Electronic Supporting Information

A comprehensive study of electronic, optical, mechanical and piezoelectric properties of Li-based Tin-halide perovskites from GGA, Meta-GGA and HSE06

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Mulliken Population Analysis:

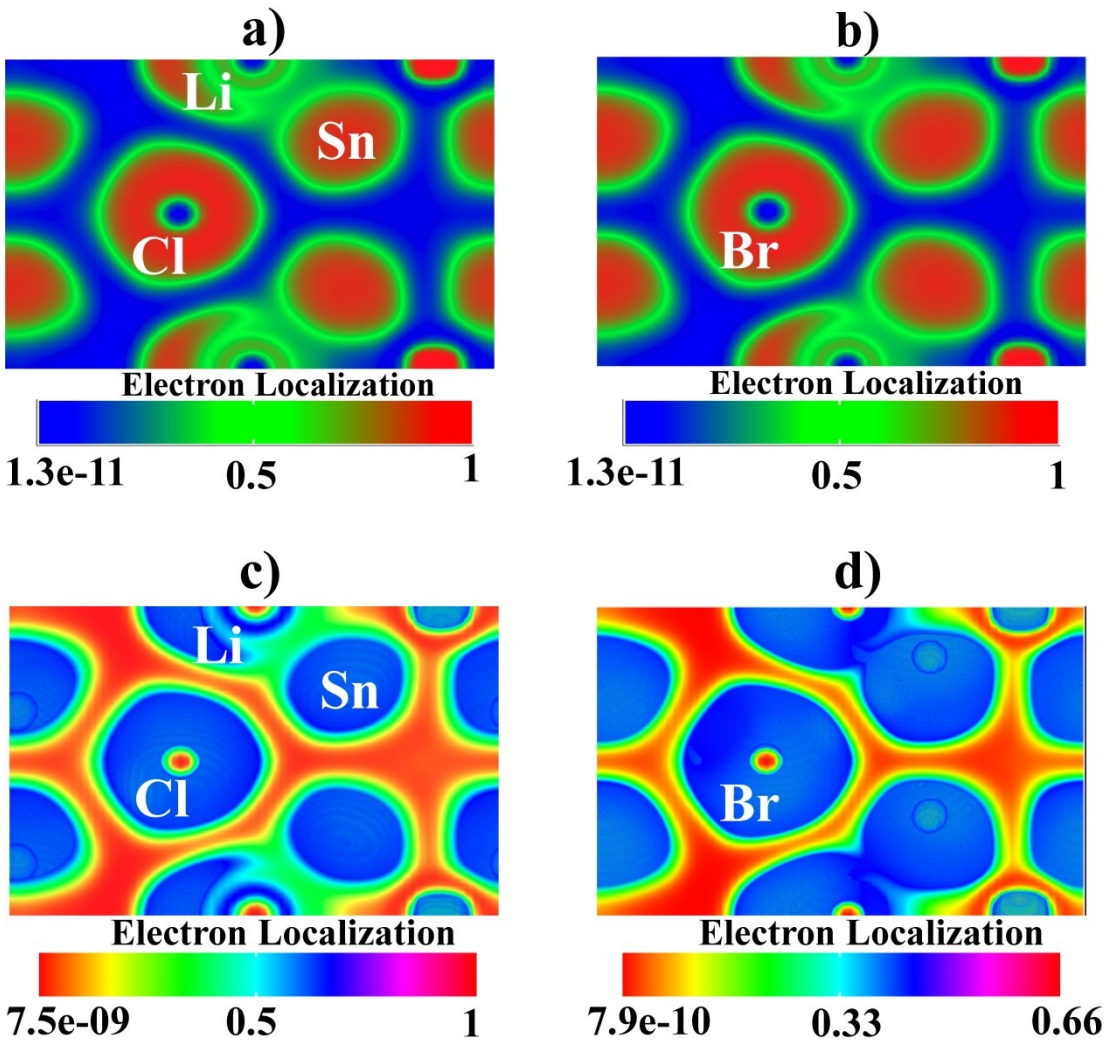
To understand the inter-atomic bonding within the compounds, we have utilized the mulliken population analysis (MPA) [1]which provides an insight of bonding between atoms and charge distributions among the atoms within the materials. Herein, Table S1 we report the analyzed populations, charges and bond lengths of the studied halide perovskites-LiSnCl3 and LiSnBr3 using GGA and mGGA. The contributions of all atoms are given in terms of their charges of s- and p-orbitals. The presence of negative charge values in Cl/Br atom is a result of charge accumulation which has a direct indication of charge transfer from Sn/Li→Br/Cl, creating charge depletion around Sn/Li atoms. The results of charge depletion (+) and charge accumulation (-) by using GGA and mGGA are given in Table S1

