Abnormal behavior of Cs polyoxides and core reaction under pressure

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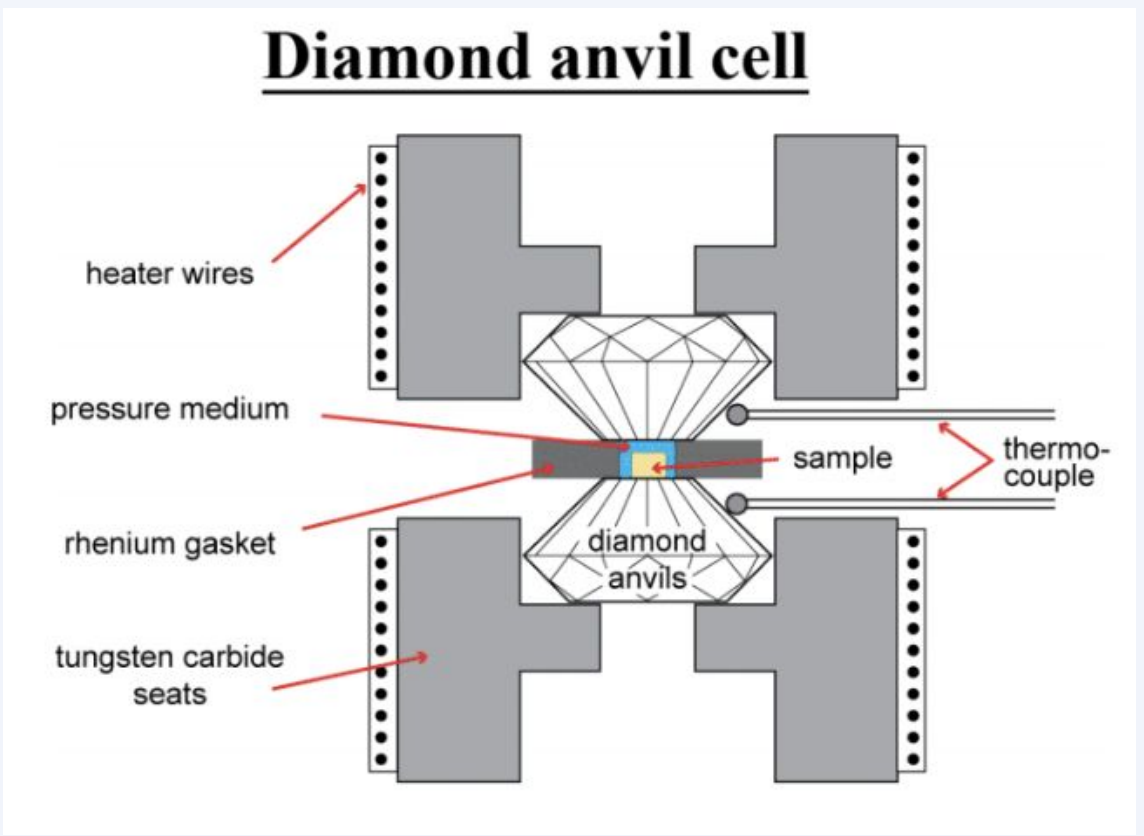
Abstract

- Pressure can significantly alter chemical bonds and oxidation states in compounds.
- Many unconventional structures have been discovered through pressure modulation.
- **Core electrons can be activated and form bonds under pressure.**
- Using Density Functional Theory and a Crystal Structure Search method, the behavior of Cs polyoxides under varying pressure levels was analyzed.
- Unlike other polyoxides, increased pressure causes O-O bonds in Cs polyoxides to break apart, forming new structures through Cs-O covalent interactions.
- Notably, the CsO peroxide system transitions at a pressure of 221 GPa to form Cs-O covalent interactions, within the range of current high-pressure experimental techniques.

