Novel $Cs_2Au^IM^{III}F_6$ (M = As, Sb) double halide perovskites: sunlight and industrial wasted heat management device applications

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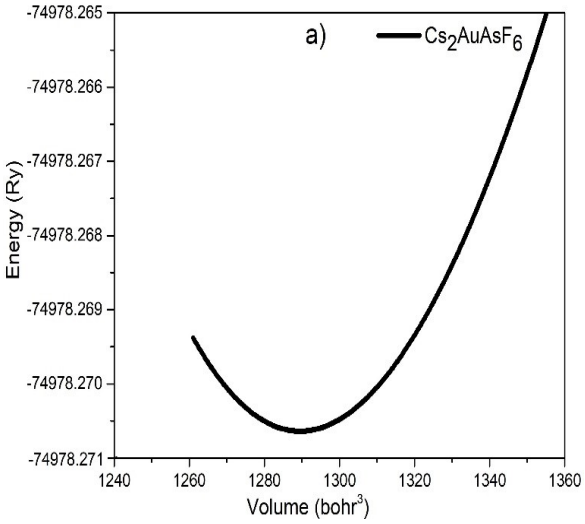

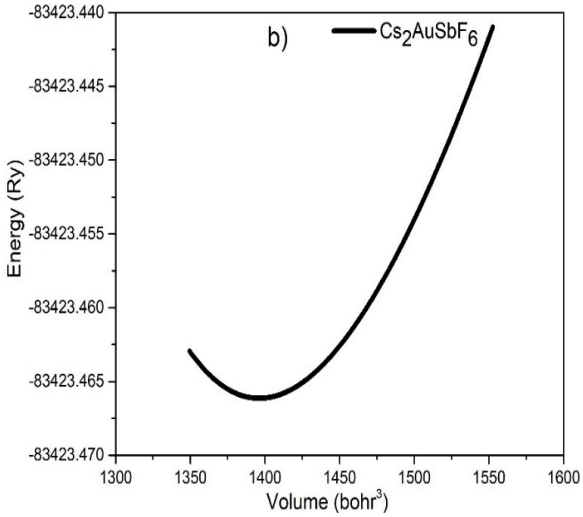

Fig. 1S: Minimum energy (E) vs. volume (V) optimization curve.

Thermo-mechanical properties

Elastic properties and mechanical stability

The elastic parameters of the material, which reflect its stiffness, anisotropy, stability, and durability, are crucial in determining the effectiveness of perovskite materials for energy harvesting applications. C_{11}, C_{12}, and C_{44} are three different elastic coefficients that, together, can properly define the elastic tensor C_{ij} of a cubic crystal structure (1). The elastic constants estimated for Cs_2AuMF_6 (M = As, Sb) materials are all positive and shown in **Table 1s**. Additionally, C_{11} is greater than C_{12}, and C_{12} is greater than C_{44} for all materials, which represent the stiffness (C_{11}) of the materials, the volume that can be maintained under stress (C_{12}), and the slightly lower stiffness against shearing forces (C_{44}).

The resulting C_{ij} values are then used to calculate the bulk and shear modulus using the following equations:

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

$$G = \frac{(C_{11} - C_{12} + 3C_{44}) \times \{4C_{44} + 3(C_{11} - C_{12})\}}{25C_{44}(C_{11} - C_{12})}$$

The formulae used to compute the Young's modulus (Y), Poisson's ratio (ν) and anisotropic behavior are as follows:

$$Y = \frac{9BG}{3B + G}, \quad \nu = \frac{3B - Y}{6B} \quad and \quad A = \frac{2C_{44}}{C_{11} - C_{12}}$$

A material's bulk modulus (B) and shear modulus (G) measure its resistance to uniform compression and shear deformation under external force. The computed values for Cs_2AuMF_6 imply a stronger shear deformation resistance. The Young's modulus measures the degree of rigidity exhibited by a substance. It is a material's relationship between tensile stress (force per unit area) and tensile strain (proportional deformation in length). Therefore, as shown in **Table 1S**, the computed Y value of the titled compounds demonstrated high stiffness compared to Cs_2SbAuX_6 (X= Cl, Br, I) (2).

The B/G ratio represents Pugh's ratio, which characterizes the ductile and brittle qualities shown by the material Cs_2AuMF_6 (M = As, Sb). Pugh's ratio categorizes materials as ductile if their value exceeds 1.75 and as brittle if their value falls below 1.75 (3). For the current

combination, the Pugh's ratio values are significantly greater than 1.75, indicating the ductile properties of the investigated materials. Poisson's ratio (ν) serves as another criterion for ductility, classifying a material as ductile if its value exceeds 0.26. The studied compounds of (ν) values are greater than 0.26, indicating a ductile characteristic. A value above zero is considered stable material, which dictates by Cauchy pressures (*CP).* The shear anisotropy (*A*) values for the double perovskite materials Cs_2AuMF_6 (M = As, Sb) are 0.56 and 0.49, respectively. This indicates that these materials have anisotropic behavior.

The Born-Huang stability criteria can be employed to assess mechanical stability in these scenarios: $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$ and $C_{11} + 2C_{12} > 0$ (4). The results of our investigation satisfy the specified criteria, demonstrating that the materials possess mechanical stability.

Table 1S: Elastic coefficient, stiffness (*B*, *G*, *Y*), Pugh's ratio (*B/G*), Poisson's ratio (ν), Cauchy Pressure (*CP*), Anisotropy (*A*), and thermal data of studied compounds.

