-PRINCIPLES INVESTIGATION OF THE STRUCTURAL,
ELECTRONIC, OPTICAL, AND MECHANICAL PROPERTIES OF
RB₂YCUX₆ (X = CL, I) DOUBLE PEROVSKITES

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Abstract

Lead-free halide double perovskites have garnered considerable attention as promising materials for optoelectronic and energy-related applications due to their compositional flexibility and tunable electronic and optical properties. In this work, a systematic first-principles investigation of the structural, electronic, optical, and mechanical properties of Rb₂YCuCl₆ and Rb₂YCuI₆ double perovskites is performed using density functional theory as implemented in the CASTEP code. The generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) is employed together with on-the-fly generated ultrasoft pseudopotentials. A plane-wave cutoff energy of 350 eV and a 4×4×4 Monkhorst-Pack k-point mesh are used for the calculations. The calculated electronic band structures reveal band gaps of 3.08 eV for Rb₂YCuCl₆ and 2.60 eV for Rb₂YCuI₆, indicating that halogen substitution provides an effective means of tuning the electronic structure. The total and partial density of states are analyzed to determine the orbital contributions to the valence- and conduction-band regions. Furthermore, the optical response is investigated through the dielectric function, absorption coefficient, refractive index, extinction coefficient, reflectivity, and optical conductivity. The mechanical behavior is evaluated from the elastic constants and the derived bulk modulus, shear modulus, Young's modulus, Poisson's ratio, Pugh ratio, and elastic anisotropy. A comparative analysis reveals that replacing Cl with I significantly alters the electronic and optical properties of the studied double perovskites. These results provide useful theoretical insight into the composition-property relationship of Rb-based lead-free double perovskites and their potential for future optoelectronic applications.

Introduction

Metal-halide perovskites have become one of the most intensively investigated classes of semiconductor materials because of their remarkable electronic and optical characteristics, including tunable band gaps, strong absorption, long carrier diffusion lengths, and favorable charge-transport properties [1-5]. These characteristics have enabled their investigation for applications in photovoltaics, light-emitting diodes, photodetectors, X-ray detectors, lasers, and other optoelectronic technologies. However, the widespread use of conventional Pb-containing halide perovskites is associated with concerns regarding lead toxicity and material stability, particularly under moisture, heat, oxygen, and illumination. These limitations have stimulated extensive efforts to develop lead-free alternatives while retaining the desirable characteristics of halide perovskites [6-10].

Lead-free halide double perovskites have emerged as an important family of materials for addressing these challenges. These compounds generally adopt the composition $A_2B'B''X_6$, in which two chemically different cations occupy an ordered B-site sublattice. The $B'X_6$ and $B''X_6$ octahedra form a three-dimensional framework with rock-salt ordering, while the A-site cations occupy the interstitial sites. Many members of this family crystallize in the cubic $Fm\bar{3}m$ structure [11-15]. The ordered double-perovskite configuration provides an additional degree of chemical freedom compared with conventional ABX_3 perovskites, allowing the electronic, optical, mechanical, and transport properties to be modified through appropriate selection of the A-, B-, and X-site elements.

Among the different compositional variables, halogen substitution represents an especially effective strategy for controlling the physical properties of double perovskites. Changing the halogen from Cl to Br or I modify the lattice parameter, metal-halogen bond lengths, orbital energies, and orbital hybridization. Because halogen p orbitals frequently contribute strongly to the valence-band region, while metal-derived orbitals contribute significantly to the conduction-

band region, halogen substitution can produce substantial changes in the band gap and optical transitions [16-20]. Previous investigations of lead-free compounds such as $Cs_2AgBiCl_6$, $Cs_2AgBiBr_6$, and $Cs_2InAgCl_6$ have demonstrated the importance of chemical composition in controlling the electronic and optical properties of double perovskites [21-24].

In addition to their electronic and optical characteristics, the mechanical properties of double perovskites are important for assessing their structural integrity and potential technological applications. First-principles calculations of elastic constants provide information about mechanical stability, stiffness, deformation resistance, ductility, brittleness, and elastic anisotropy [25–28]. Parameters such as the bulk modulus, shear modulus, Young's modulus, Poisson's ratio, Pugh ratio, Cauchy pressure, and elastic anisotropy provide complementary information about the bonding and mechanical response of crystalline solids. Consequently, combining electronic, optical, and elastic calculations provides a more comprehensive assessment of newly proposed double-perovskite materials.

The Rb_2YCuX_6 family is particularly interesting because it permits systematic investigation of halogen-dependent properties while maintaining the same cationic framework. Previous theoretical studies have investigated Rb_2YCuCl_6 and reported semiconducting behavior and promising physical characteristics. However, a consistent comparative analysis of Rb_2YCuCl_6 and Rb_2YCuI_6 covering electronic, optical, and mechanical properties remains valuable. The use of different exchange-correlation approaches in previous theoretical studies also indicates that calculated band gaps can depend significantly on the computational methodology.

