Supporting Information

From Molecular Salt to Layered Network: Cation-Driven Tuning of Band Gap, Structure, and Charge Transport in $A_3Bi_2I_9$ (A= Cs, Rb) Perovskites

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Supplementary Equations

$$\alpha = \alpha_0 \, e^{\left(\frac{h\nu}{E_u}\right)} \qquad (S1)$$

where α_0 represents a fixed value.

$$n_{trap} = \frac{2\varepsilon\varepsilon_0 V_{TFL}}{eL^2} \qquad (S2)$$

where :

- Vacuum permittivity (ε_0) : A universal constant representing the permittivity of free space (8.85×10^{-12} F/m).
- Dielectric constant (ε) : This parameter reflects the ability of $A_3Bi_2I_9$ (A = Cs, Rb) to store electrical energy compared to a vacuum, which equal to 4.3 and 20.8 for $Cs_3Bi_2I_9$ and $Rb_3Bi_2I_9$, respectively [1, 2].

- Elementary charge (e) : A fundamental constant representing the charge of an electron (1.6 × 10^{-19} C).
- Sample thickness (L) : The distance taken across the space-charge region (SC) within $A_3Bi_2I_9$ (A = Cs, Rb) (~1 mm for both material).

$$Z(\omega) = Z'(\omega) + jZ''(\omega) \quad (S3)$$

$$\sigma_{AC} = \omega\varepsilon'\varepsilon_0 \tan\delta \quad (S4)$$

where ε0 denotes the permittivity of vacuum.

$$\sigma_{AC}(\omega) = \sigma_{DC} + \sigma_0 f^s \quad (S5)$$

The equation incorporates separate terms for DC (direct current) and AC (alternating current) conductivity, represented by σ_{DC} and σ_{AC}, respectively. Additionally, a constant term (σ_0) and a frequency-dependent term are included.

The frequency-dependent term accounts for the influence of frequency on the overall conductivity. It involves a parameter, "s," which reflects the degree of interaction between charge carriers and the crystal lattice of $A_3Bi_2I_9$ (A = Cs, Rb). This parameter "s" can range from 0 to 1, where:

- s closer to 0 indicates weaker interaction between charge carriers and the lattice, resulting in a more significant contribution from AC conductivity.
- s closer to 1 signifies stronger interaction, leading to a dominant DC conductivity component.

$$\sigma_{DC} = \sigma_0 e^{\frac{-E_a}{k_B T}} \quad (S6)$$

Where :

- Activation energy (E_a): This parameter represents the minimum energy barrier that charge carriers must overcome to participate in conduction. A higher activation energy signifies a lower conductivity at a given temperature.
- Pre-exponential factor (σ_0): This constant term reflects the intrinsic conductivity of the material and the conduction mechanism. It essentially represents the theoretical conductivity at infinitely high temperature.
- Boltzmann constant (k_B): This fundamental constant (approximately 1.38×10^{-23} J/K) relates the average kinetic energy of particles to temperature.
- Absolute temperature (T): This parameter is measured in Kelvin (K) and influences the mobility and concentration of charge carriers within the material. Higher temperatures generally lead to increased conductivity due to enhanced thermal excitation of charge carriers.

$$W_H = W_{H0} \times \left(1 - \frac{r_p}{R}\right) \qquad (S7)$$

Where :

- Polaron hopping energy (W_H): This parameter represents the minimum energy required for a charge carrier (polaron) to overcome the energy barrier and hop from one lattice site to another. A higher W_H signifies a more significant energy obstacle for hopping and potentially lower conductivity.
- Large polaron radius (r_P): This parameter reflects the extent of lattice distortion surrounding a polaron. A larger radius (r_P) can indicate stronger polaron-lattice interaction, potentially affecting hopping mobility.

$$W_{H0} = \frac{e^2}{4 \varepsilon_p r_p} \qquad (S8)$$

- Effective dielectric constant (ε_P): This parameter reflects the overall ability of the material to store electrical energy, accounting for both the intrinsic lattice polarization and any additional contributions from polarizable species within the material.
- Intersite separation (R): This parameter represents the average distance between neighboring lattice sites where charge carriers can potentially hop. A smaller intersite separation (R) can facilitate hopping due to the closer proximity of available sites.

The expression of AC conductivity according to the OLPT model:

$$\sigma_{ac} = \frac{\pi^4 e^2 \mathrm{k_B^2 T^2} \alpha^{-1} \omega \left[\mathrm{N(E_F)}\right]^2 R_\omega^4}{12\,(2\,\alpha\,\mathrm{k_B T} + W_{\mathrm{H0}} r_p / R_\omega^2)} \qquad \textit{(S9)}$$

$$(R_\omega^{'})^2 + (\beta W_{\mathrm{H0}} + \ln(\omega \tau_0))\, R_\omega^{'} - \beta W_{\mathrm{H0}}\, r_{\mathrm{p}}^{'} = 0 \qquad \textit{(S10)}$$

where $R_\omega' = 2\alpha R_\omega$, $\beta = 1/k_B T$ and $r_P' = 2\alpha r_P$.

The expression of the parameter s according to the OLPT model:

$$s = 1 - \frac{8\alpha R_\omega + \dfrac{6 W_{\mathrm{H0}} r_p}{R_\omega k_B T}}{\left[2\alpha R_\omega + \dfrac{W_{\mathrm{H0}} r_p}{R_\omega k_B T}\right]^2} \qquad \textit{(S11)}$$

The expression of the parameter s according to the NSPT model:

$$s = 1 + \frac{4 k_B T}{W_m} \qquad \textit{(S12)}$$

where :

- Polaron transfer energy (W_m): This parameter represents the minimum energy barrier required for a polaron (a quasiparticle formed by a charge carrier and its surrounding lattice distortion) to move from one lattice site to another. A higher W_m signifies a greater energy obstacle for hopping and potentially lower conductivity.