Compound(s)	**Functionals**	**Species**	**Atomic Population**			**Mulliken charge (*e*)**	**Bond**	**Bond length (Å)**
			Total	**s**	**p**			
$LiSnCl_3$	GGA	Li	2.39	2.06	0.32	(+)0.61	Li-Sn	3.41
							Li-Cl	2.67
		Sn	13.35	0.15	11.41	(+)0.65	Sn-Cl	2.63
		Cl	7.41	1.93	5.48	(-)0.41	Cl-Cl	3.46
$LiSnBr_3$	GGA	Li	2.51	2.15	0.37	(+)0.49	Li-Sn	3.62
							Li-Br	2.85
		Sn	13.49	1.95	11.54	(+)0.51	Sn-Br	2.77
		Br	7.33	1.94	5.39	(-)0.33	Br-Br	3.72
$LiSnCl_3$	mGGA	Li	2.53	2.15	0.38	(+)0.47	Li-Sn	3.98
							Li-Cl	2.44
		Sn	13.38	1.90	11.48	(+)0.62	Sn-Cl	2.58
		Cl	7.37	1.90	5.49	(-)0.37	Cl-Cl	3.39
$LiSnBr_3$	mGGA	Li	2.56	2.21	0.35	(+)0.44	Li-Sn	3.59
							Li-Br	2.69
		Sn	13.46	1.92	11.55	(+)0.54	Sn-Br	2.73
		Br	7.32	1.93	5.39	(+)0.32	Br-Br	3.70

Table S1: Calculated the atomic populations, mulliken charge and bond lengths of $LiSnX_3$ (X = Cl, and Br) using GGA and mGGA

Electron Localization Function

The electron localization function (ELF) [2] has become an effective tool for qualitatively comprehending the behaviour of electrons within the atomic system during the course of crystalline formation. A wide range of bonding scenarios can be explained, from the most common covalent to the metallic bond. The ELF does not solely depend on the employed basis sets and computational techniques. ELF plays a crucial role in understanding the chemical bond formation providing vital information about the electrons localization. We have displayed the 2D and 3D ELF maps of LiSnCl3 and LiSnBr3 employing GGA and mGGA in Fig.S1. As seen from the figures obtained using GGA, the region with the red colour reveals higher electron localization while the blue colour displays the regions with lower electron localization [see Fig. S1 (a-b) & Fig. S1 (e-f)]. Whereas, the representation of colour coding is just the opposite for mGGA as compared to GGA [see Fig.S1 (c-d) & Fig. S1(g-h)]. The charge localizations are more in Cl- and Br-atoms due to their higher level of electronegativity than Li and Sn atoms. Thus, these findings support the results of the Mulliken population analysis.