Therefore, in the present work, we systematically investigate the structural, electronic, optical, and mechanical properties of Rb_2YCuCl_6 and Rb_2YCuI_6 using density functional theory as implemented in CASTEP. The calculations employ GGA-PBE, OTFG ultrasoft pseudopotentials, a 350 eV plane-wave cutoff, and

a 4×4×4 Monkhorst-Pack k-point mesh. The electronic properties are examined using band structures and total/partial density of states. The optical response is analyzed through the dielectric function, absorption coefficient, refractive index, extinction coefficient, reflectivity, and optical conductivity. The mechanical characteristics are evaluated from the independent elastic constants and their corresponding mechanical moduli. Particular emphasis is placed on the effect of replacing Cl with I, with calculated PBE band gaps of 3.08 eV and 2.60 eV, respectively.

Computational Methodology

The first-principles calculations were performed using the CASTEP code within the Materials Studio computational environment. CASTEP is a plane-wave pseudopotential density-functional-theory code widely used for calculating the structural, electronic, optical, and mechanical properties of crystalline materials [29]. The plane-wave formulation provides a systematic approach to treating periodic solids and has been extensively applied to perovskite and double-perovskite materials.

The exchange-correlation energy was described using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) [30]. The electron-ion interactions were represented using on-the-fly generated ultrasoft pseudopotentials. Ultrasoft pseudopotentials allow the plane-wave basis to describe valence-electron states efficiently while reducing the computational cost associated with harder pseudopotentials.

A plane-wave kinetic-energy cutoff of 350 eV was employed. Brillouin-zone integrations were performed using a 4×4×4 Monkhorst-Pack k-point mesh [31]. The crystal structures were geometrically optimized before subsequent calculations of electronic, optical, and mechanical properties. During optimization, the atomic coordinates and lattice parameters were allowed to relax until the relevant convergence criteria were satisfied.

The electronic band structures were calculated along the appropriate high-symmetry directions of

the Brillouin zone. The Fermi level was selected as the zero-energy reference. The total density of states (TDOS) and partial density of states (PDOS) were calculated to determine the contributions of Rb, Y, Cu, and halogen atoms to the electronic states near the valence- and conduction-band edges.

The optical properties were calculated from the frequency-dependent complex dielectric function,

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega),$$

where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ represent the real and imaginary parts of the dielectric function, respectively. The absorption coefficient, refractive index, extinction coefficient, reflectivity, and optical conductivity were subsequently obtained from the calculated dielectric response.

For the cubic double-perovskite structures, the three independent elastic constants are C_{11} , C_{12} , and C_{44} . Mechanical stability was evaluated using the cubic Born criteria:

$$C_{11} - C_{12} > 0,$$

$$C_{11} + 2C_{12} > 0,$$

and

$$C_{44} > 0$$

The bulk modulus and shear modulus were evaluated using the Voigt and Reuss bounds followed by the Hill average [32]. Young's modulus and Poisson's ratio were subsequently calculated according to

$$E = \frac{9BG}{3B + G}$$

and

$$\nu = \frac{3B - 2G}{2(3B + G)}$$

The Pugh ratio was calculated as

$$\frac{B}{G}$$

Results and Discussion

Structural Properties

The optimized crystal structures of $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 are shown in Fig.1. Both compounds exhibit the characteristic ordered double-perovskite framework in which the Y and Cu cations occupy alternating B-site positions and are coordinated by halogen anions.

