Poster Presentation

Understanding of the Band Gap Transition in $Cs_3Sb_2Cl_{9-x}Br_x$: Anion Site Preference Induced Structural Distortion

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Energy demand is growing rapidly with economic and population growth, which needs to be fulfilled. Among all kind of energies, solar energy is inexhaustible and easily available for use. In order to convert the solar energy to electrical energy, efficient materials must be developed and some device should be fabricated. The required properties of a material for its suitable applications in photovoltaics are, the material should be a better solar light absorber, it must have higher power conversion efficiency and less toxicity, etc. The discovery of lead halide based hybrid perovskite, with greater power conversion efficiency and good solar light absorber than that of traditional silicon solar cell materials, revolutionize the search for alternative photovoltaic material. The greater power conversion efficiency of these materials is due to their exceptional optoelectronic properties like; suitable band gap, high absorption coefficient, and low exciton binding energy. However, these lead-based perovskites suffer roadblock towards the commercialization of these materials because of the highly toxic nature of lead and instability of these compounds. Search for lead-free perovskite led to the discovery of Bi and Sb-based perovskites, which are very good alternative lead-free halide perovskites. These compounds do not form normal AMX_3 (A=Alkali metal; M=Pb; X=Halides) type perovskite with corner shared MX_6 Polyhedra, rather have $A_3M_2X_9$ (A=Alkali metal; M=Bi, Sb; X= Halide) composition with defect halide perovskite structure. In these type of materials direct Band gap materials are suitable candidates for better photovoltaic materials compared to indirect band gap materials. Herein we have synthesized $Cs_3Sb_2Cl_9$, and Br substituted $Cs_3Sb_2Cl_9$ using solution method. The detail structural, optical, electronic properties of these Br substituted $Cs_3Sb_2Cl_9$ compounds as well as a suitable explanation from both experimental and theoretical study for the band gap transition from indirect to direct with Br substitution in $Cs_3Sb_2Cl_9$ will be presented.

1.**Pradhan, A.**; Jena, M. K.; Samal, S. L. Understanding of the Band Gap Transition in $Cs_3Sb_2Cl_{9-x}Br_x$: Anion Site Preference-Induced Structural Distortion. ***ACS Appl. Energy Mater***. **2022**, *5* (6), 6952–6961.

Understanding of the Band Gap Transition in $Cs_3Sb_2Cl_{9-x}Br_x$: Anion Site Preference Induced Structural Distortion