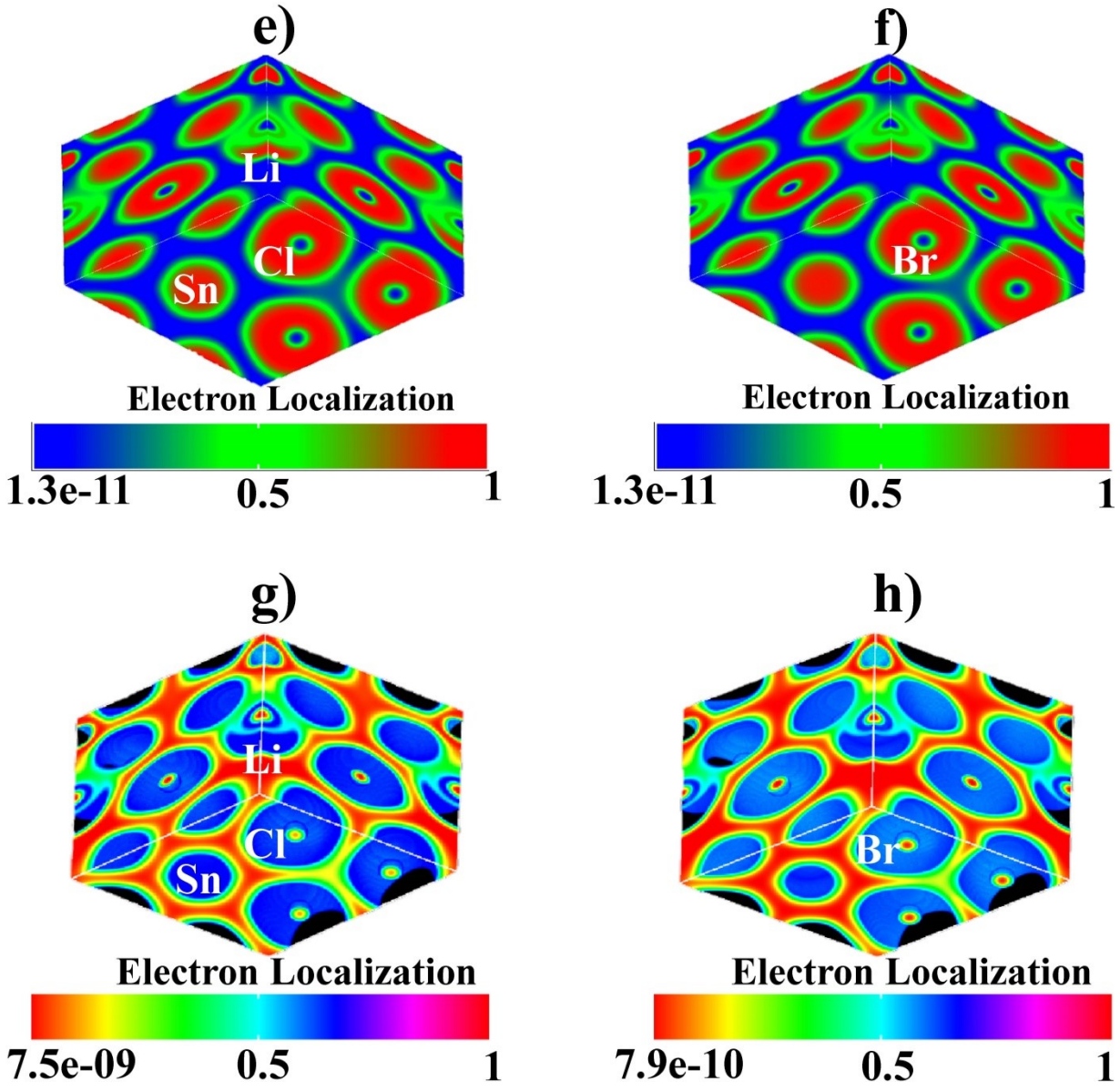
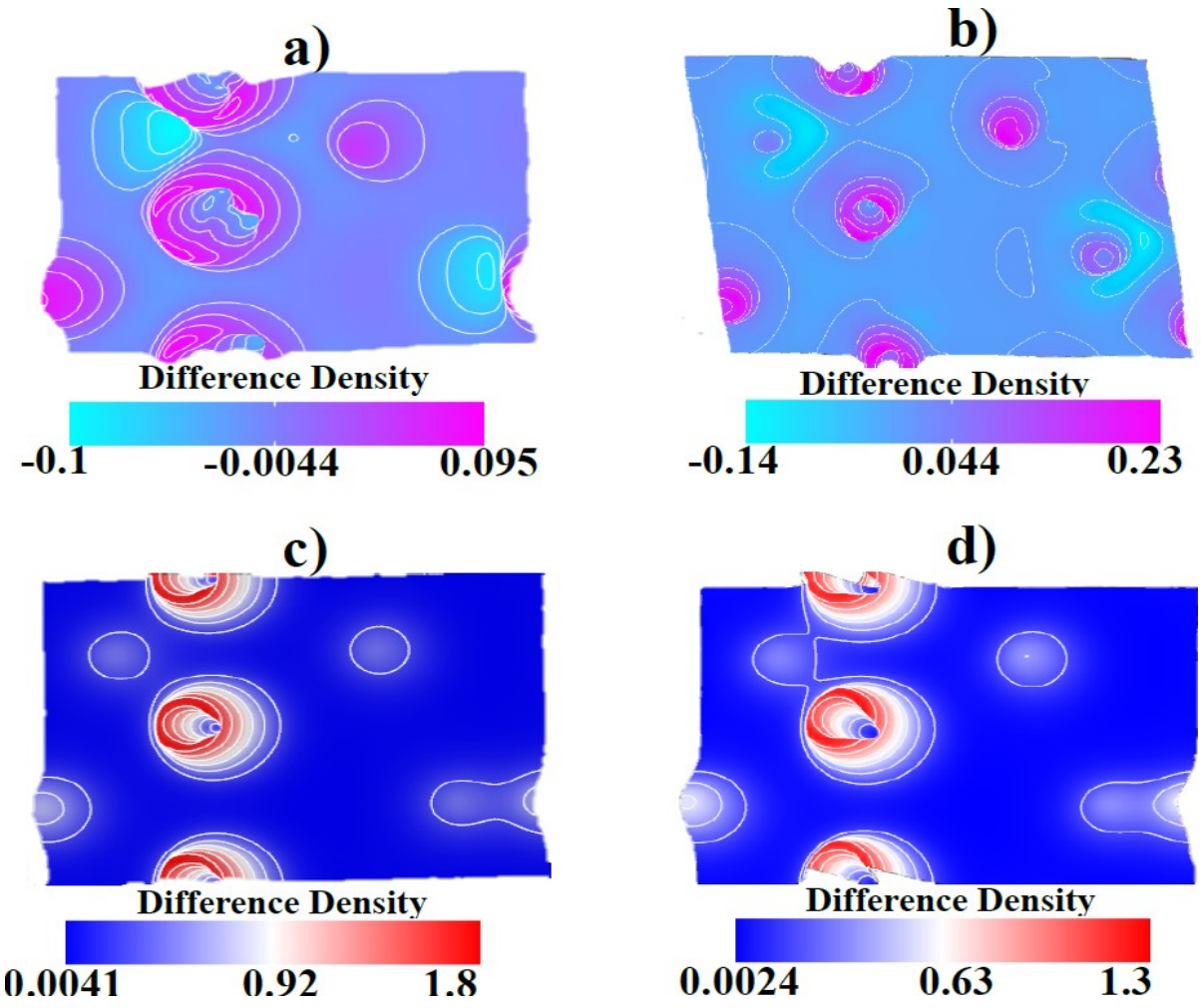