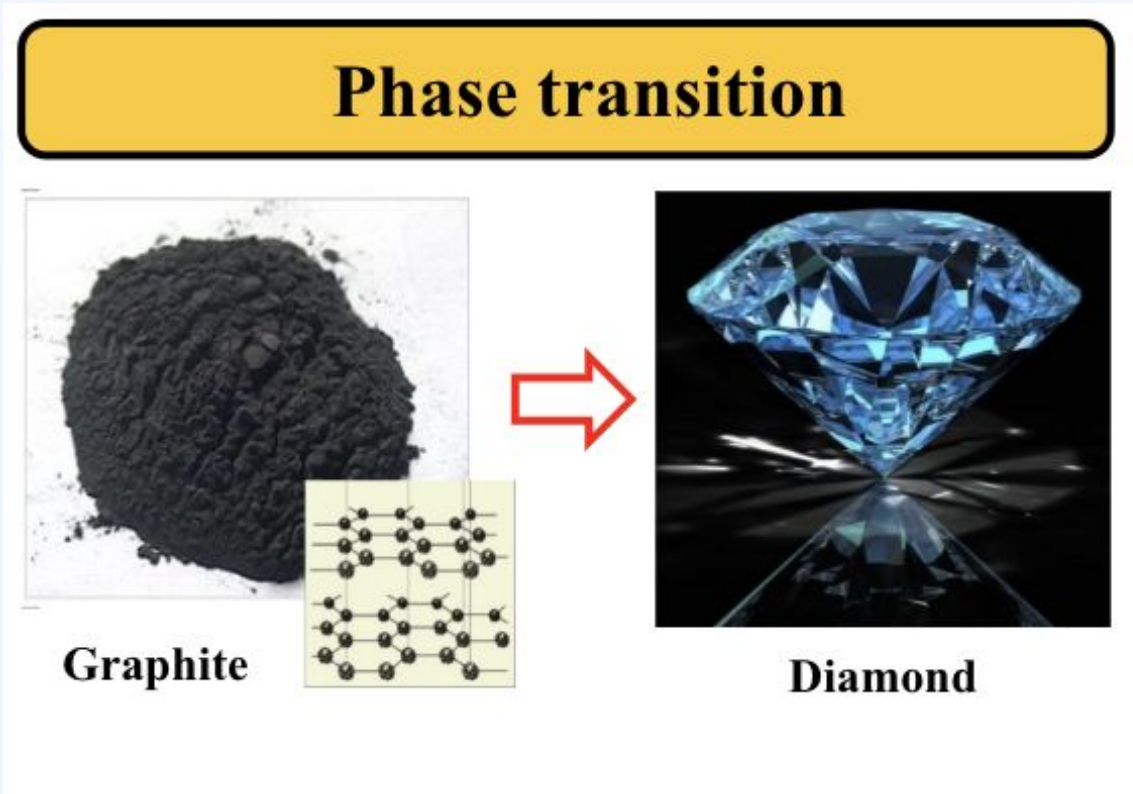
High Pressure Chemistry

- High-pressure chemistry enables unique material structures and compounds unobservable at standard pressures, leading to discoveries like phase transitions and unusual stoichiometries.
- Advanced computational simulations predict new compounds and explore novel chemistry under high pressure.
- High pressures can induce superconductivity, transform the typical chemistry of elements, and stabilize compounds with distinctive electronic, mechanical, and optical characteristics.