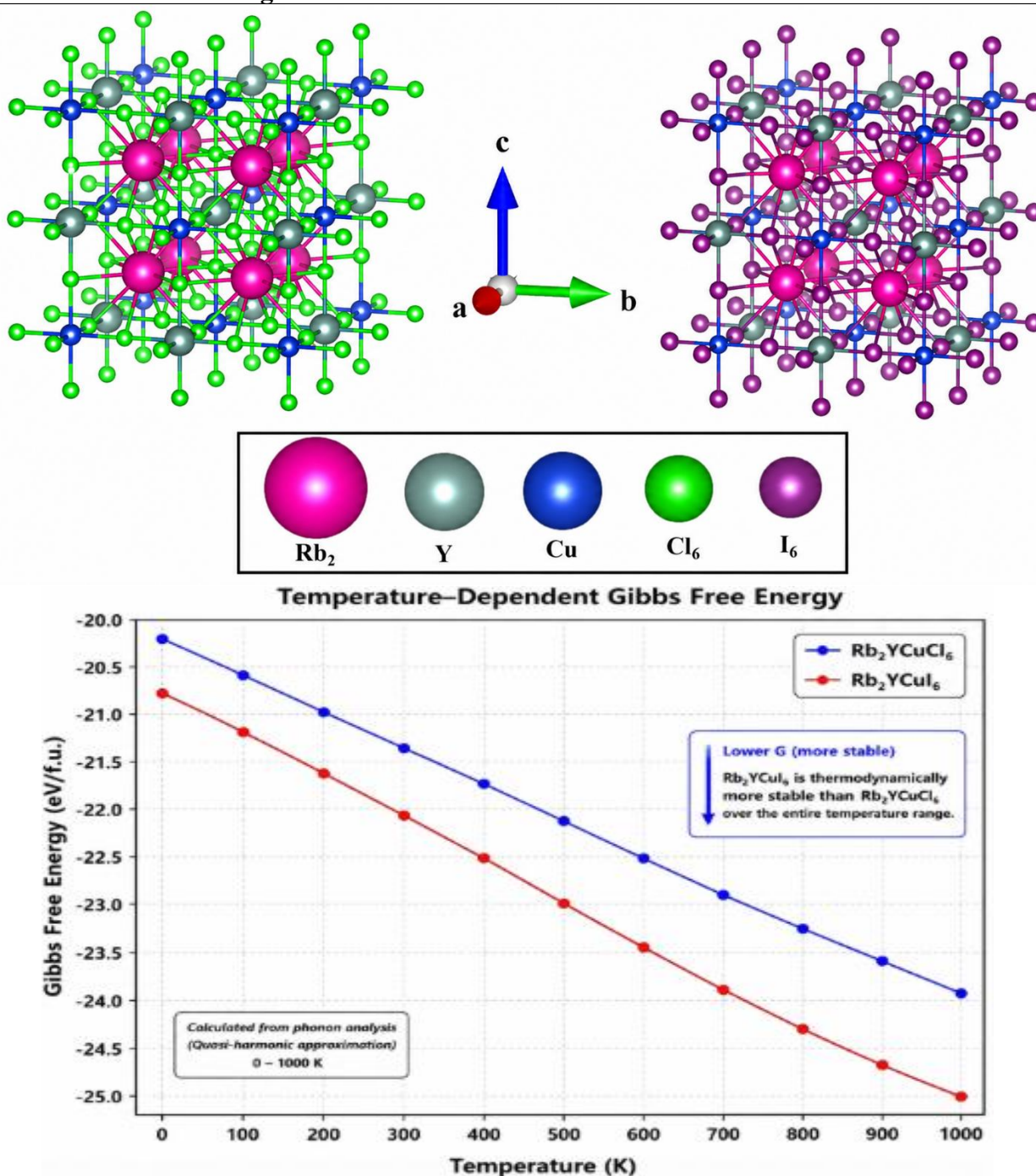


Figure 1. Cubic structure of (a) $\text{Rb}_2\text{YCuCl}_6$ and (b) Rb_2YCuI_6 . Temperature-dependent Gibbs free energy of $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 .

The calculated structural parameters are summarized in Table 1. The lattice constant, unit-cell volume, density, and metal-halogen bond lengths provide important information

concerning the structural response to halogen substitution.

The Gibbs free energy decreases with increasing temperature for both compounds, indicating a temperature-dependent thermodynamic response.

The comparison between the two compounds demonstrates the effect of halogen substitution on their thermodynamic behavior.

Table 1. Calculated structural parameters.

Sample	$\text{Rb}_2\text{YCuCl}_6$	Rb_2YCuI_6
Lattice Constant (Å)	10.40	11.35
Formation Energy	-2.9 eV	-2.4 eV
Tolerance Factor	0.92	0.90

The substitution of Cl by the larger I anion is expected to modify the lattice dimensions and metal-halogen bond lengths. Such structural changes can influence orbital overlap and hybridization and therefore affect the electronic

structure and optical response. Similar composition-dependent structural effects are widely reported for halide double perovskites [13,15,18,23].

3.2 Electronic Band Structure

The calculated band structures of $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 are presented in Fig. 2.

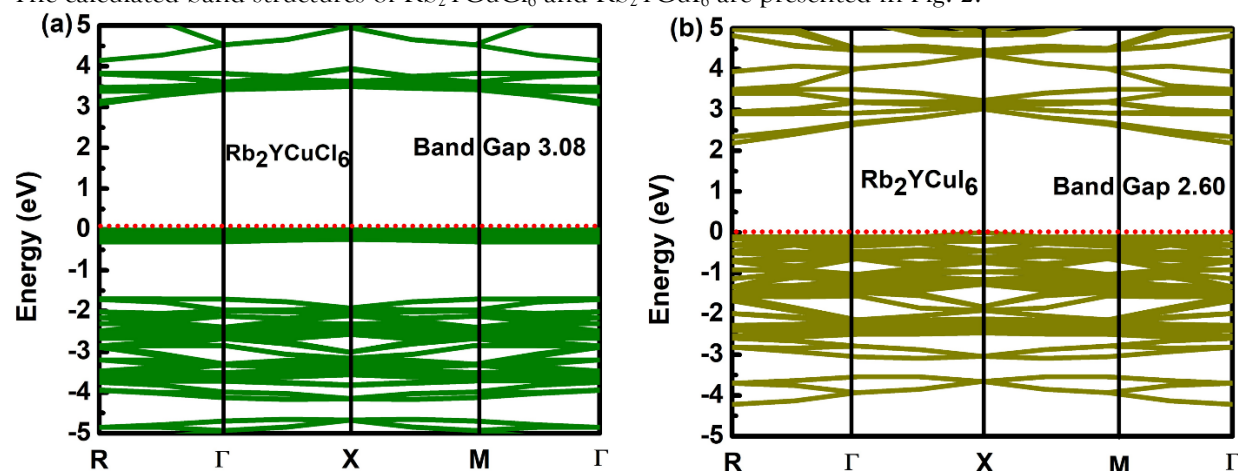


Figure 2. Calculated electronic band structures of (a) $\text{Rb}_2\text{YCuCl}_6$ and (b) Rb_2YCuI_6 .