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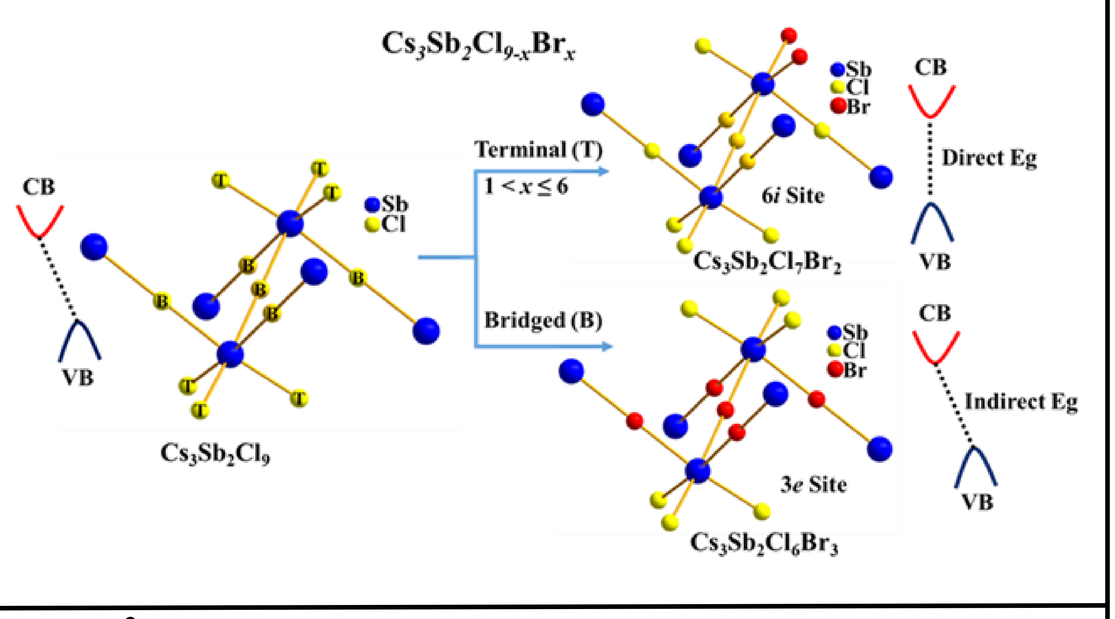
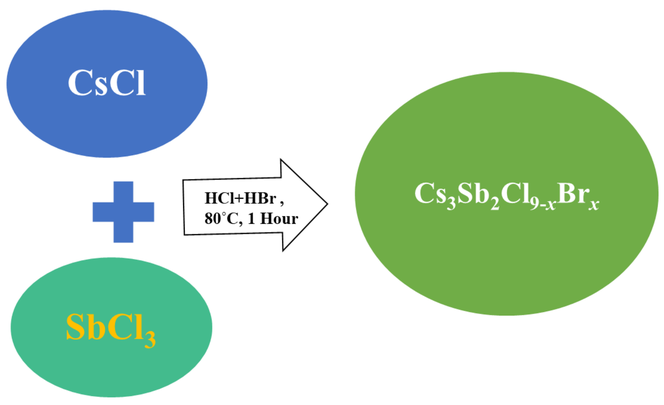
Abstract: Herein, we have studied an indirect to direct band gap transition in $Cs_3Sb_2Cl_{9-x}Br_x$ with Br substitution and a possible explanation is provided from both experimental and theoretical studies. Rietveld refinement of powder X-ray diffraction data revealed that Br prefers the terminal position over the bridging position with initial substitution and induces a distortion in the $Sb(Cl/Br)_6$ polyhedral. Theoretical study confirms that $Cs_3Sb_2Cl_9$ is an indirect band gap material, which undergoes a transition to direct band gap type with minimal (two moles) substitution of Br in $Cs_3Sb_2Cl_{9-x}Br_x$. The splitting of *p*-states of halides and Sb just above the Fermi level induced by the change in the terminal Cl/Br–Sb–Cl/Br bond angle is observed to be the primary reason for the transition.

Introduction: Lead Free Metal Halide Perovskites show remarkable properties which leads to different optoelectronic applications. Understanding of the effect of substitution/doping on the electronic properties and the structure in these compounds is highly essential to design materials with improved optoelectronic properties and hence for practical applications. Systematic introduction of structural distortion in these kind of materials show variable properties. The introduction of distortion is one of the efficient ways to improve the broadband emission in these halide perovskites.