Elastic and Mechanical properties		
Parameter	**Cs_2AuAsF_6**	**Cs_2AuSbF_6**
$C_{11} + 2C_{12}$	171.48	150.54
$C_{11} - C_{12}$	49.56	48.81
C_{11} (GPa)	90.20	82.72
C_{12} (GPa)	40.63	33.91
C_{44} (GPa)	13.84	12.05
B (GPa)	57.16	50.18
G (GPa)	17.51	16.05
Y (GPa)	47.67	43.51
B/G	3.26	3.12
ν	0.36	0.36
$CP = C_{12}$-C_{44}	26.79	21.86
A	0.56	0.49
Thermal properties		
Density, ρ (g/cm^3)	5.66	5.60
Elastic Debye temperature, θ_D (K)	220.77	207.11
Transverse sound velocity, V_t (m/s)	1758.50	1692.38
Longitudinal sound velocity, V_l (m/s)	3770.65	3573.23
Averaged sound velocity, V_m (m/s)	1980.06	1904.15
Melting point, T_m (K)	1086.08	1042.65
Minimum thermal conductivity, K_{min} (Wm^{-1}K^{-1})	0.38	0.35
Lattice thermal conductivity at 300K k_L (Wm^{-1}K^{-1})	0.32	0.29

Thermo-physical properties

The thermal properties of titled double perovskite cubic compounds are essential for understanding their behavior in various applications, especially in thermoelectric material. The Debye temperature is a characteristic temperature that provides insights into the phonon spectrum of a material. It is related to the highest frequency (or energy) of vibration in a solid. It is crucial for understanding the heat capacity, thermal conductivity, and other thermal properties at low temperatures. The Debye temperature (θ_D) can be estimated using elastic constants since it depends on the sound velocities in the material, which are related to the elastic moduli (bulk modulus, shear modulus). The relationship can be expressed as (5):

$$\theta_D = \frac{h}{k_\beta}\left[\frac{3n}{4\pi V}\right]^{\frac{1}{3}} V_m$$

V is the volume of the unit cell. V_m is the mean sound velocity, which depends on the longitudinal and transverse sound velocities derived from the elastic constants as:.

$$V_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right]^{-\frac{1}{3}}\right.$$

Longitudinal (V_l) and transverse (V_t) sound velocities can be derived from the bulk modulus (B) and shear modulus (G) as the following (1):

$$V_l = \left(\frac{3B + 4G}{3\rho}\right)^{\frac{1}{2}}, V_t = \left(\frac{G}{\rho}\right)^{\frac{1}{2}}$$

Where ρ is the density of the material.

The melting temperature (T_m) indicates the stability of a compound at high temperatures. It is crucial for determining the operational temperature range of materials in practical applications. There is an empirical relationship between the melting temperature and elastic constants (6).

$$T_m = \left\{553 + 5.91\left(\frac{k}{GPa}\right) \times C_{11}\right\}$$

Generally, higher elastic moduli imply a higher melting temperature, indicating a more stable and robust lattice structure. In a similar way, the compounds under investigation, Cs_2AuAsF_6 and Cs_2AuSbF_6, have melting temperatures of 1086.08 K and 1047.65 K, respectively. The minimum thermal conductivity (K_{min}) is an important parameter in determining the lower limit of thermal conductivity in disordered or highly anharmonic systems. It provides a benchmark for comparing the thermal transport properties of materials. The minimum thermal conductivity can be estimated using the following relation, which are influenced by the elastic constants. It is given by the David R. Clarke's model as follows (7):

$$K_{min} = k_B V_m \left[\frac{M}{n\rho N_A}\right]^{-2/3}$$

Where, k_B is the Boltzmann constant, and $\hbar$ is the reduced Planck constant. The studied DPs of Cs_2AuAsF_6 and Cs_2AuSbF_6 have very low values of K_{min}, making them the most suitable for the creation of renewable energy devices. The lattice thermal conductivity (k_L) represents the ability of a material to conduct heat through its lattice vibrations (phonons). It is vital for applications in thermo-electrics and heat management in electronics. The lattice thermal conductivity is influenced by the phonon mean free path and phonon scattering rates, which depend on the elastic properties of the material. Materials with higher elastic constants typically

exhibit higher sound velocities, leading to higher lattice thermal conductivity. It may be calculated by the effective slack's model which is (8):

$$k_L = \frac{A\Theta_D^3 V^{1/3} m}{\Upsilon^2 \bar{N}^{2/3} T}$$

Where, A is a constant dependent on γ, δ is the mean atomic volume of cubic root, M_{av} is the mean atomic mass, θ_D is the Debye hardness, γ corresponds to the Gruneisen parameter, n stands for the unit cell atom, and T represents the absolute temperature in kelvin. The thermoelectric section (3.5) graphically displays the k_L values, and **Table 1S** reports the calculated values at room temperature.

References

1. Schreiber E, Anderson OL, Soga N, Bell JF. Elastic constants and their measurement. 1975;
2. Al-Muhimeed TI. Study of mechanical, thermodynamic, thermoelectric, and optical properties of Cs_2SbAuX_6 (X= Cl, Br, I) for energy harvesting applications. Mater Sci Semicond Process. 2024;178:108443.
3. Pugh SF. XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. London, Edinburgh, Dublin Philos Mag J Sci. 1954;45(367):823–43.
4. Born M, Huang K, Lax M. Dynamical theory of crystal lattices. Am J Phys. 1955;23(7):474.
5. Anderson OL. A simplified method for calculating the Debye temperature from elastic constants. J Phys Chem Solids. 1963;24(7):909–17.
6. Fine ME, Brown LD, Marcus HL. Elastic constants versus melting temperature in metals. Scr Metall. 1984;18(9):951–6.
7. Clarke DR, Levi CG. Materials design for the next generation thermal barrier coatings. Annu Rev Mater Res. 2003;33(1):383–417.
8. Slack GA. The thermal conductivity of nonmetallic crystals. Solid state Phys. 1979;34:1–71.