Supplemental Material – First-principles study on structural, electronic and optical properties of perovskite solid solutions $KB_{1-x}Mg_xI_3$ (B = Ge, Sn) toward water splitting photocatalysis

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Computational details for mechanical property

We determined the bulk and shear moduli using the stiffness constants within the Voigt approximation as follows,

$$\begin{aligned} B_{\mathrm{V}} &= \frac{2C_{11} + C_{33} + 2(C_{12} + 2C_{13})}{9}, \\ G_{\mathrm{V}} &= \frac{2C_{11} + C_{33} - (C_{12} + 2C_{13}) + 3(2C_{44} + C_{66})}{15} \end{aligned} \tag{1}$$

Within Reuss approximaion, we could also be calculated using the compliance constants as follows,

$$\begin{aligned} B_{\mathrm{R}} &= \frac{1}{2S_{11} + S_{33} + 2(S_{12} + 2S_{13})}, \\ G_{\mathrm{R}} &= \frac{15}{4(2S_{11} + S_{33}) - 4(S_{12} + 2S_{13}) + 3(2S_{44} + S_{66})} \end{aligned} \tag{2}$$

Within Hill approximation, the real moduli are estimated by average values as follows,

$$B = \frac{B_{\mathrm{V}} + B_{\mathrm{R}}}{2}, G = \frac{G_{\mathrm{V}} + G_{\mathrm{R}}}{2} \tag{3}$$

Then, the Young's modulus and Poisson's ratio (ν) are estimated from the calculated bulk and shear moduli as follows,

$$E = \frac{9BG}{3B + G}, \nu = \frac{3B - 2G}{6B + 2G} \tag{4}$$

We determined the longitudinal (υ_l) and transverse (υ_t) elastic wave velocities with elastic moduli as follows,

$$\upsilon_l = \sqrt{\frac{3B + 4G}{3\rho}}, \upsilon_t = \sqrt{\frac{G}{\rho}} \tag{5}$$

where ρ is the density. With these values, we evaluated the average sound velocity υ_m as follows,

$$\upsilon_m = \left[\frac{1}{3}\left(\frac{2}{\upsilon_t^3} + \frac{1}{\upsilon_l^3}\right)\right]^{-1/3} \tag{6}$$

With the following relation, we estimated the Debye temperature θ_{D}, which is an very important parameter for checking the degree of mechanical properties,

$$\theta_{\mathrm{D}} = \frac{h}{k_{\mathrm{B}}}\left[\frac{3N}{4\pi V}\right]^{1/3} \upsilon_m \tag{7}$$

where h and k_{B} are the Plank's and Boltzmann's constants, N the number of atoms in the unit cell and V the unit cell volume.

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Table S1. Lattice constants (a, b, c) and lattice angle (α) of $CsGeI_3$ and $CsSnI_3$, calculated with PBE functional.

		Lattice constants(Å)			Lattice angle (deg)		
Compound	Space group	Our cal.	Other cal.	Exp.	Our cal.	Other cal.	Exp.
$CsGeI_3$	$R3m$	$a = b = c = 5.93$	6.13[a]	5.98[b]	88.67	88.28[a]	88.60[b]
$CsSnI_3$	$Pnma$	a=8.60, b=8.62, c=12.41	–	8.69, 8.64, 12.38[c]	–	–	–

[a]Calculated with the PBE functional [1]
[b]Ref. [2]
[c]Ref. [3]

Table S2. Band gaps (unit: eV) in $CsGeI_3$, $CsSnI_3$, $CsMgI_3$ calculated with PBE and HSE06 functionals with and without SOC effect. Cal. and Exp. stand for calculation and experiment.

	Our cal.					
Compound	PBE	PBE+SOC	HSE06	HSE06+SOC	Other cal.	Exp.
$CsMgI_3$	1.40	1.31	2.08	1.44	1.7 (LDA), 3.4 (GW)[a]	
$CsGeI_3$	0.89	0.82	1.64	1.54	1.41[b]	1.63[d]
$CsSnI_3$	0.80	0.71	1.28	1.12	0.50[c]	1.30[e]

[a]Ref. [4]
[b]HSE06+SOC [1]
[c]LDA [6]
[d]Ref. [5]
[e]Ref. [7]

Table S3. Elastic stiffness constants (C_{ij}), bulk modulus (B), shear modulus (G), Young's modulus (E), Pugh's ratio (B/G), and Poisson's ratio (ν) of the systems, calculated with PBE functional.