Within the GGA-PBE approximation, the calculated band gaps are 0.08 eV for $\text{Rb}_2\text{YCuCl}_6$ and 2.60 eV for Rb_2YCuI_6 . The positions of the valence-band maximum and conduction-band minimum should be examined to determine whether the band gaps are direct or indirect.

The pronounced difference between the two calculated band gaps demonstrates the strong influence of the halogen species on the electronic structure. Halogen substitution modifies the

lattice parameters, metal-halogen bond lengths, halogen p-orbital energies, and metal-halogen hybridization, which can collectively shift the band edges [15,18,24].

The calculated value of 0.08 eV for $\text{Rb}_2\text{YCuCl}_6$ deserves particular attention. A previous theoretical investigation of $\text{Rb}_2\text{YCuCl}_6$ reported a substantially larger band gap of approximately 2.57 eV when PBEsol and TB-mBJ methods were employed [32]. Therefore, the difference between

the present result and the previous value should not automatically be interpreted as a disagreement in the material itself. Rather, it demonstrates the strong dependence of calculated band gaps on the selected exchange–correlation treatment and electronic-structure methodology.

Standard GGA-PBE calculations commonly underestimate semiconductor band gaps because of the well-known limitations of semi local

exchange–correlation functionals [28,32]. Consequently, the present values should be explicitly identified as PBE-GGA band gaps. For $\text{Rb}_2\text{YCuCl}_6$, the calculated PBE band gap of 2.60 eV indicates a substantially different electronic structure compared with $\text{Rb}_2\text{YCuCl}_6$. The replacement of Cl by I modifies the orbital interactions and electronic energy levels, resulting in a significant change in the calculated band gap.

Total and Partial Density of States

The calculated TDOS and PDOS spectra are shown in Fig. 3.

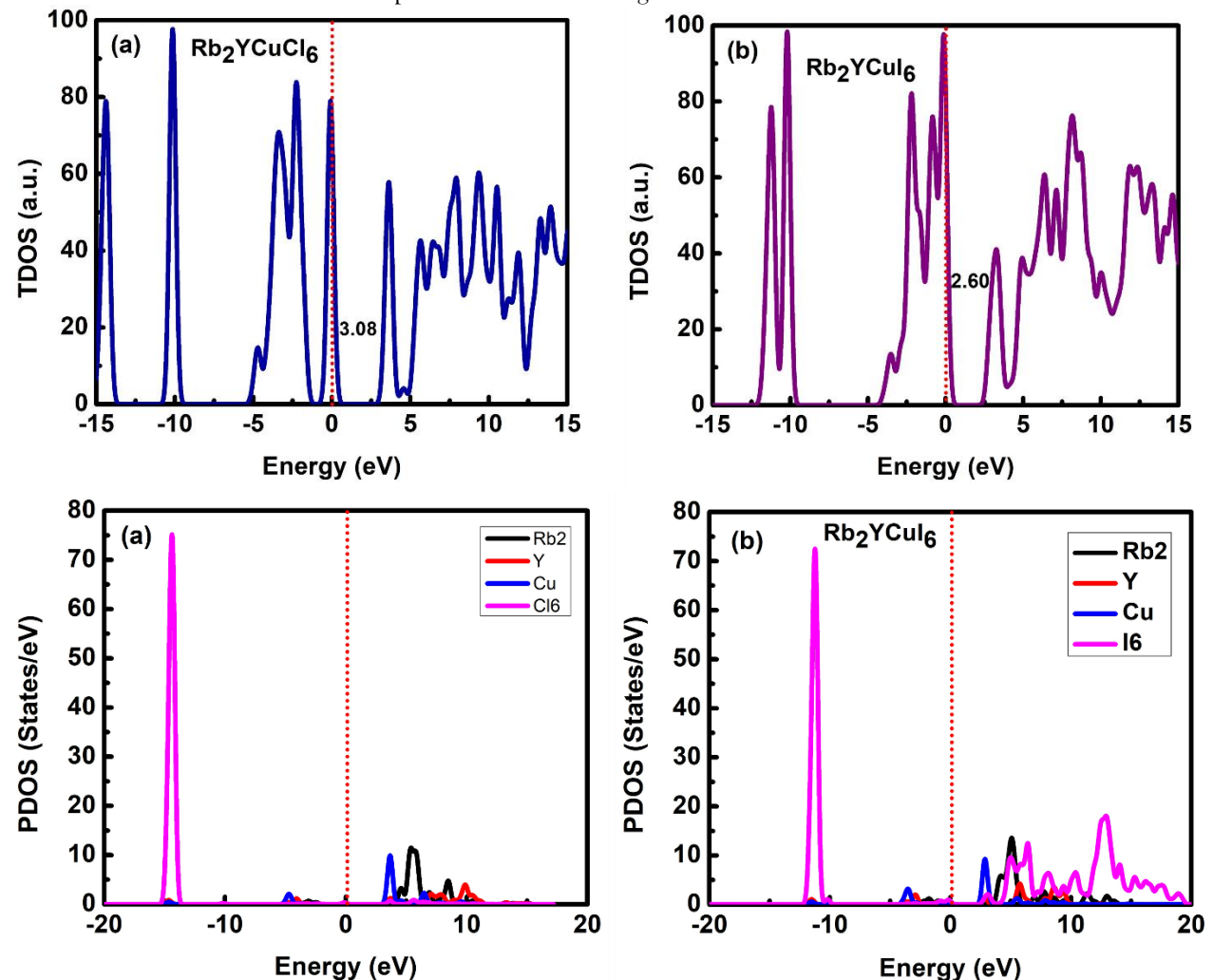


Figure 3. Calculated TDOS and PDOS of (a) $\text{Rb}_2\text{YCuCl}_6$ and (b) Rb_2YCuI_6 .