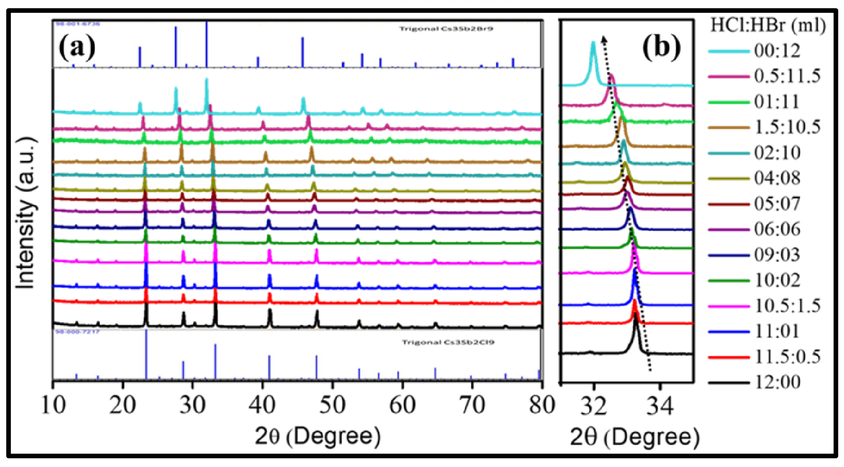


Results and Discussion

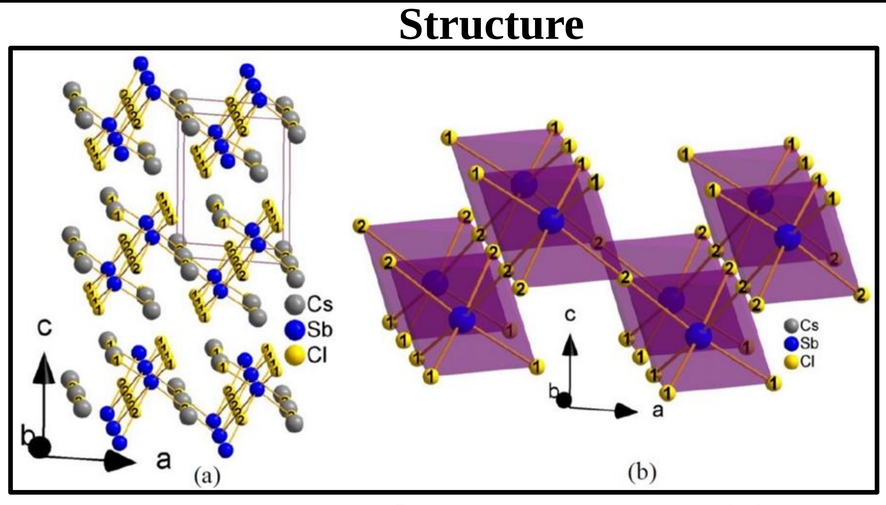
Synthesis



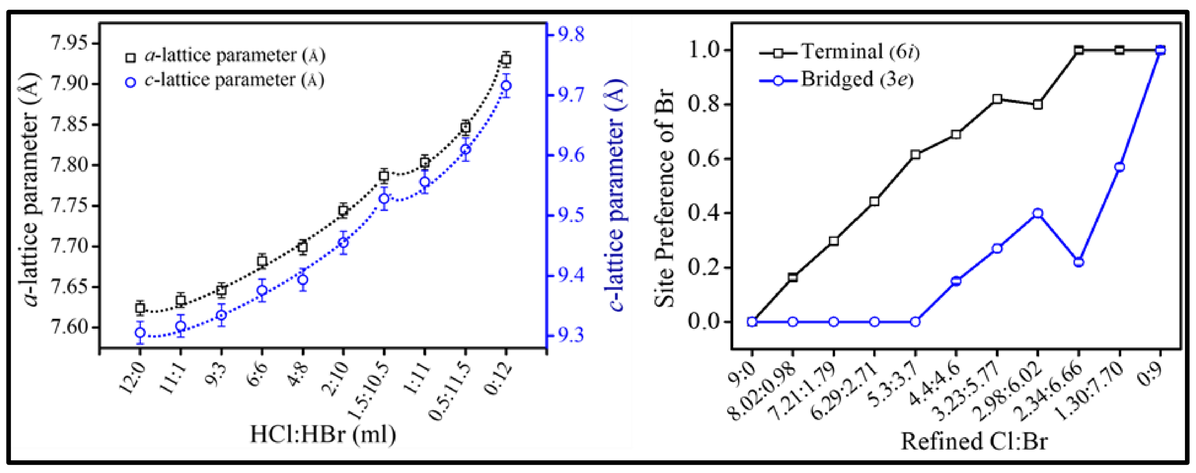
PXRD



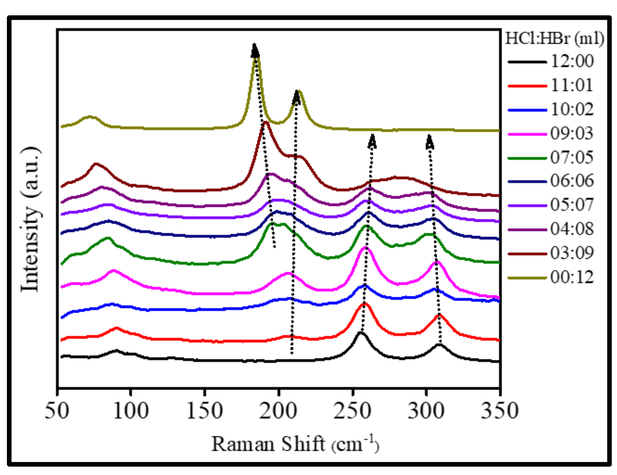
Structure



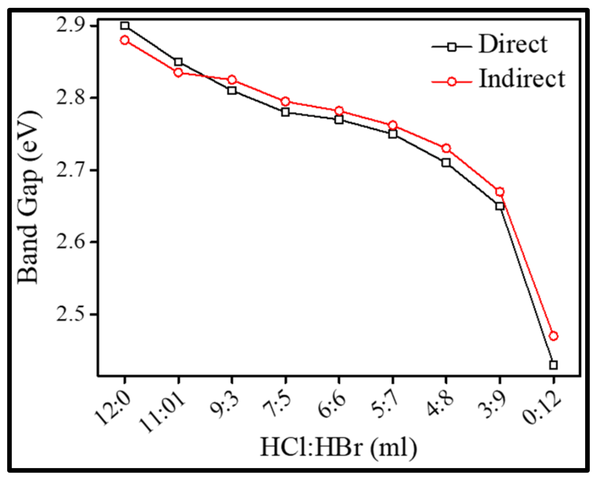
Preferential Substitution of Br