Fig.S1: 2D & 3D schematic presentation of Electron Localization Function (ELF) for $LiSnX_3$ where Fig.(a-b & e-f) are obtained using GGA and Fig.(c-d & g-h) are obtained using mGGA

Electron Difference Density (EDD):

Electron Difference Density (EDD)[3] also plays a vital role in chemical bonding as it compares the electron densities between the atoms within the materials. EDD provides valuable information about the electronic structures with the allocations of the charge between Li, Sn, Cl, and Br atoms. Within the system, the recombination of atoms will produce charge transfer which produces fascinating outcomes. The obtained figures in 2D and 3D, using GGA FigS2.(a-b, e-f) & Fig.(c-d, g-h) using mGGA, depicts the distribution of charge within the materials. From our output figures obtained using GGA, we have observed that the regions with magenta color reveals higher densities of electrons while regions having light blue color depicts lower in densities of the electrons. But in the 3D contour plot Fig.S2.(g), we observed that there are atleast two lower points which shows less accumulation of charge as compared to the other regions. These particular areas are considered to be having the weakest bond while the crystalline formation. Likewise, from the figures obtained employing mGGA, we also noted the regions tends to red color are considered to have accumulated more electrons then the ones tending towards the blue color. Therefore, we have come to know that the findings of MPA, ELF and EDD are in good agreements with another.