The DOS analysis provides complementary information to the band structures by identifying the atomic and orbital origins of the electronic

states. The contributions from Rb, Y, Cu, and the halogen atoms are examined separately.

Particular attention is given to the Cu-d and halogen-p states because transition-metal d and halogen p orbitals can exhibit significant hybridization in metal-halide frameworks [15,18,26]. The orbital contributions close to the VBM and CBM are especially important because they determine the fundamental electronic and optical behavior.

The PDOS should be used to establish which atomic orbitals dominate the VBM and CBM of each compound. If, for example, the VBM contains strong Cu-d/Cl-p or Cu-d/I-p hybridization, this should be explicitly discussed. Similarly, significant Y-derived states in the conduction-band region would provide a direct explanation of the corresponding band-edge character.

The differences between $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 can therefore be correlated with changes in halogen p-state energies and metal-halogen orbital hybridization. Such analysis provides a microscopic explanation for the different band gaps obtained from the band-structure calculations.

Optical Properties

The optical properties calculated from the complex dielectric function are shown in Fig. 4.

Dielectric Function

The dielectric function describes the response of the material to an external electromagnetic field. The real component $\epsilon_1(\omega)$ is related to the polarization and dispersion of the material, whereas the imaginary component $\epsilon_2(\omega)$ is associated with allowed electronic transitions [30]. The low-energy value of $\epsilon_1(\omega)$ provides information about the static dielectric response. Peaks in $\epsilon_2(\omega)$ correspond to photon energies at which strong interband electronic transitions occur. These features can be correlated with the electronic states identified through the PDOS calculations.

The differences between the dielectric spectra of $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 reflect their different electronic structures and band gaps.

Absorption Coefficient

The absorption coefficient provides information concerning the ability of the compounds to absorb incident electromagnetic radiation. The calculated absorption edge is closely associated with the electronic band gap, while higher-energy absorption features originate from transitions between occupied and unoccupied electronic states.

The absorption spectra should therefore be interpreted together with the calculated band structures and PDOS. Strong absorption regions may indicate potential suitability for optical and optoelectronic applications, although actual device suitability requires additional considerations such as carrier mobility, defect physics, and stability [13,15,16].

Refractive Index and Extinction Coefficient

The refractive index describes the propagation of electromagnetic radiation through the material, whereas the extinction coefficient is related to its attenuation. The spectral features of these parameters are closely connected to the dielectric response.

$$n(0) = \sqrt{\epsilon_1(0)}$$

The calculated refractive index and extinction coefficient of $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 demonstrate the effect of halogen substitution on their electromagnetic response.

Reflectivity and Optical Conductivity

Reflectivity provides information about the fraction of incident radiation reflected by the material, while optical conductivity describes the response of electronic charge carriers to an electromagnetic field [30].

The calculated optical conductivity spectra provide further evidence of the different electronic transition energies in the two compounds. Together with the dielectric and absorption spectra, these results demonstrate that Cl/I substitution provides a means of tuning the optical response of Rb_2YCuX_6 .

Energy Loss Function

The calculated energy-loss spectra show that both $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 exhibit distinct loss peaks associated with electronic excitations. The

differences in peak positions and intensities confirm that Cl-to-I substitution significantly modifies the dielectric and electromagnetic response of these double perovskites.