The expression of AC conductivity according to the NSPT model:

$$\sigma_{ac} = \frac{(\pi e)^2 k_B T \alpha^{-1} \omega \left[\mathrm{N}(\mathrm{E_F})\right]^2 R_\omega^4}{12} \qquad (S13)$$

where

$$R_\omega = \frac{1}{2\alpha}\left[\ln(\frac{1}{\omega\tau_0}) - \frac{W_m}{k_B T}\right] \qquad (S14)$$

where :

- Density of states at the Fermi level ($N(E_F)$): This parameter represents the number of available electronic states per unit energy near the Fermi level (the energy level at which the probability of finding an electron is 50%). A higher density of states ($N(E_F)$) can facilitate tunneling due to the increased availability of unoccupied states for electrons to tunnel into.
- Spatial extension of the polaron (α^{-1}): This parameter reflects the inverse of the polaron size, essentially indicating the extent of the wavefunction associated with the polaron. A smaller polaron size (larger α^{-1}) can potentially enhance tunneling probability due to a more localized wavefunction and increased overlap with neighboring sites.
- Tunneling distance (R_ω): This parameter represents the distance between the initial and final positions of the charge carrier during the tunneling event. A smaller tunneling distance (R_ω) generally increases the tunneling probability due to the weaker energetic barrier that needs to be overcome.

Supplementary Tables

Table S1. Raman Spectrum Assignment for $A_3Bi_2I_9$ (A = Cs, Rb) Perovskites.

$Cs_3Bi_2I_9$			
Vibration	*Symmetry*	*Description*	*Frequency (cm^{-1})*
ν_1	A_1'	terminal Bi-I symmetric stretch mode	144
ν_{15}	E''	terminal Bi-I asymmetric stretch mode	126
ν_{10}	E'	terminal Bi-I asymmetric stretch mode	121
ν_2	A_1^1	bridge Bi-I symmetric stretch mode	111
ν_7	E''	bridge Bi-I asymmetric stretch mode	92
		Bi-I bending mode	59
unidentified: Cs-[Bi_2I_9] elongation or alternate deformation mode			44
$Rb_3Bi_2I_9$			
ν_1	A_{1g}	Bi-I symmetric stretch mode	141
ν_2	E_g	Bi-I asymmetric stretch mode	127
ν_5	F_{2g}	Bi-I bending mode	73
unidentified: Bi − I bending or lattice distortion mode			66
			58
			50

Table S2. Temperature Dependence of Equivalent Circuit Model Parameters for $A_3Bi_2I_9$ (A = Cs, Rb) Perovskites.

$Cs_3Bi_2I_9$						
Temperature (K)	R_g (Ω)	C_g (nF)	R_{gb} (Ω)	C_{gb} (pF)	CPE_e (μF)	α_e
300	262	2.25	2502	5.47	0.58	0.748
325	256	2.47	2148	8.05	0.87	0.715
350	248	2.68	1794	11.25	1.25	0.698
375	242	2.80	1444	13.94	1.77	0.635
400	237	3.14	1095	16.58	1.96	0.607
$Rb_3Bi_2I_9$						
Temperature (K)	R_g (Ω)	C_g (nF)	R_{gb} (Ω)	C_{gb} (pF)	CPE_e (μF)	α_e
300	193	1.87	1884	3.96	0.21	0.784
325	162	2.06	1635	7.11	0.35	0.763
350	134	2.36	1383	9.65	0.64	0.721
375	103	2.59	1137	12.39	0.85	0.702
400	75	2.99	885	15.72	1.08	0.695

Table S3. Frequency-Dependent OLPT Parameters for Charge Transport in $Cs_3Bi_2I_9$ Perovskite.

Frequency (Hz)	*α (Å^{-1})*	*W_{HO} (eV)*	*N (cm^{-3})*	*r_p (Å)*	*R_ω (Å)*
10^2	0.631	0.512	5.73×10^{28}	1.241	4.302
10^3	0.654	0.509	6.15×10^{28}	1.208	4.279
10^4	0.682	0.487	6.37×10^{28}	1.174	4.255
10^5	0.718	0.464	6.96×10^{28}	1.159	4.234
10^6	0.745	0.451	7.44×10^{28}	1.146	4.212

Table S4. Frequency Dependence of Dielectric Permittivity (ε_p) and Hopping energy (W_H) in $Cs_3Bi_2I_9$.

Frequency (Hz)	ε_p *(F.m^{-1})*	W_H *(eV)*
10^2	5.95×10^{-9}	0.294
10^3	6.21×10^{-9}	0.286
10^4	6.74×10^{-9}	0.273
10^5	7.08×10^{-9}	0.259
10^6	7.25×10^{-9}	0.231

Table S5. Frequency Dependence of Charge Transport Parameters Extracted from the NSPT Model for $Rb_3Bi_2I_9$.

Frequency (Hz)	α (Å^{-1})	N(E_F) (eV^{-1} cm^{-3})	R_ω (Å)
10^2	0.619	8.47×10^{28}	4.214
10^3	0.674	9.62×10^{28}	3.963
10^4	0.725	1.15×10^{29}	3.767
10^5	0.768	3.58×10^{29}	3.534
10^6	0.801	4.99×10^{29}	3.312

References

[1] W. Li, X. Wang, J. Liao, Y. Jiang and D. Kuang, Advanced Functional Materials, 2020, 30, 1909701.

[2] M. Xia, J. Yuan, G. Niu, X. Du, L. Yin, W. Pan, J. Luo, Z. Li, H. Zhao, K. Xue, X. Miao and J. Tang, Advanced Functional Materials, 2020, 30, 1910648.