Effects of pressure on the electronic properties of KSnX3 (X=Cl,Br,I) perovskites

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INTRODUCTION

The halide perovskites are known to have good power conversion efficiencies and hence can be utilized for various opto-electronic applications such as photovoltaics, light emitting diodes, sensors, lasers and radiation detectors. (Eperon et al., 2016; Khan et al., 2021; Mcmeekin et al., 2016). The effect of pressure on enhancing the electronic properties, has been widely studied for halide perovskites (Wang et al., 2021). One of the common tools in atomistic simulations is Density functional theory (DFT) (Sholl & Steckel, 2009), which is based on the Kohn-Sham equations (Kohn & Sham, 1965) and a solution of the Schroedinger equation. Khan et al. applied DFT studied the electronic property of KSnCl3 and KSnBr3, Perdew-Burke-Ernzerhof Generalized Gradient (PBE-GGA) and Tran-Blaha modified Becke-Johnson (TB-mBJ) approximations. (Khan et al., 2021). The interest in KSnX3 (X=Cl,Br,I) perovskites is because it is a potential material for solar cell applications. Hence, the goal of this work was to study the electronic properties of KSnCl3, KSnBr3 and KSnI3 perovskites under pressures ranging from 0 to 50 GPa.

COMPUTATIONAL DETAILS

In this work, the structure relaxation and self-consistent field calculations are performed using plane wave-based DFT method (Perdew et al., 1996) as implemented in the open-source Quantum espresso suite (P. Giannozzi et al., 2017; Paolo Giannozzi et al., 2009).

The hybrid Perdew-Burke-Ernzerhof functional (PBE0) is used to describe the exchange correlation energy of the interacting electrons. The Monkhorst–Pack method (Monkhorst & Pack, 1976) is used to sample the k-points in the Brillouin zone. The brillouin zone is sampled with the Γ-centered k-point grid of 10×10×10.

The k-space integral and the plane-wave basis are chosen to ensure that the total energy is converged at 0.1m Ry level. The kinetic energy cut off for the plane-wave expansion is found to be optimal at 60 Ry.

The solution of the Murnaghan equation is obtained by fitting optimal cell volume, bulk modulus and the derivative of bulk modulus to predict calculated total energies at different lattice constants.

In order to ensure that the relationship between external pressure and cell volume is accurate, the fitted structural properties are ensured to have chi-squared errors of less than 0.001.

The Wannier 90 code was used to plot bandstructures. (Pizzi et al., 2020)

$$E(V) = E_0 + B_0 V_0 \left[\frac{1}{B_0'(B_0'-1)} \left(\frac{V}{V_0}\right)^{1-B_0'} + \frac{1}{B_0'}\frac{V}{V_0} - \frac{1}{B_0'-1} \right] \quad (1)$$

$$B_0 = -V\left(\frac{\partial P}{\partial V}\right)_T \quad (2)$$

$$P = -\left(\frac{\partial E}{\partial V}\right)_S \quad (3)$$

$$B_0' = \left(\frac{\partial B_0}{\partial P}\right)_T \quad (4)$$

- E – Energy
- E_0 – Energy at ground state
- P – Pressure
- S – Entropy
- B_0 – Bulk modulus
- B_0' – Pressure derivative of the Bulk modulus
- V – Volume
- V_0 – Volume at ground state