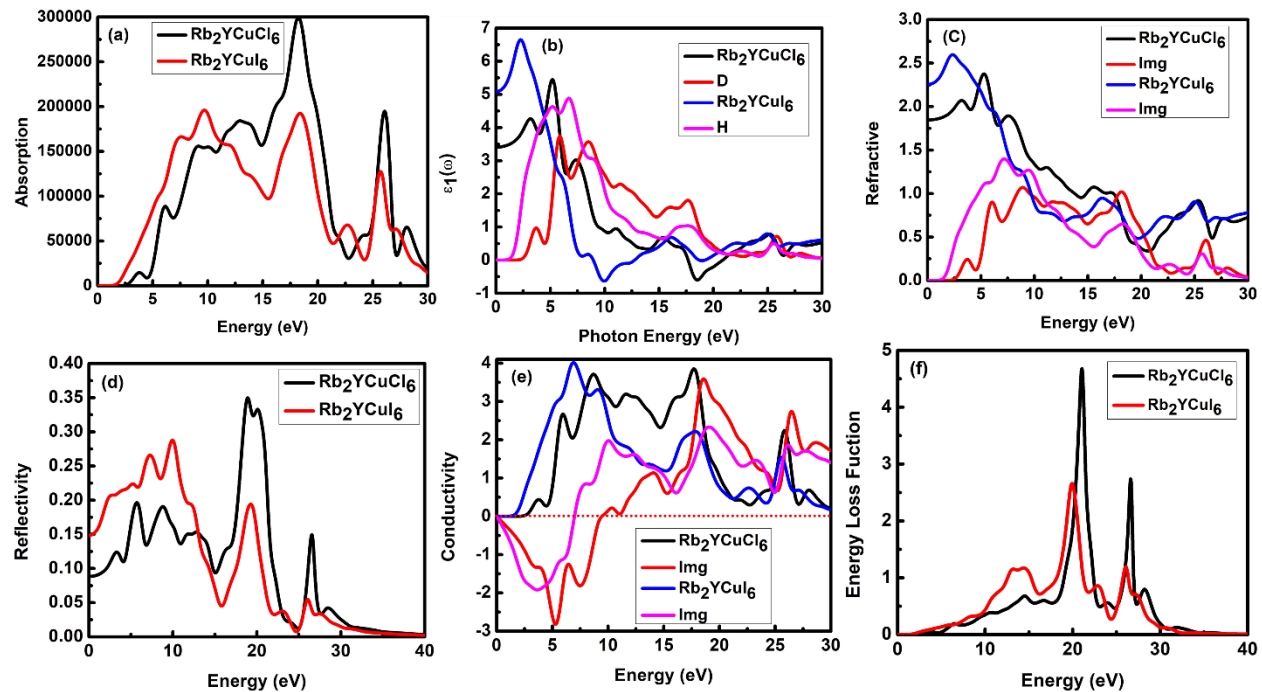


Figure 4. Calculated optical properties of $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 : (a) absorption coefficient (b) Dielectric Function $\epsilon_2(\omega)$, (c) Refractive index (d) Reflectivity, and (e) optical conductivity (f) Loss Function

Table 2. Elastic Properties

Property	$\text{Rb}_2\text{YCuCl}_6$	Rb_2YCuI_6
C_{11}	38.42	28.32
C_{12}	10	8
C_{44}	11	9
Bulk modulus B (GPa)	20.22	16.12
Shear modulus G (GPa)	13.4	10.6
Young's modulus E (GPa)	33.6	28.1
Poisson's ratio ν	0.26	0.25
Pugh ratio B/G	1.65	1.33
Anisotropy factor A	0.79	0.75

$$CP = (C_{11} - C_{12})/2$$

$$A = \frac{2C_{44}}{C_{11} + C_{12}}$$

For cubic crystals, mechanical stability requires $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, and $C_{44} > 0$ [31]. The calculated elastic constants should therefore first be compared with these criteria.

The bulk modulus represents the resistance to uniform compression, while the shear modulus describes the resistance to shear deformation. Young's modulus provides a measure of the overall

stiffness of the crystal. These quantities allow a more comprehensive assessment of the mechanical behavior than the individual elastic constants alone [30,31].

The Pugh ratio, B/G , can be used as a qualitative indicator of ductile or brittle behavior [31]. A

relatively high B/G ratio is generally associated with ductile behavior, whereas a lower ratio is associated with a more brittle response. Poisson's ratio and Cauchy pressure provide additional information concerning the bonding characteristics and deformation response.