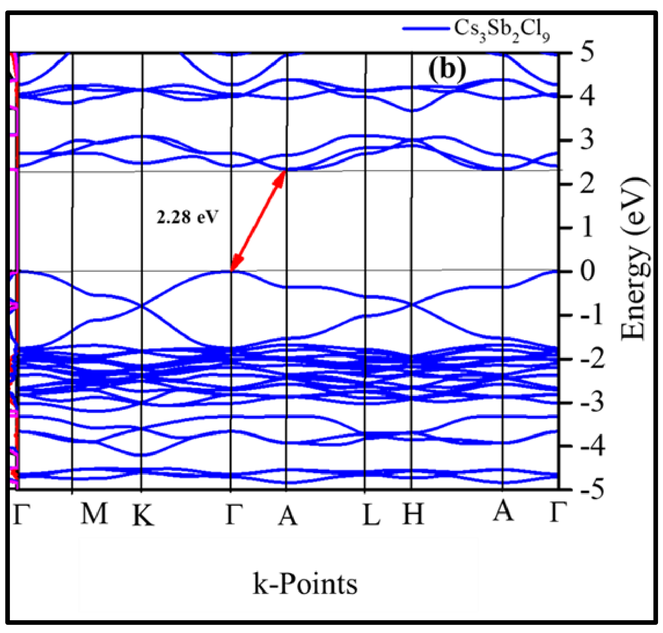
Raman

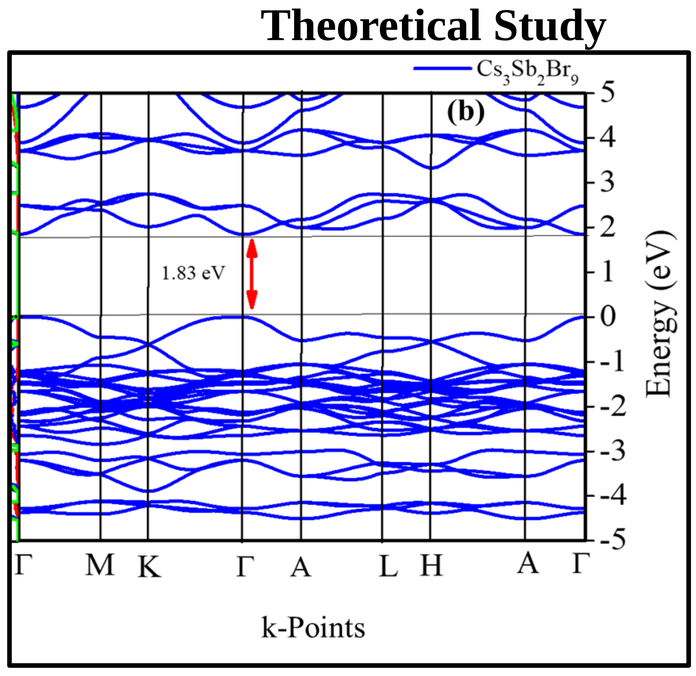


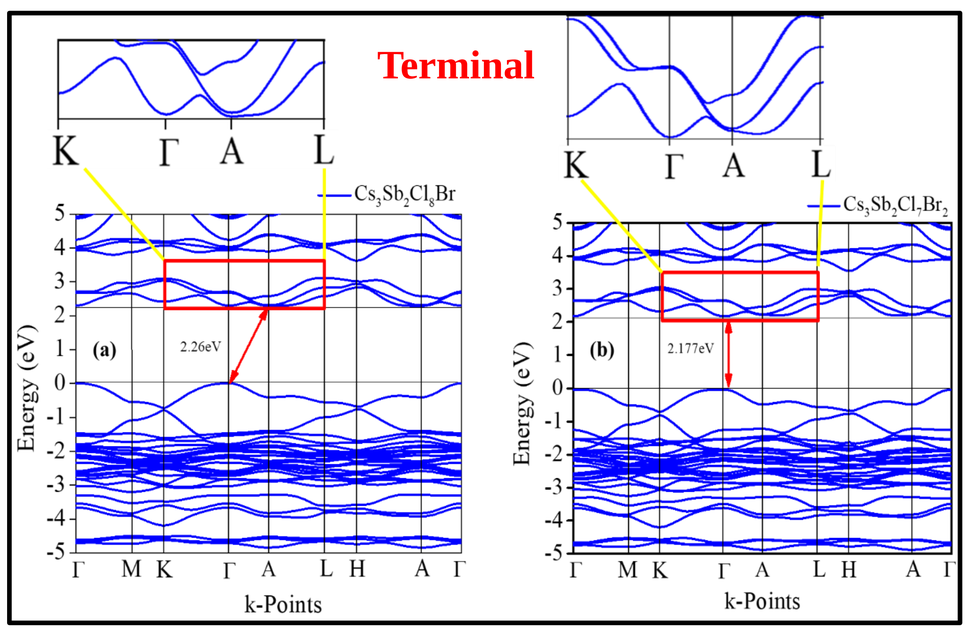
Band Gap vs Composition

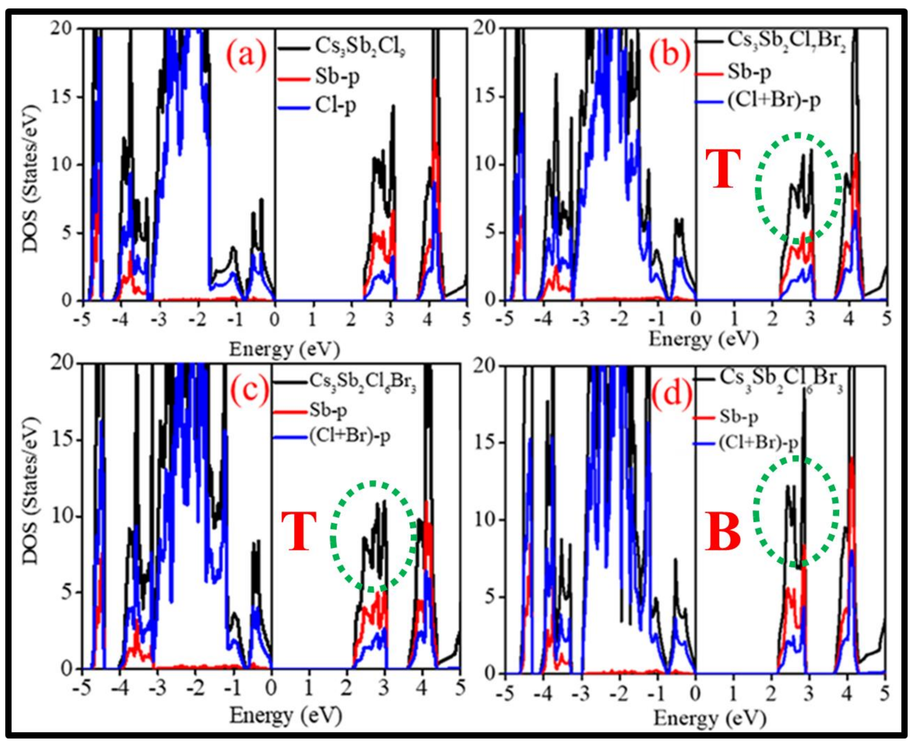


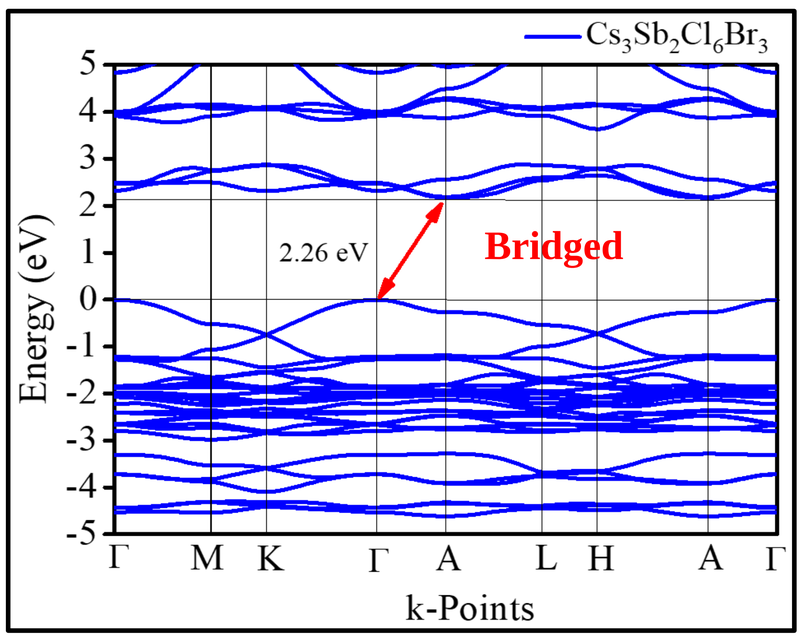
Theoretical Study



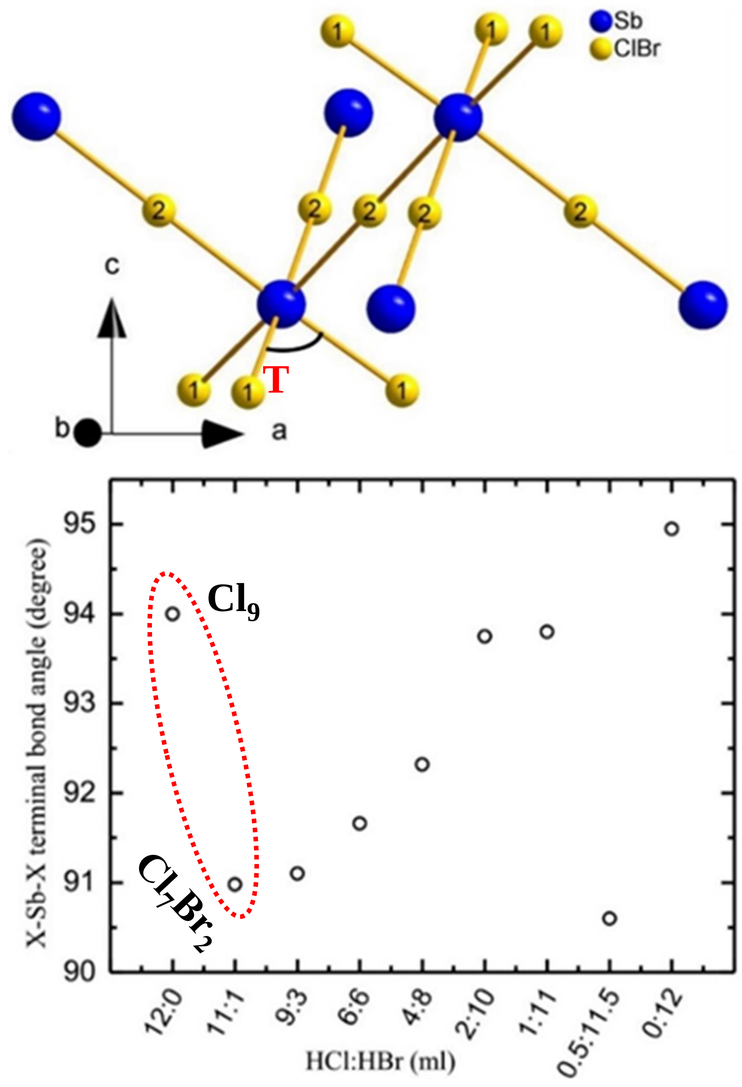








Structural Analysis



Conclusion: $Cs_3Sb_2Cl_{9-x}Br_x$ compounds were successfully synthesized using ion exchange method. Br^- prefers terminal position over the bridging position during initial substitution in $Cs_3Sb_2Cl_{9-x}Br_x$. Substitution of Br at the terminal position results in significant change in the terminal Cl/Br–Sb–Cl/Br bond angle and splitting of halide *p*-states lying above Fermi. Which causes the a transition from an indirect band gap to direct band gap with Br (2 mol) substitution.

Reference: **A. Pradhan,** *et al. ACS Appl. Energy Mater.* **2022**, *5* (6), 6952–6961