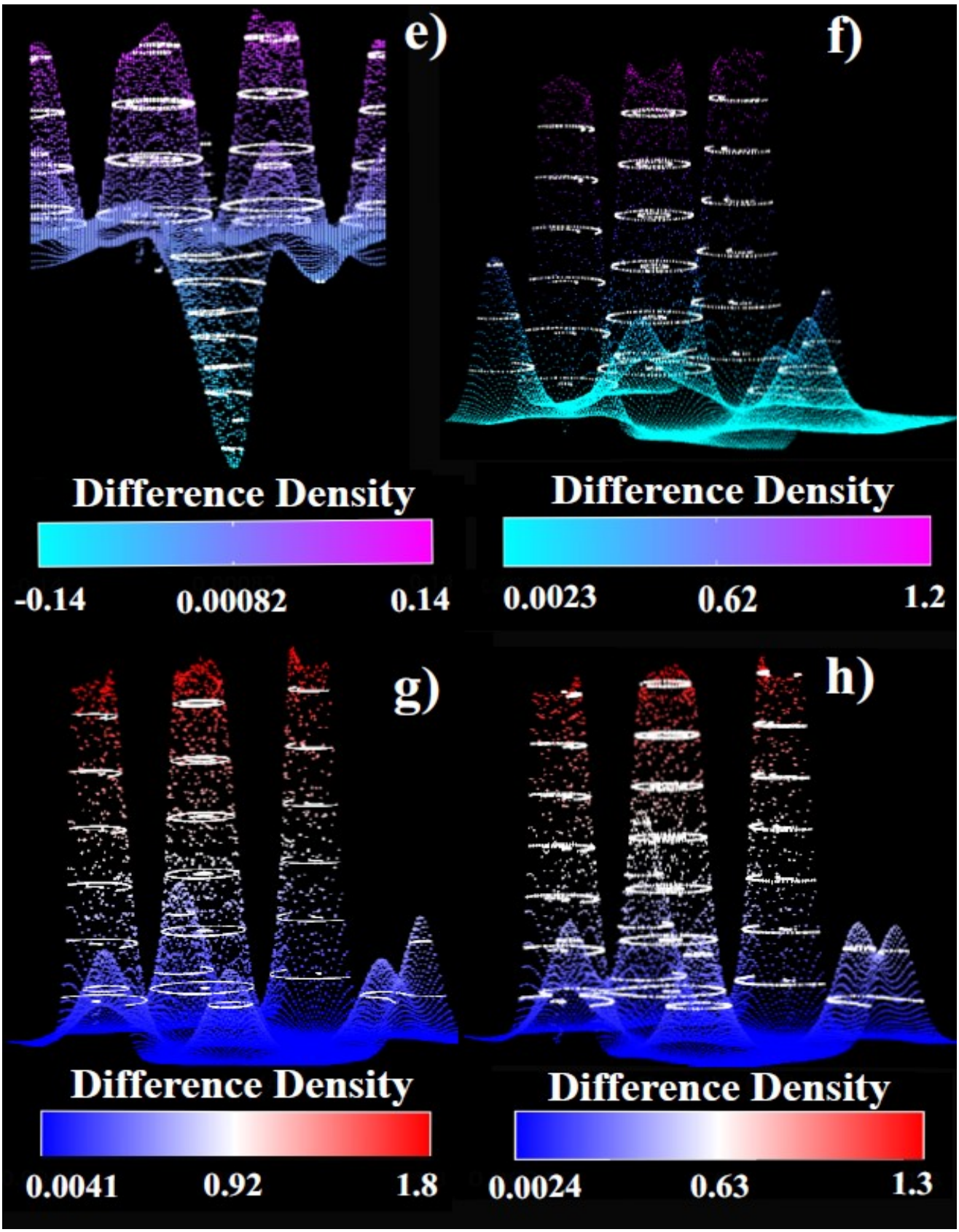


Fig.S2: 2D & 3D schematic presentation of Electron Difference Density (EDD) for $LiSnX_3$ where Fig.(a-b & e-f) are obtained using GGA and Fig.(c-d &g-h) are obtained using mGGA

Optical Properties: Dielectric constants, Absorption Coefficients, and Optical Conductivities (all along zz-direction) and Refractive Indices of $LiSnX_3$ (X = Cl and Br)

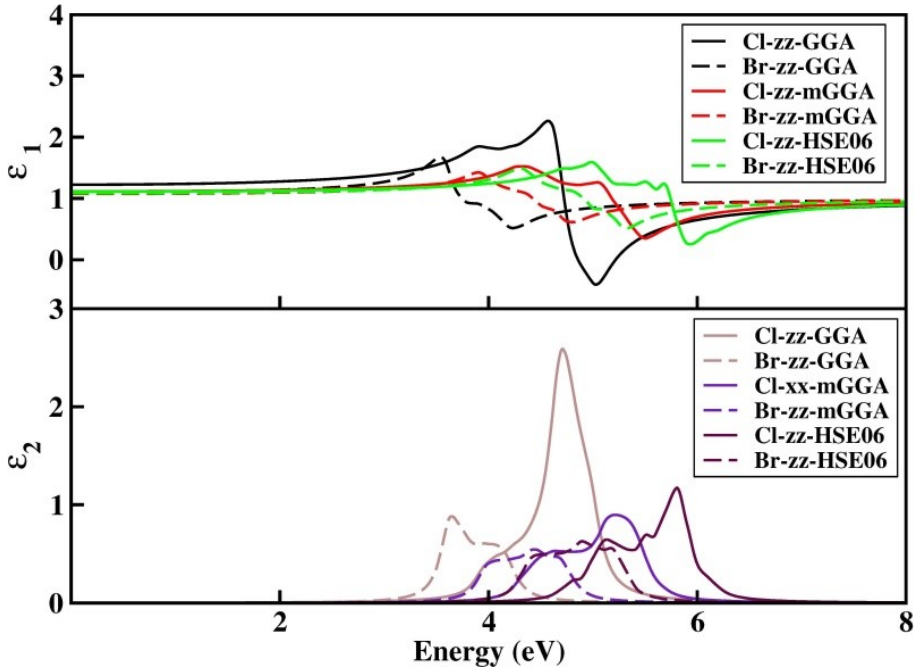


Fig.S3: Calculated Dielectric Constants of $LiSnX_3$ (X= Cl and Br) using GGA, mGGA and HSE06