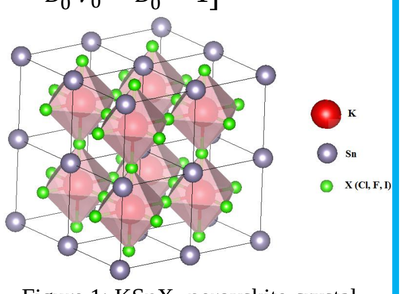

Figure 1: $KSnX_3$ perovskite crystal

RESULTS

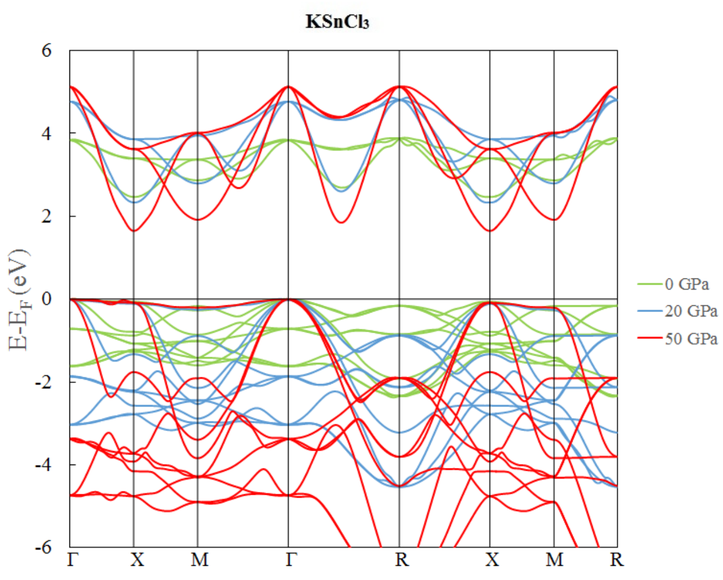

Figure 3: Electronic Bandstructure for $KSnCl_3$

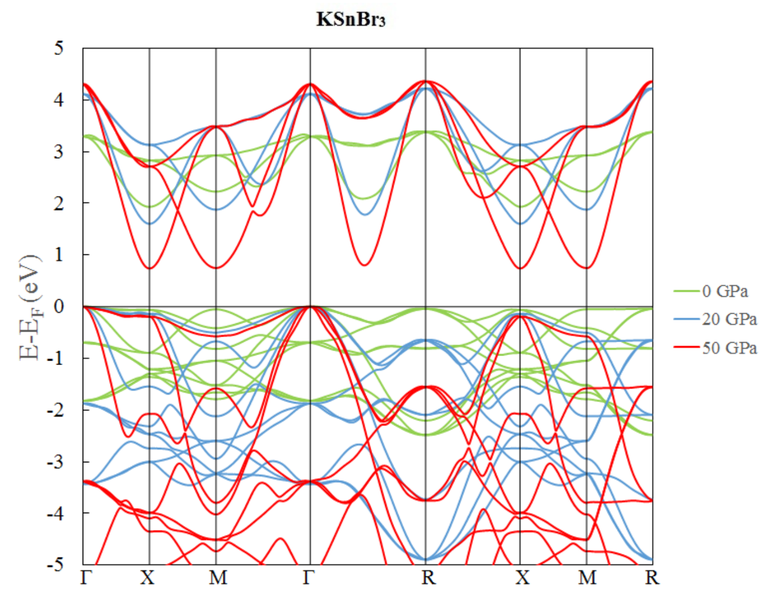

Figure 4: Electronic Bandstructure for $KSnBr_3$

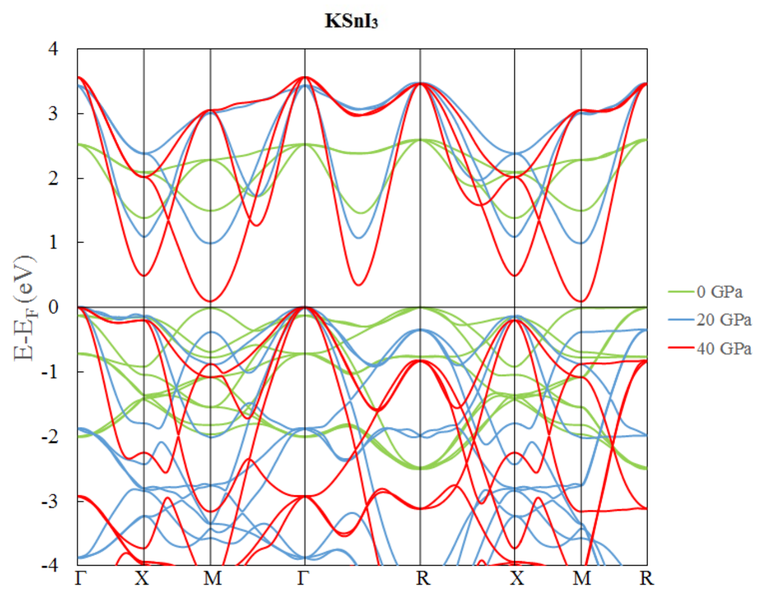

Figure 5: Electronic Bandstructure for $KSnI_3$

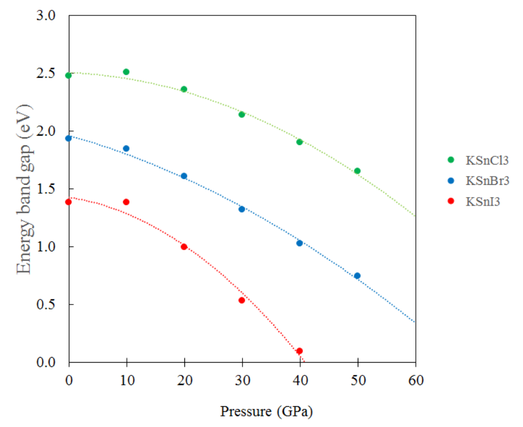

Figure 6: Dependence of Energy band gap on pressure

Table 1: Comparison of results with similar work

Compound	Energy band gap (eV)	
	This work	Khan et al.
KSnCl3	2.47	0.89 (PBE-GGA) 1.48 (TB-mBJ)
KSnBr3	1.93	0.57 (PBE-GGA) 0.93 (TB-mBJ)

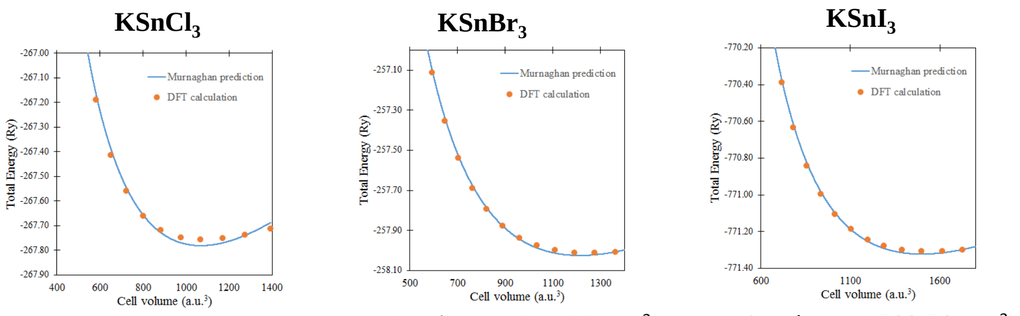

Figure 2: Dependence of total energy on cell volume

CONCLUSION

The effect of hydrostatic pressure on the electronic properties of KSnX3 has been studied using DFT-PBE. All the systems were found to be semiconducting within the pressure considered except KSnI3 that exhibited metallic behavior at 40 GPa. The band gap was found to decrease with pressure. The systems under pressure can absorb in the visible region making them potential materials for solar cell and optoelectronic applications.

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