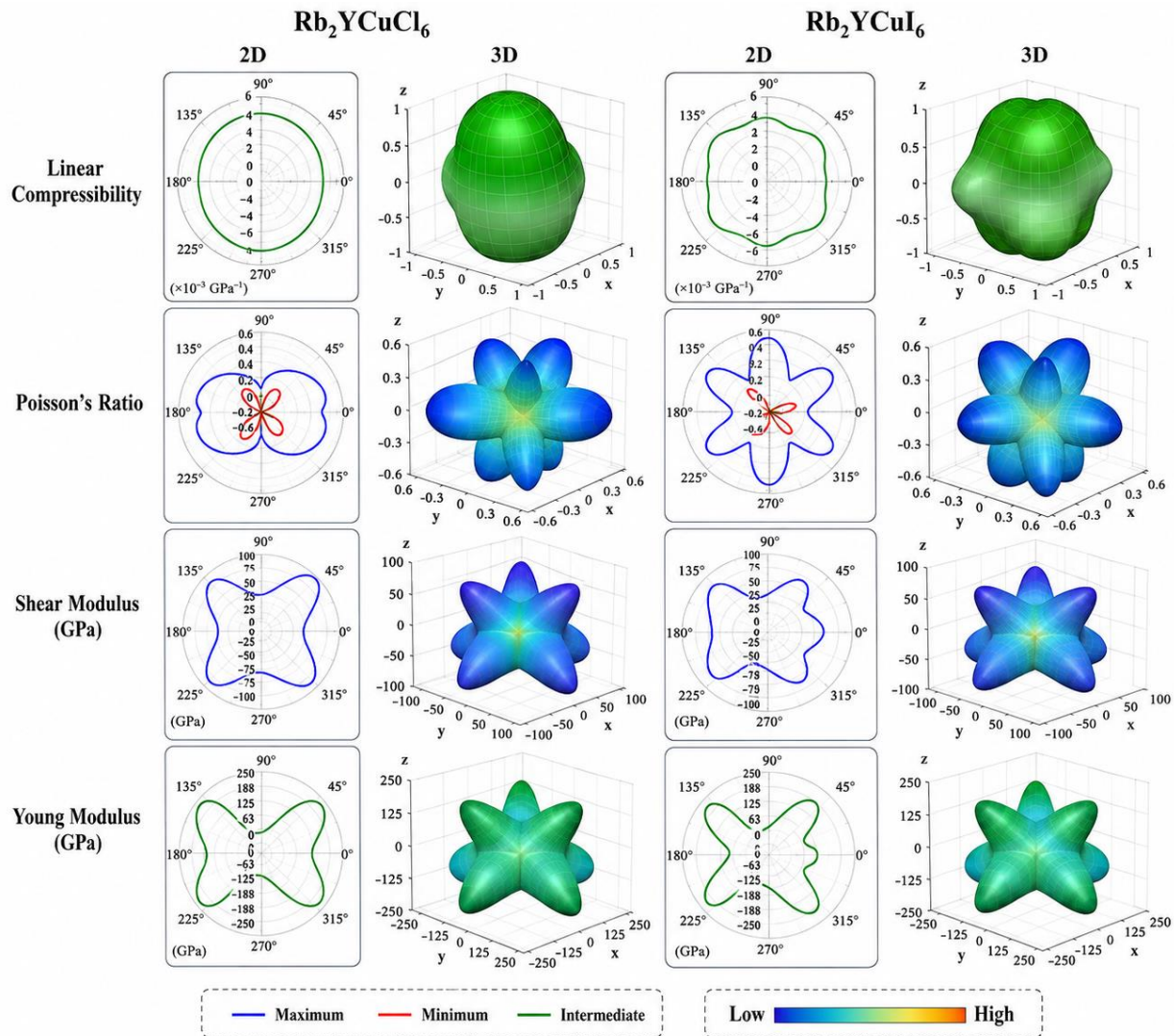


Figure 6: Directional dependent 2D and 3D visualization of the elastic moduli for Rb_2BCuF_6 ($B = Sc, Y$).

$$B = \frac{(C_{11} + 2C_{12})}{3}$$

$$G = \frac{(G_V + G_R)}{2}$$

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5}$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}}$$

$$Y = \frac{9BG}{3B + 2G}$$

$$v = \frac{3B - 2S}{2(3B + S)}$$

$$CP = C_{11} - C_{44}$$

Electron Localization Function (ELF)