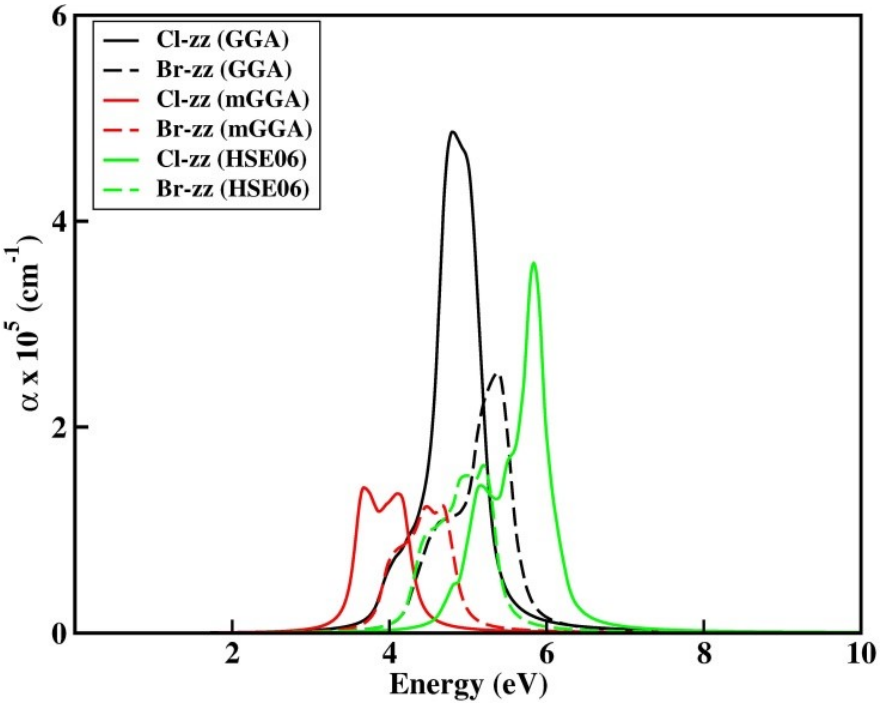


Fig.S4: Calculated Absorption coefficients of $LiSnX_3$ (X= Cl and Br) using GGA, mGGA and HSE06

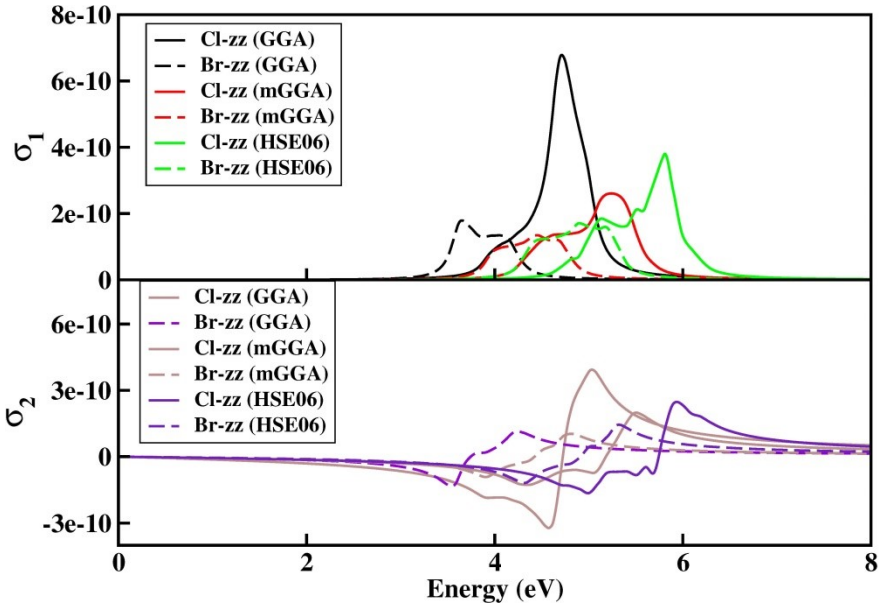


Fig.S5: Calculated Optical Conductivities of $LiSnX_3$ (X= Cl and Br) using GGA, mGGA and HSE06