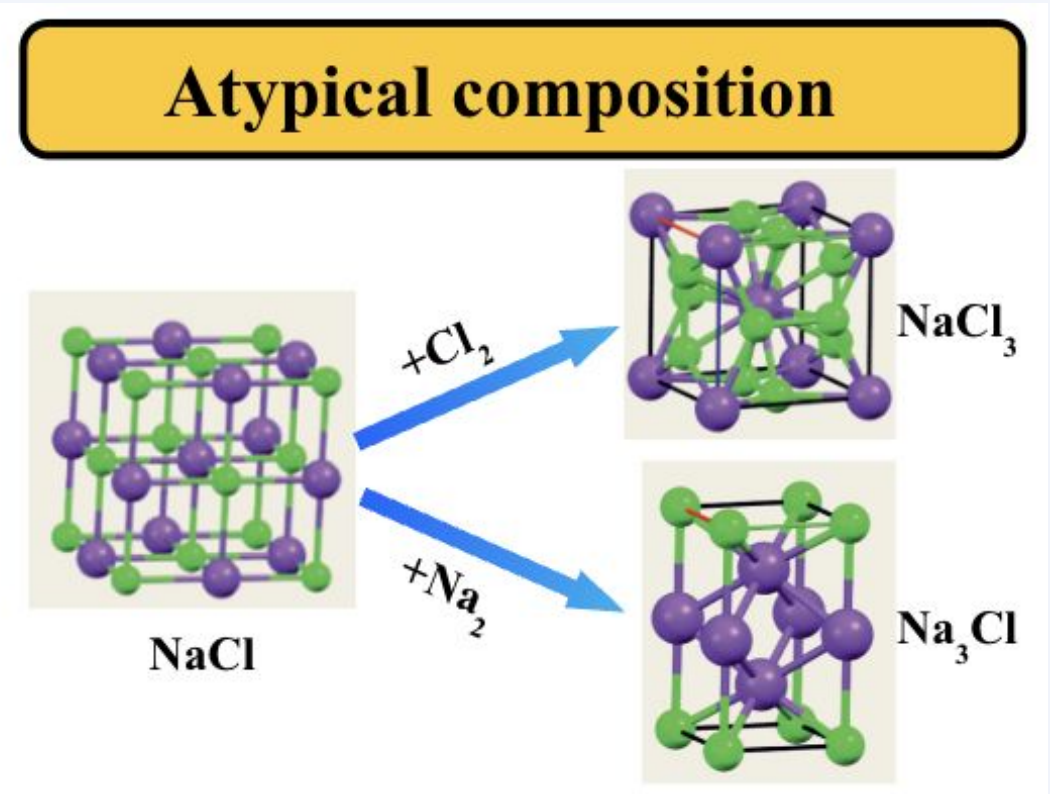
Diamond anvil cell



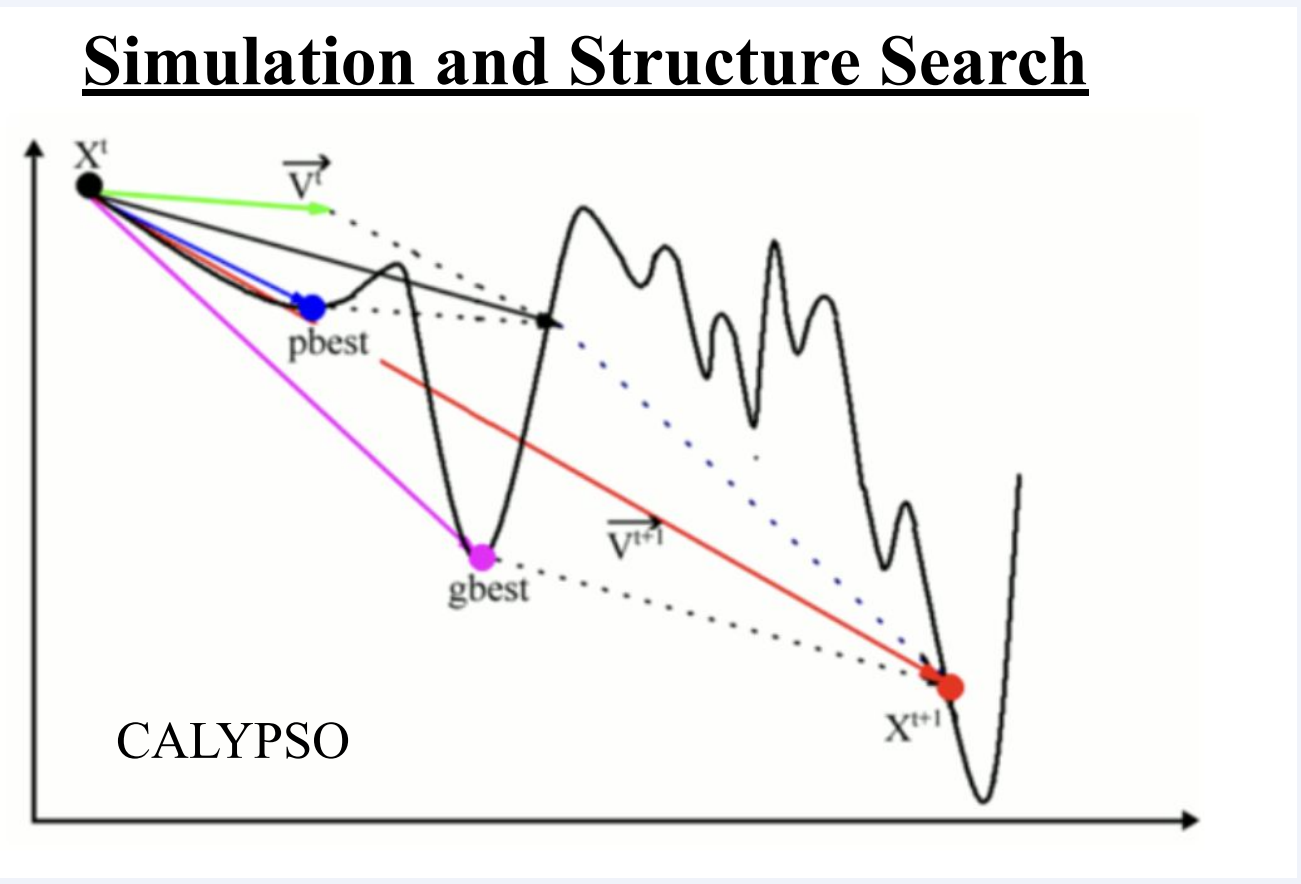
Phase transition



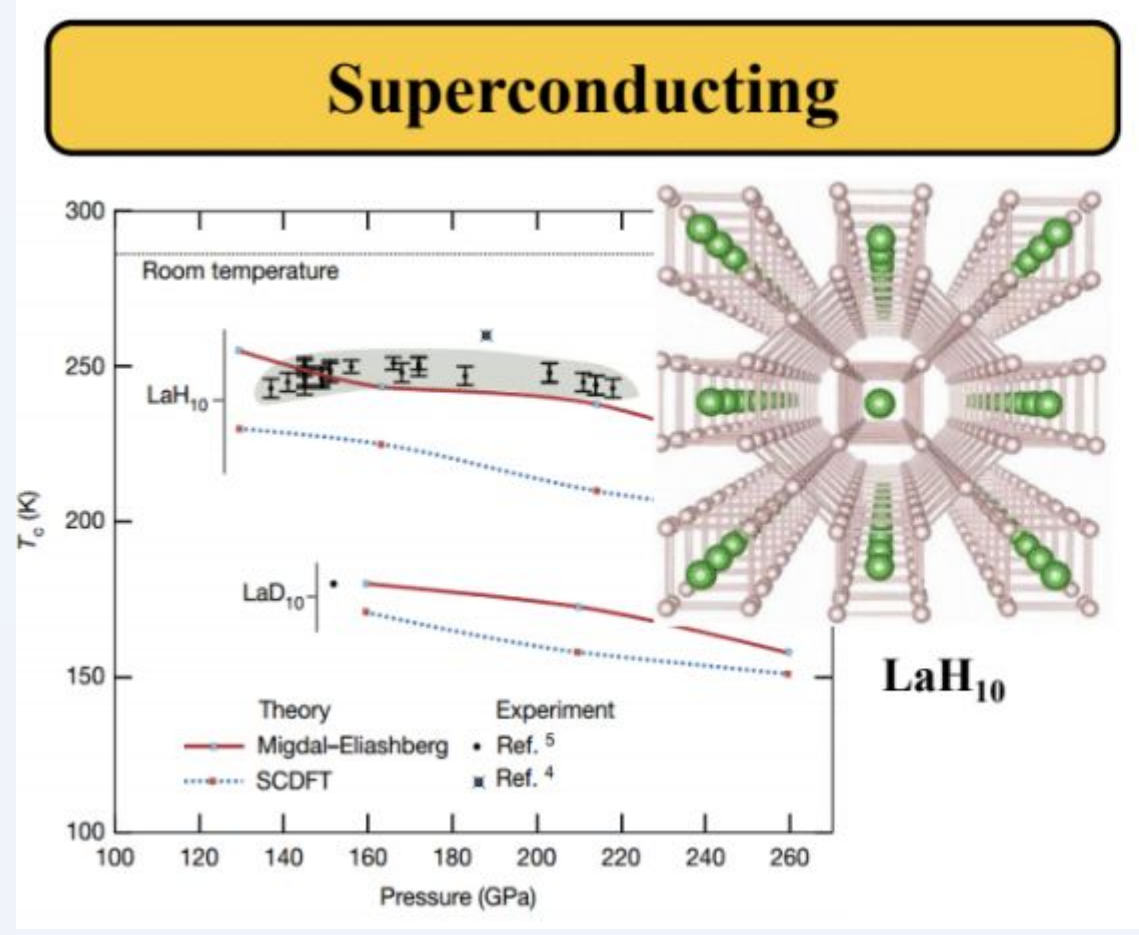
Atypical composition



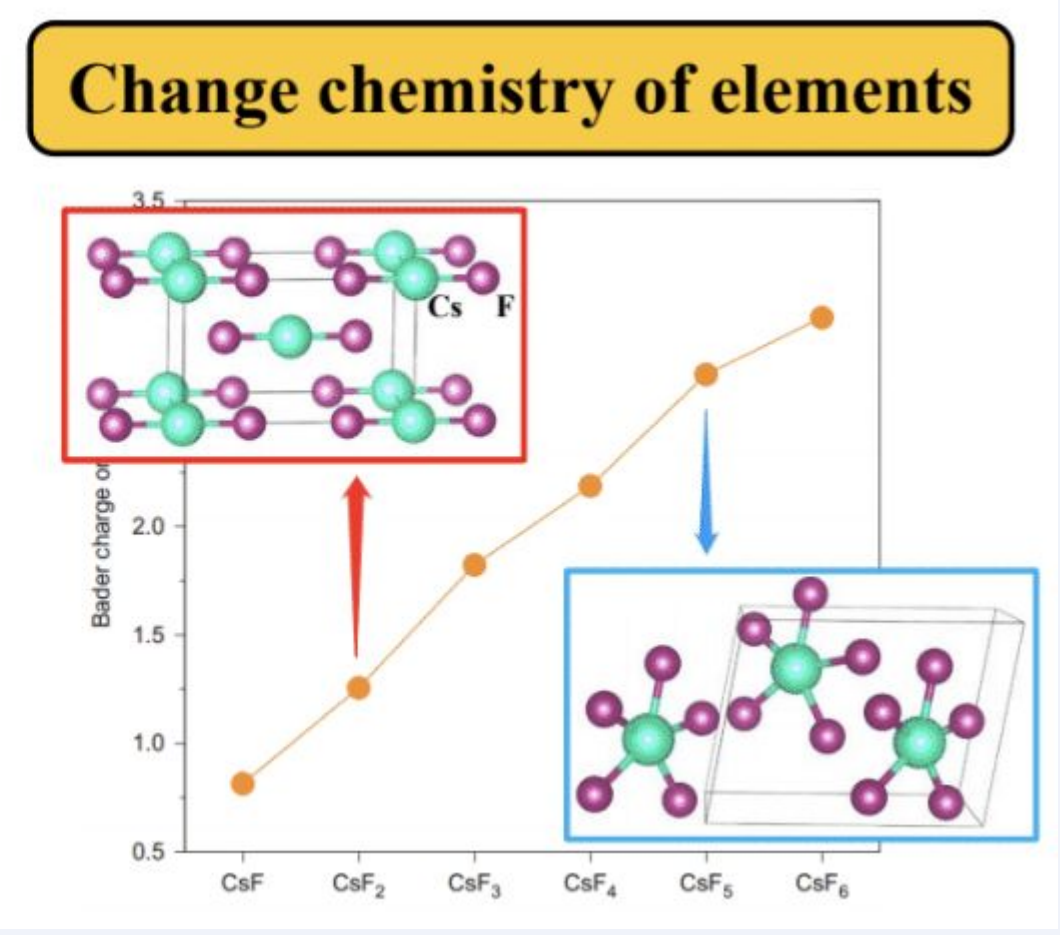
Simulation and Structure Search