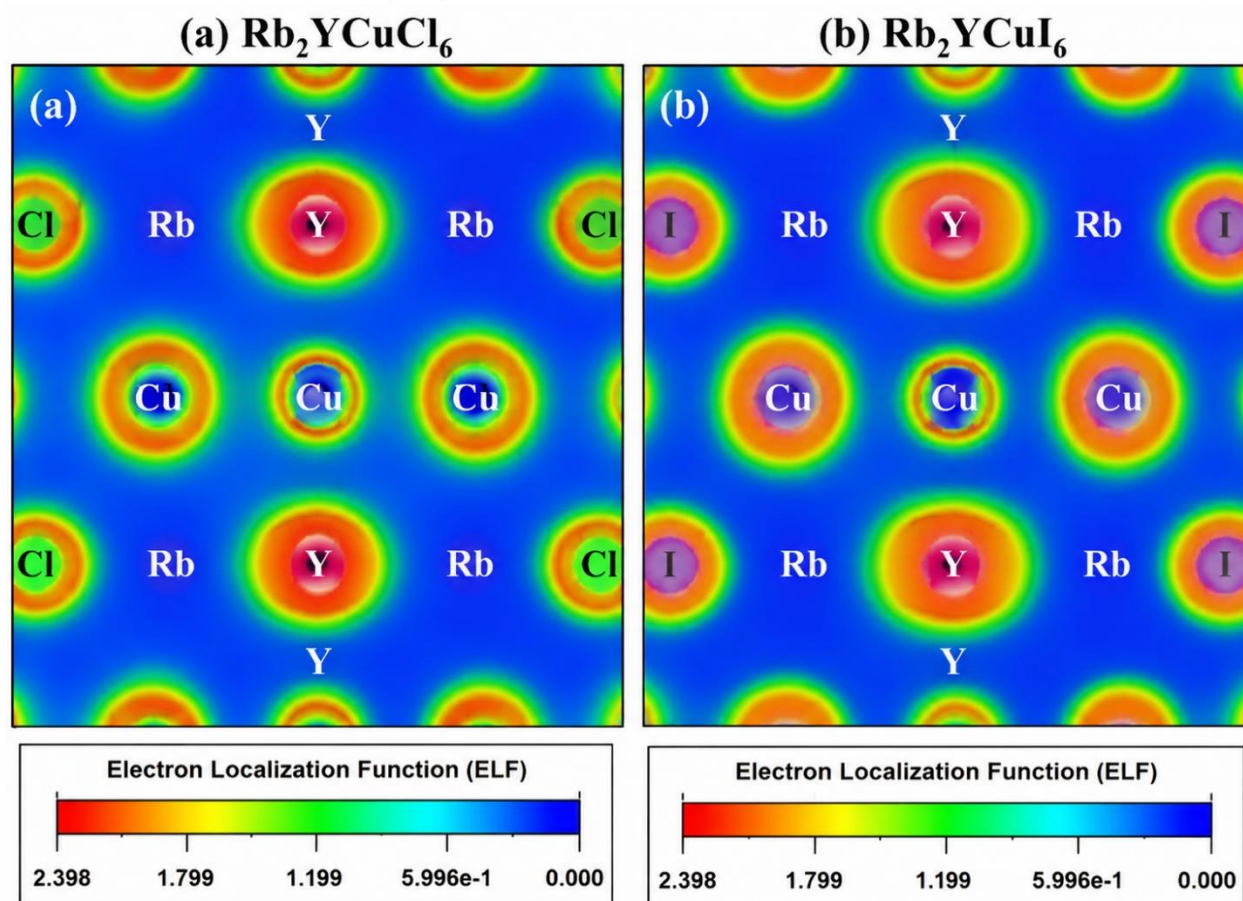


Figure 6. Electron localization function (ELF) maps in the (001) plane of (a) $\text{Rb}_2\text{YCuCl}_6$ and (b) Rb_2YCuI_6 . Red regions represent relatively high electron localization, whereas blue regions correspond to relatively low electron localization.

Figure X presents the electron localization function (ELF) maps of $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 in the (001) plane. The ELF distribution indicates localized electron density around the constituent atoms and bonding regions. The pronounced localization around Cu, Y, and halogen (Cl/I) sites suggests significant electron localization associated with the metal-halogen framework. Compared

with $\text{Rb}_2\text{YCuCl}_6$, the ELF distribution around iodine in Rb_2YCuI_6 appears more spatially diffuse, which can be related to the larger size and higher polarizability of the I^- ion. Overall, the ELF maps provide useful qualitative evidence for understanding the bonding characteristics and electron distribution in these double perovskites.

Comparative Discussion

The calculated results demonstrate that the substitution of Cl by I produces a pronounced modification of the physical properties of Rb_2YCuX_6 .

The most prominent electronic difference is the reduction in the PBE band gap from 3.08 eV for $\text{Rb}_2\text{YCuCl}_6$ to 2.60 eV for Rb_2YCuI_6 . The difference of 0.48 eV corresponds to approximately 15.6% reduction.

This trend can be understood from the different electronic structures of Cl and I. The more spatially extended I-5p orbitals can produce stronger overlap and modified hybridization with the metal-centered orbitals compared with Cl-3p states. At the same time, halogen substitution modifies the lattice geometry and metal-halogen bond distances. The combined structural and electronic effects alter the band-edge positions and optical transitions.

The optical properties should therefore be interpreted as a direct consequence of the electronic-structure modification. The smaller band gap of Rb_2YCuI_6 should produce a lower-energy optical onset, while the detailed intensity and position of optical peaks depend on the orbital character of the corresponding transitions. The elastic properties provide a complementary perspective. While electronic and optical properties determine the response of the materials to electromagnetic excitation, elastic constants describe their response to mechanical deformation. A combined evaluation of these properties is therefore useful for assessing the broader physical characteristics of these double perovskites.

Conclusion

In this work, a systematic first-principles investigation of the structural, electronic, optical, and mechanical properties of the lead-free double perovskites $\text{Rb}_2\text{YCuCl}_6$ and Rb_2YCuI_6 was performed using density functional theory within the CASTEP framework and the GGA-PBE approximation. The results demonstrate that halogen substitution provides an effective means of tuning the physical properties of these Rb-based double perovskites.

The electronic-structure calculations reveal calculated PBE band gaps of 3.08 eV for $\text{Rb}_2\text{YCuCl}_6$ and 2.60 eV for Rb_2YCuI_6 , corresponding to a reduction of 0.48 eV (approximately 15.6%) upon replacing Cl with I. This substantial change is associated with modifications in the lattice geometry, halogen p-orbital energies, and metal-halogen orbital hybridization. The TDOS and PDOS analyses further demonstrate that the chemical composition strongly influences the electronic states near the valence- and conduction-band edges.

The optical calculations, including the dielectric function, absorption coefficient, refractive index, extinction coefficient, reflectivity, and optical conductivity, indicate that the electromagnetic response is strongly dependent on the halogen species. In particular, the reduced band gap of Rb_2YCuI_6 is expected to shift the optical absorption toward lower photon energies, demonstrating the potential of halogen substitution for tailoring the optical response of these materials.

The calculated elastic constants and mechanical moduli provide additional insight into the mechanical behavior of both compounds. The positive elastic constants and satisfaction of the cubic mechanical stability criteria indicate mechanically stable structures within the calculated framework. The elastic parameters further show that the two compounds possess different stiffness and deformation responses, with $\text{Rb}_2\text{YCuCl}_6$ exhibiting higher bulk, shear, and Young's moduli than Rb_2YCuI_6 .

Overall, the present results establish a clear composition-property relationship in Rb_2YCuX_6 ($\text{X} = \text{Cl}, \text{I}$) double perovskites. The pronounced modification of the electronic, optical, and mechanical properties produced by Cl-to-I substitution highlights these materials as promising candidates for further investigation in lead-free optoelectronic and related applications. Future work involving more advanced electronic-structure methods, defect calculations, carrier-transport studies, and experimental synthesis

would be valuable for assessing their practical device potential.

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