Refractive Indices

The refractive index (η) [4]describes how light travels from one material to another. It illustrates how light's velocity drops when the refractive index of a material increases. This could be due to the interplay of atoms in the substrate and their effect on light. Herein, we obtained all the refractive indices of $LiSnCl_3$ and $LiSnBr_3$ using GGA, mGGA, and HSE06 functionals which are depicted in Fig.S6. The obtained figures are plotted in both xx- and zz- directions. From the figures, under the employed functional GGA, we observed that for X = Cl along the xx- and zz-axes, the spectral peak reaches upto 1.52 a.u and 1.64 a.u at 3.86 eV and 4.75 eV, respectively. And for X = Br (GGA), both the spectral peaks reaches upto 1.82 a.u at 3.85 eV and 1.31 a.u at 3.56 eV along xx- and zz- axes. Under employed mGGA, we also observed the peak upto 1.73 a.u and 1.17 a.u at 4.23 eV and 4.12 eV along xx- and zz-axes, respectively, for X = Cl. And for X = Br, the xx- and zz- direction reaches the level upto 1.38 a.u and 1.33 a.u at 3.89 eV and 3.68 eV. Similarly, for HSE06, we observed that the spectral peaks reaches upto 1.64 a.u and 1.23 a.u at 4.92 eV and 5.12 eV, respectively, along xx-and zz-axes ,for X = Cl. For X = Br, the peaks extends upto 1.52 a.u and 1.21 a.u at 4.23 eV and 4.12 eV along the xx- and zz- directions. The obtained index spectra closely resemble with the real parts (ε_1) of the dielectric constant, with the high peaks falling inside the vis-UV region.

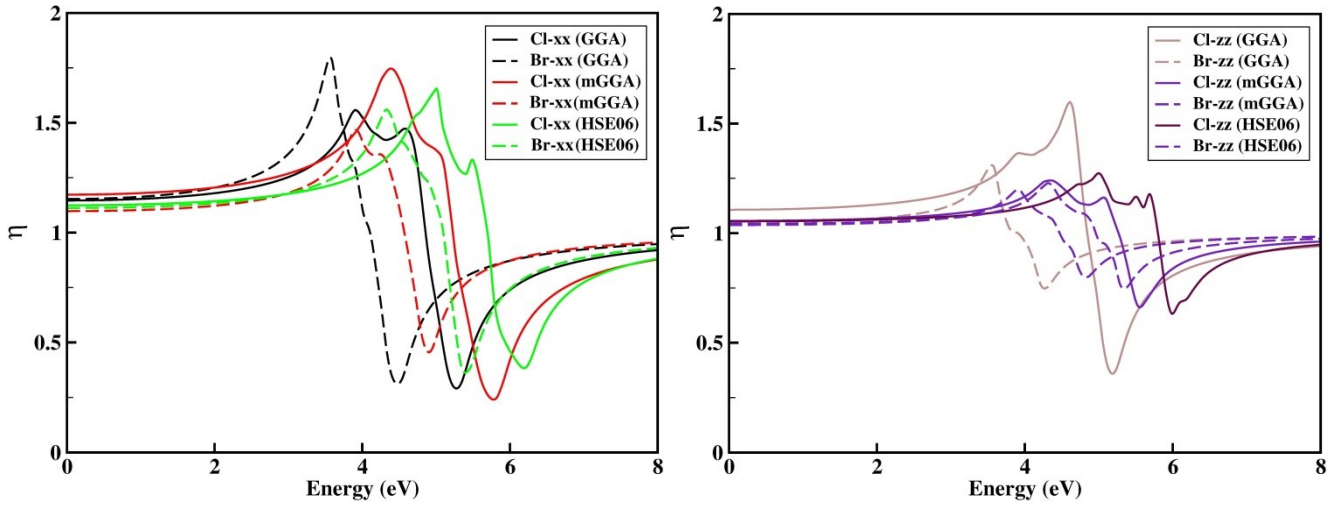


Fig.S6: Calculated refractive index of $LiSnX_3$ (X = Cl and Br) along xx- and zz-axes using GGA, mGGA, and HSE06

Melting Temeperature

Understanding a material's melting point is essential for real world applications. In addition to simulating atomic and ionic radii, the temperature parameter is crucial for structural stability. Using the following equation, we have obtained the melting temperatures (Tm) of the compounds studied[5].

$$Tm = 553 + 5.911C_{11} \pm 300 \quad \text{(i)}$$

As shown in Table S2, the calculated Tm values using GGA and mGGA are aligned, where $LiSnCl_3$ in both functionals have higher melting temperatures than $LiSnBr_3$. Among them X = Cl (mGGA) has the highest value up to 723.06 ± 300 K which simply means that it can out-stand its structural integrity even at high temperatures comparing with the others' values.