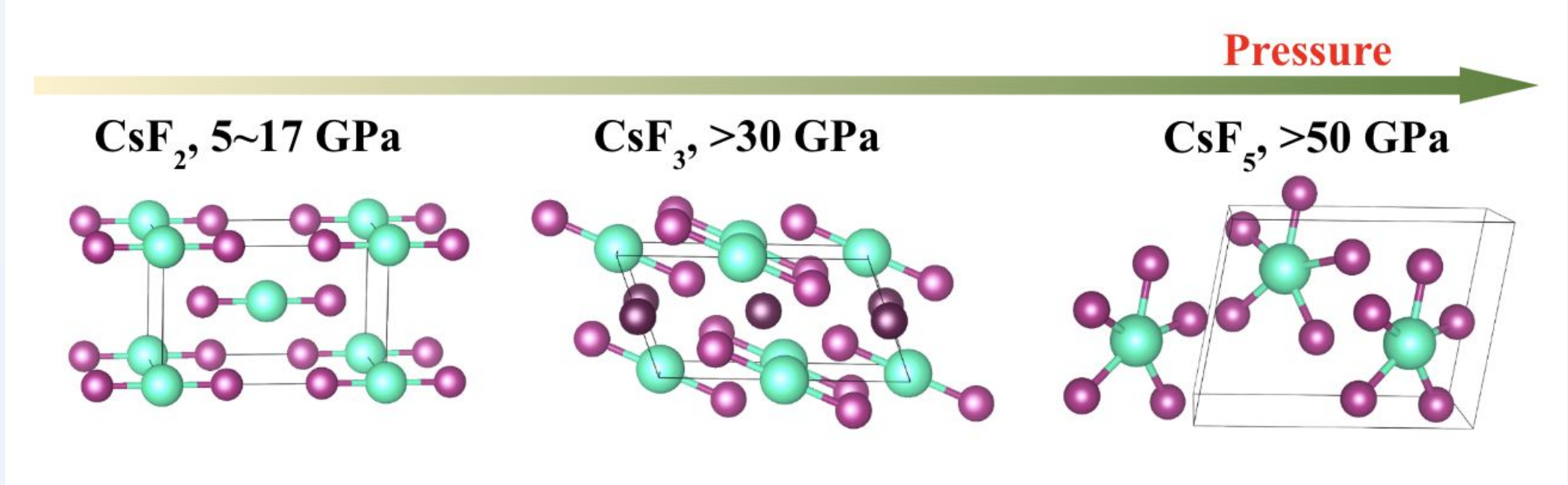
Superconducting



Change chemistry of elements

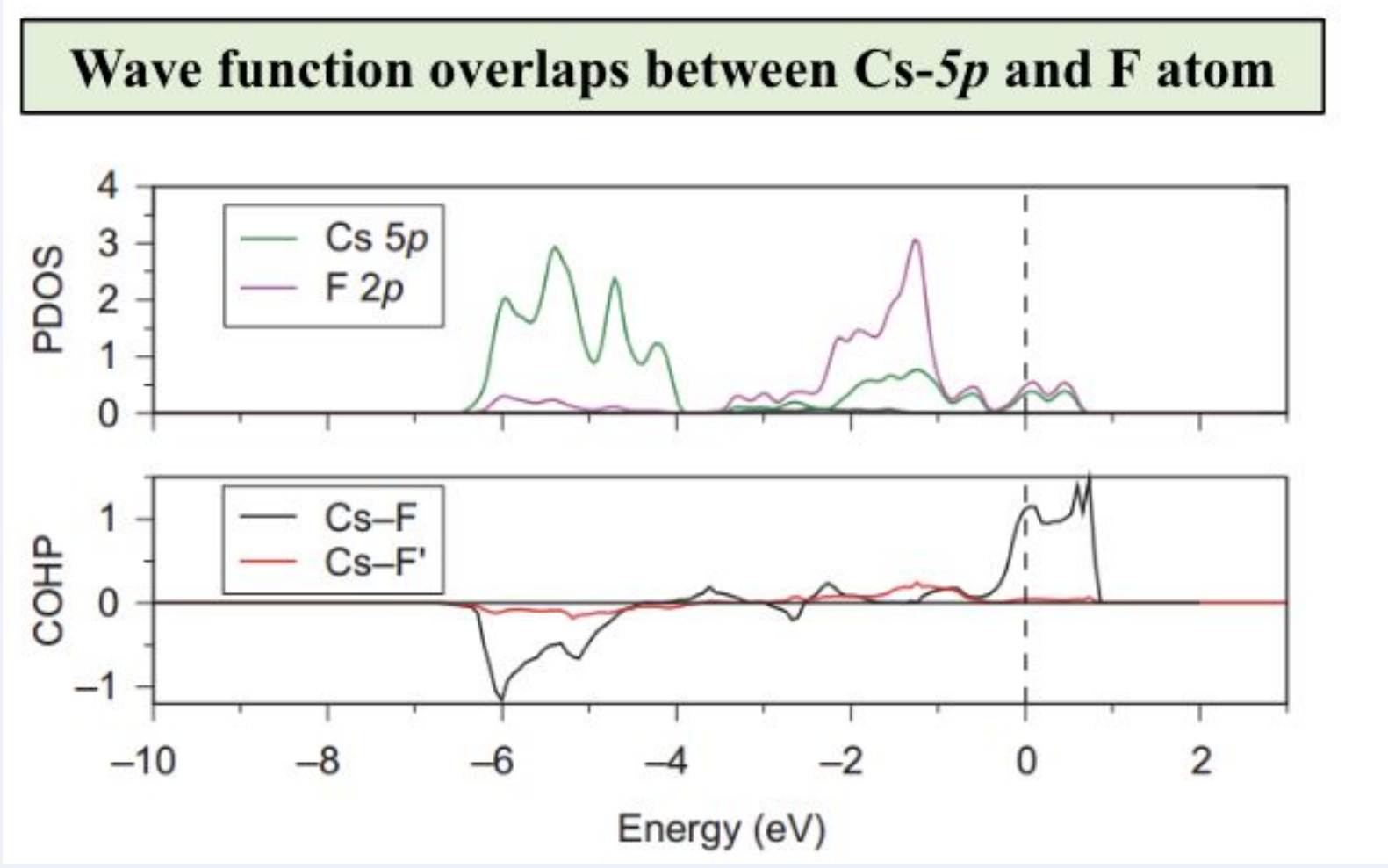


Reactivity of Core Electrons in Cs-F system

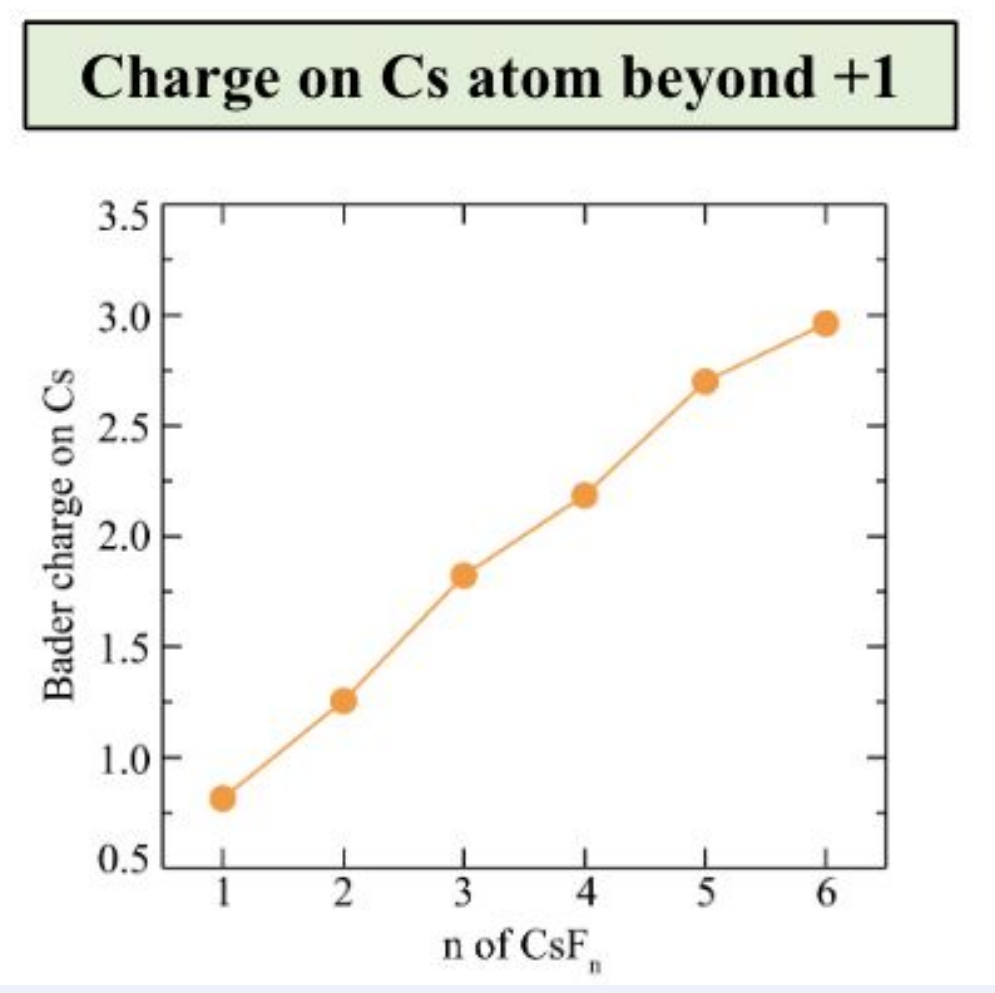