Sound Velocity

Determining sound velocities is one of the important parameters in estimating mechanical properties[6]. They can be obtained by using the crystal symmetry and the direction of propagation. The longitudinal velocities, $v_l = [(B + 4G/3)/\rho]1/2$ and transverse velocities, $v_t = (G/\rho)1/2$, also known as the seismic-compression and shear waves are used to obtain the mean sound velocities v_m

$$v_m = [(1/v^3p + 2/v^3s)/3]^{-1/3} \quad \text{(ii)}$$

Our calculated results for vl, vt and vm are presented in Table S2. We observed that among the compounds studied, X = Cl (GGA) has the highest v_l value while X = Cl (mGGA) has the highest v_t value. The highest mean sound velocities are obtained by X = Cl (mGGA) with the value of 1450 m/s. The true forms of hexagonal crystals can only be obtained in [100] and [001] directions. These can be derived using the following equations

$$\begin{aligned} [100] : [100]v_l &= \sqrt{(C_{11} - C_{12})/2\rho} \\ [010]v_{t1} &= \sqrt{C_{11}/\rho} \quad \text{(iii)} \\ [001]v_{t2} &= \sqrt{C_{44}/\rho} \\ [001] : [001]_{vl} &= \sqrt{(C_{33}/\rho)} \\ [100]v_{t1} &= \sqrt{(C_{44}/\rho)} \quad \text{(iv)} \\ [010]v_{t2} &= \sqrt{(C_{44}/\rho)} \end{aligned}$$

Utilizing the above two equations (iii) and (iv), we obtained the sound velocities values for these compounds in the directions of x[100] and z[001], respectively. In the equations, the first and second transverse modes are represented by v_{t1} and v_{t2}, respectively. As listed in Table S3, along the [100] propagation direction, X= Cl (GGA) has the highest sound velocity at [010]vt1 polarization direction while the smallest value results along [001]v_{t2} polarization direction of X = Br (GGA). Along the propagation direction [001], again X = Cl (GGA) tops the sound velocity and the polarization directions along [100]v_{t1} and [010]v_{t2} possess identical sound velocities. Thus, in the study of sound velocities, GGA has a greater impact on these compounds studied.

X	**Functional**	V_l	V_t	V_m	T_m	V_D	Θ_D
Cl	GGA	2960	1250	1410	717.08	3.4	163.1
Br	GGA	1500	1030	1120	684.93	2.8	134.3
Cl	mGGA	2400	1290	1450	723.06	3.5	167.9
Br	mGGA	1620	940	1040	631.67	2.5	119.9

Table S2: Calculated values of longitudinal wave (V_l), transverse wave (V_t) and mean sound velocities (V_m). All waves and sound velocities are in m/s. Melting temperature (Tm, ± 300) (in K), machinability index (μ), Debye's frequency(V_D)($\times 10^{12}$) in Hz and Debye's Temperature(θ_D) in K.

Debye's Temperature and Frequency

In material science, Debye temperature (θ_D) is a crucial metric that helps to understand how materials behave under extreme heat and cold. It also sheds light on the mechanical and thermal characteristics of materials. The θ_D also indicates the toughness of a material and can even dictate the number of active phonon modes through its relationship with sound velocities, density and

mass of the material. This phenomenon can be activated by the crystal's structure, chemical composition, and other external factors such as pressure and temperature. Using the following equation, we can obtain the Debye's temperature of the materials.

$$\theta_D = \frac{hv_D}{k} \qquad \text{(v)}$$

where *h* is the Planck's constant, v_D is Debye's frequency, and *k* denotes the Boltzmann constant.

In order to acquire to the value of θ_D, first we need to have the debye's frequency v_D, which depends solely on the number of atoms per unit volume and the sound velocities. The equation given below can be utilized to obtain the debye frequency.

$$v^3_D = 2\pi.9\ (N/V)\ [\frac{2}{vt^3} + \frac{1}{vl^3}]^{-1} \qquad \text{(vi)}$$

Using Equations (v) and (vi), we calculated the values of Debye's temperatures and frequencies of the lead-free halide compounds presented in Table S2. We observed that X = Cl (mGGA) has the highest values of v_D and θ_D which signifies that it has the best mechanical attributes and can stand up to temperate conditions compared to the others[7].

X	**Functionals**	**[100]**			**[001]**		
		[100]v_l	[010]v_{l1}	[001]v_{t2}	[001]v_l	[100]v_{t1}	[010]v_{t2}
Cl	GGA	1.73	3.06	0.84	2.76	0.84	0.84
Br	GGA	1.12	1.92	0.45	1.71	0.45	0.45
Cl	mGGA	1.37	2.73	1.25	2.59	1.25	1.25
Br	mGGA	0.61	1.48	0.58	1.67	0.58	0.58

Table S3: Calculated values of sound velocities for $LiSnX_3$ (X = Cl, and Br) along different directions [100] and [001].

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