- CsF_2 stable at 5-17 GPa, CsF_3 and CsF_5 stabilize at 15 GPa and 50 GPa respectively, remain stable up to 200 GPa.

Wave function overlaps between Cs-*5p* and F atom



Charge on Cs atom beyond +1



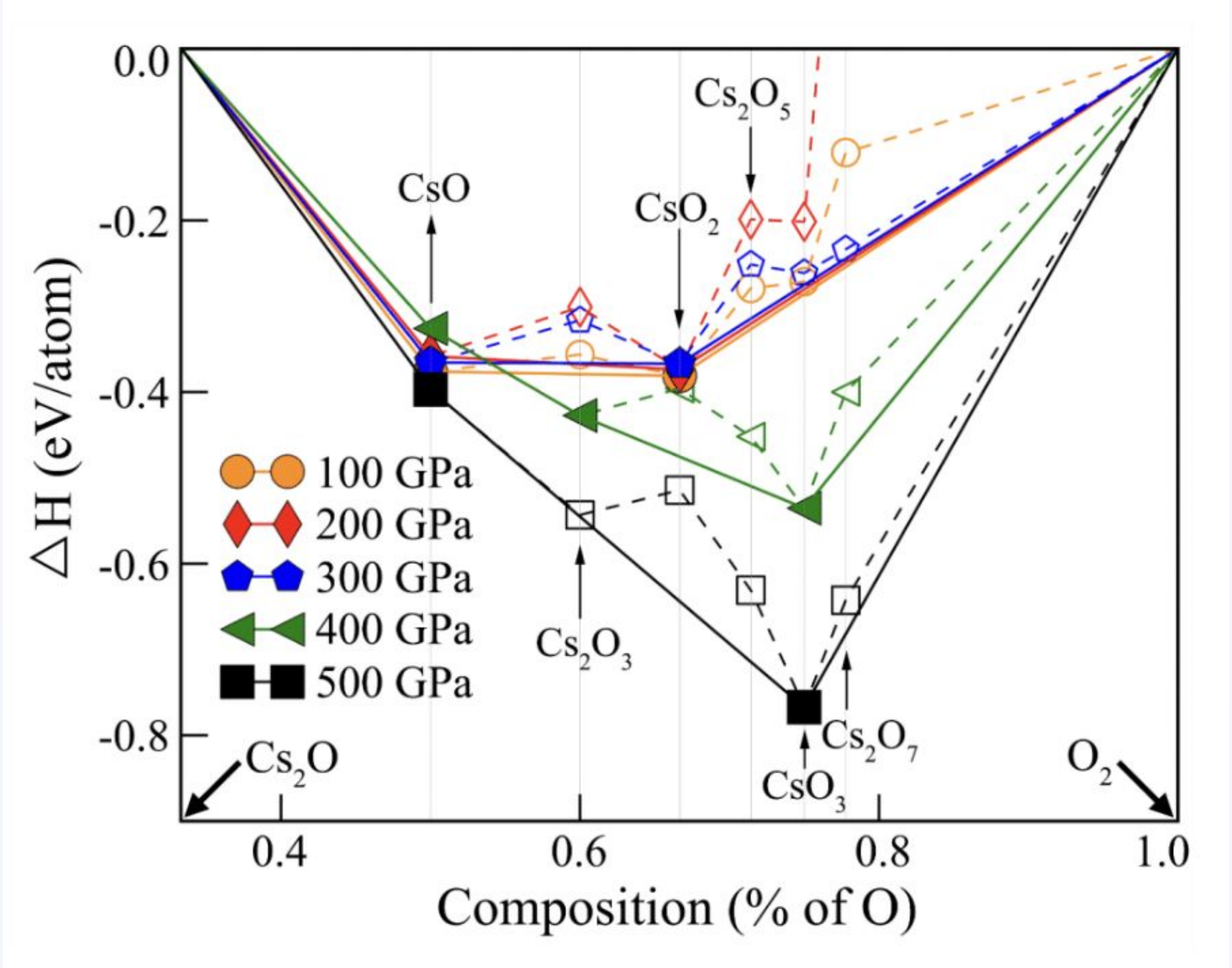
- Increasing pressure forms CsF□ compounds with higher fluorine ratios.
- Electronic structure and bond analyses distinctly show the involvement of Cs 5*p* electrons in forming Cs-F bonds.

- At 30 GPa, CsF_3 structural transition: from F_3^{2-} polyfluoride anions structure to structure without F-F bonds.

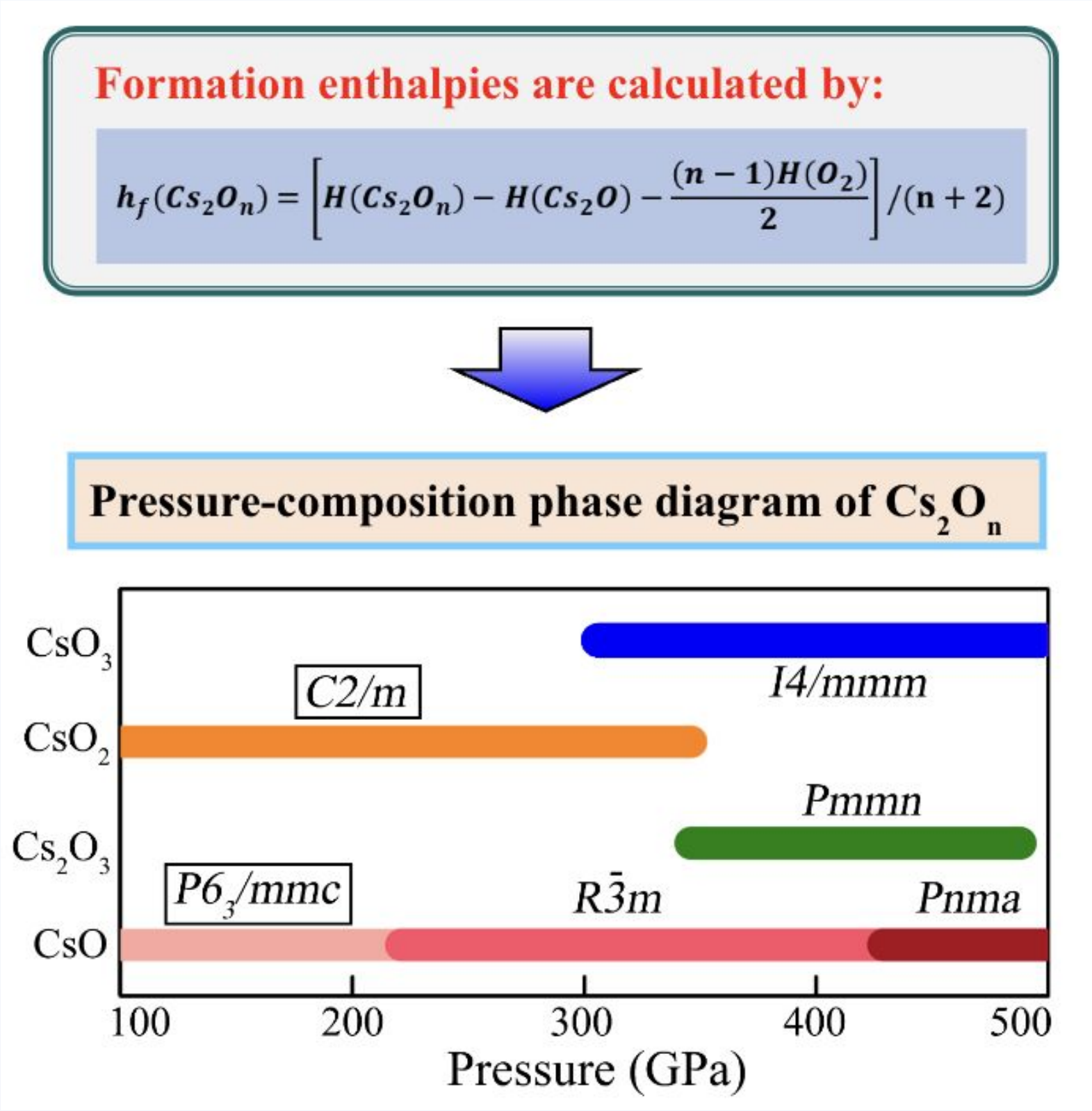
Issues with Fluorine

Fluorine is corrosive to diamond anvil cells, making the experimental verification of the above predictions extremely challenging.

Stability of Cs polyoxide structures

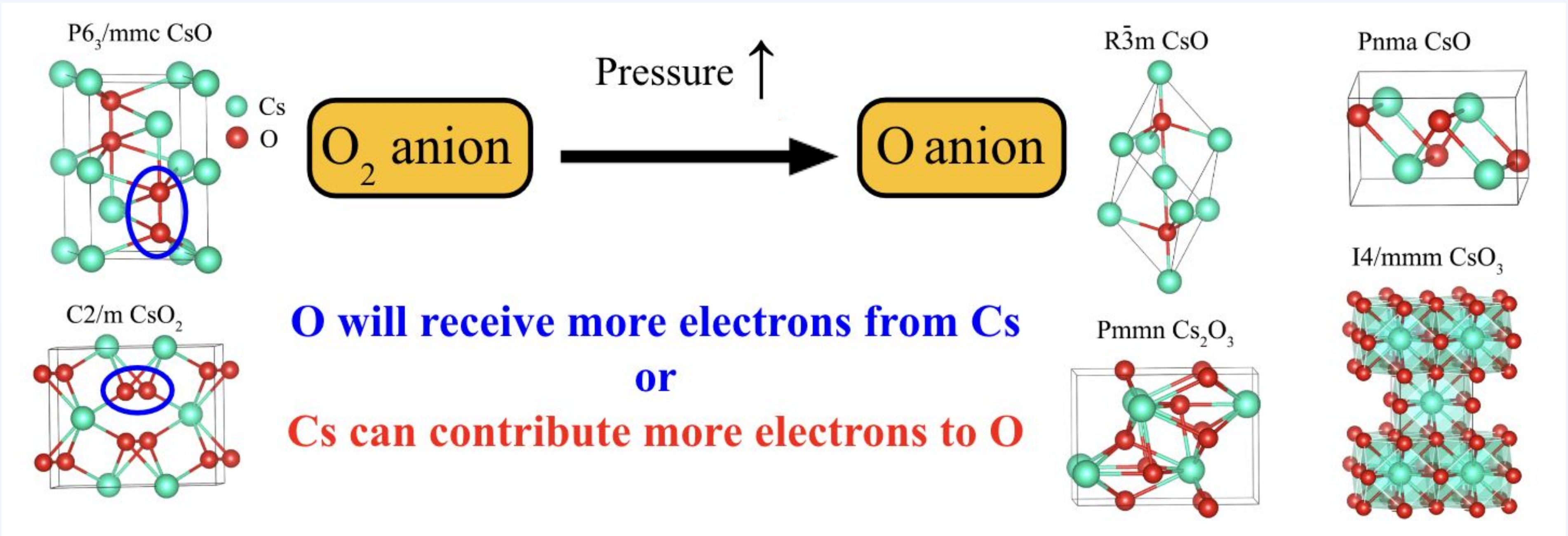


Convex Hull of Cs polyoxides


Formation enthalpies are calculated by:

$$h_f(Cs_2O_n) = \left[H(Cs_2O_n) - H(Cs_2O) - \frac{(n-1)H(O_2)}{2}\right]/(n+2)$$

Pressure-composition phase diagram of Cs_2O_n



O_2 anion $\xrightarrow{\text{Pressure} \uparrow}$ O anion

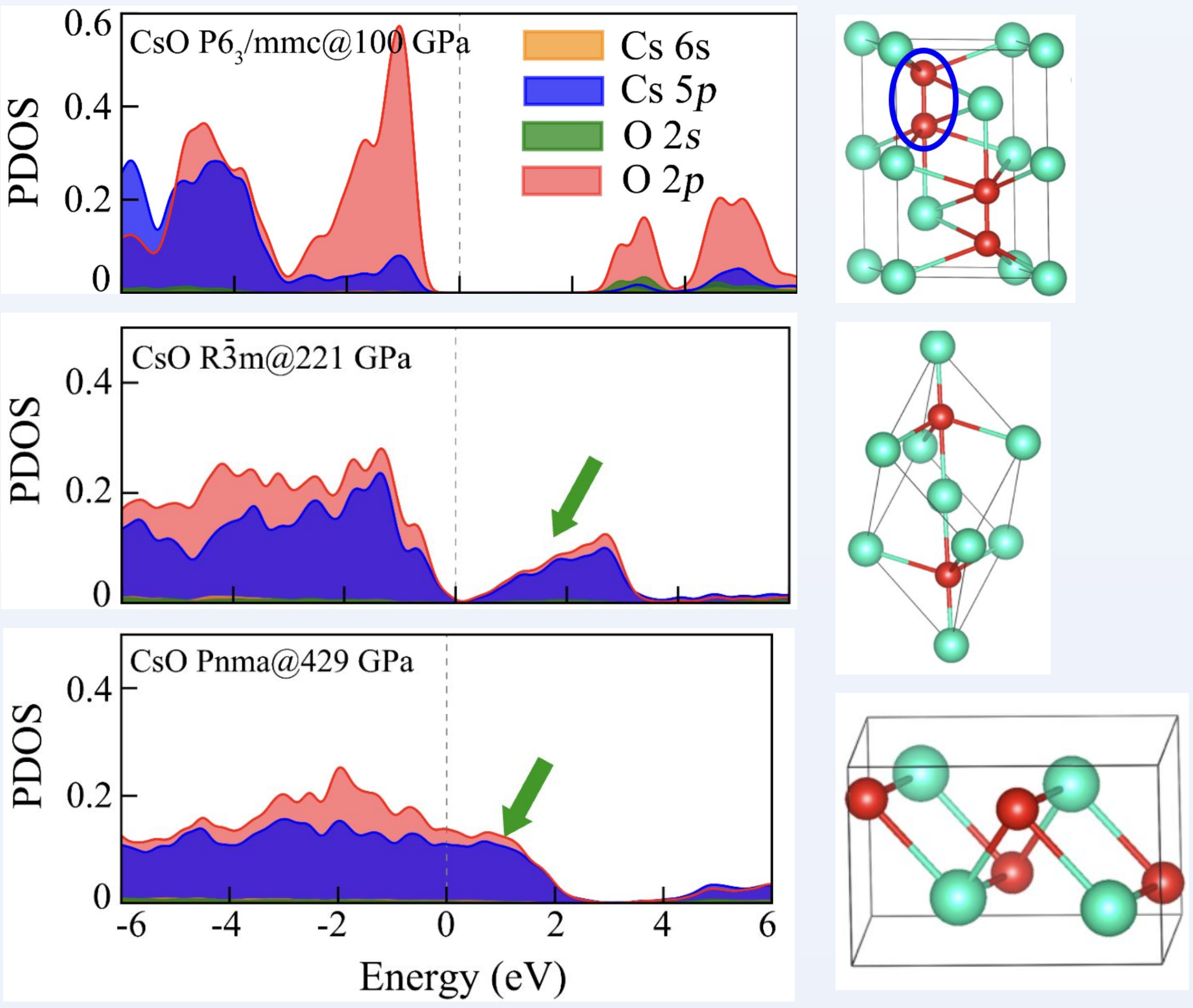
O will receive more electrons from Cs

or

Cs can contribute more electrons to O

Reactivity of Cs-5p orbital under pressure

$P6_3/mmc$ CsO $\xrightarrow{221\text{ GPa}}$ $R\bar{3}m$ CsO $\xrightarrow{429\text{ GPa}}$ Pnma CsO



- High pressure causes structural change in Cs-O compounds, eliminating polyoxygen anions (key to polyoxides).
- Abnormal behavior due to activation of Cs 5sp electrons.
- Pressure alters atomic orbital energies, potentially activating core electrons if their energies near or surpass other orbital energies.

Conclusions

- **Above 221 GPa, O atoms in Cs-O compounds will change from O_2 anion to O anion.**
- **For the compounds composed of O anion, the charge on Cs is higher than the +1 state, which denotes that the Cs 5*p* electrons participate in forming chemical bonds.**

Acknowledgements

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