		Elastic stiffness constant (GPa)						Elastic modulus (GPa)				
System	x	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	G	E	B/G	ν
$KGe_{1-x}Mg_xI_3$	0.00	262.2	162.5	97.1	431.9	150.8	73.0	184.2	103.9	262.4	1.772	0.263
	0.25	266.1	157.8	111.6	400.0	133.4	76.7	187.1	98.5	251.4	1.900	0.276
	0.50 (I)	263.9	153.2	122.5	380.9	126.8	82.8	188.3	96.3	246.9	1.954	0.281
	0.50 (II)	274.6	155.0	127.4	352.3	117.3	83.0	190.8	91.9	237.6	2.075	0.292
	0.75	278.9	150.0	132.3	348.0	111.0	89.3	192.3	92.7	239.7	2.073	0.292
	1.00	279.5	142.5	141.3	345.9	102.6	99.2	194.1	91.7	237.7	2.117	0.296
$KSn_{1-x}Mg_xI_3$	0.00	207.2	163.8	72.1	423.3	108.8	47.3	159.7	71.3	186.1	2.241	0.306
	0.25	221.4	161.7	90.2	397.6	104.8	54.8	167.9	74.2	193.9	2.264	0.308
	0.50 (I)	223.2	158.9	105.5	391.9	103.5	60.6	173.4	73.5	193.1	2.360	0.314
	0.50 (II)	241.1	153.9	114.7	353.4	109.3	66.5	177.1	78.1	204.4	2.266	0.308
	0.75	258.8	152.3	122.1	346.6	103.1	73.1	183.5	78.9	207.1	2.325	0.312
	1.00	279.5	142.5	141.3	345.9	102.6	99.2	194.1	91.7	237.7	2.117	0.296

Table S4. Elastic compliance constants (unit: GPa^{-1}).

System	x	S_{11}	S_{12}	S_{13}	S_{33}	S_{44}	S_{66}
$KGe_{1-x}Mg_xI_3$	0.00	0.006	−0.004	−0.001	0.003	0.007	0.014
	0.25	0.006	−0.003	−0.001	0.003	0.008	0.013
	0.50 (I)	0.006	−0.003	−0.001	0.003	0.008	0.012
	0.50 (II)	0.006	−0.003	−0.001	0.004	0.009	0.012
	0.75	0.005	−0.002	−0.001	0.004	0.009	0.011
	1.00	0.005	−0.002	−0.001	0.004	0.010	0.010
$KSn_{1-x}Mg_xI_3$	0.00	0.013	−0.010	0.000	0.003	0.009	0.021
	0.25	0.010	−0.007	−0.001	0.003	0.010	0.018
	0.50 (I)	0.009	−0.006	−0.001	0.003	0.010	0.016
	0.50 (II)	0.008	−0.005	−0.001	0.003	0.011	0.015
	0.75	0.006	−0.003	−0.001	0.004	0.010	0.019
	1.00	0.005	−0.002	−0.001	0.004	0.010	0.010

Table S5. Elastic moduli within Reuss (B_R and G_R) and Voigt (B_V and G_V) approximation (unit: GPa), and longitudinal (υ_l) and transverse (υ_t) elastic wave velocities, average sound velocity (υ_m) (unit: m/s) and Debye temperature θ_D (unit: K).

System	x	B_R	G_R	B_V	G_V	υ_l	υ_t	υ_m	θ_D
$KGe_{1-x}Mg_xI_3$	0.00	182.81	92.94	185.50	114.88	8969.4	5089.4	5658.9	489.5
	0.25	186.04	91.54	188.23	105.44	8967.9	4987.3	5554.2	482.4
	0.50 (I)	187.08	91.36	189.49	101.32	9004.4	4966.0	5534.0	482.5
	0.50 (II)	190.34	87.60	191.23	96.28	8946.6	4846.0	5407.6	471.8
	0.75	191.78	90.46	192.77	95.01	9038.7	4897.1	5464.6	479.0
	1.00	193.28	90.55	195.00	92.84	9105.5	4901.8	5472.4	481.9
$KSn_{1-x}Mg_xI_3$	0.00	157.83	54.22	161.53	88.30	8112.4	4291.1	4796.5	397.9
	0.25	166.42	62.19	169.40	86.11	8316.2	4384.4	4902.0	412.4
	0.50 (I)	171.38	65.22	175.34	81.73	8420.5	4381.8	4903.4	417.9
	0.50 (II)	176.17	69.10	178.02	87.19	8541.9	4502.3	5033.8	430.0
	0.75	182.93	73.48	184.13	84.37	8684.2	4540.1	5079.0	440.1
	1.00	193.28	90.55	195.00	92.84	9105.5	4901.8	5472.4	481.9

Table S6. Band gaps (unit: eV) calculated with different levels of DFT method.

		Our cal.				
Systme	x	PBE	PBE+SOC	HSE06	HSE06+SOC	Other cal.[a]
$KGe_{1-x}Mg_xI_3$	0.00	0.851	0.615	1.238	1.041	1.08
	0.25	1.227	1.059	1.713	1.551	
	0.50 (I)	1.486	1.264	2.110	1.916	
	0.50 (II)	2.057	1.955	2.679	2.648	
	0.75	2.232	2.153	3.044	2.994	
	1.00	1.981	1.892	2.920	2.801	
$KSn_{1-x}Mg_xI_3$	0.00	0.658	0.593	1.070	1.021	0.97
	0.25	1.075	0.944	1.541	1.393	
	0.50 (I)	1.066	1.047	1.659	1.640	
	0.50 (II)	2.008	1.923	2.607	2.595	
	0.75	2.295	2.064	2.886	2.862	
	1.00	1.981	1.892	2.920	2.801	

[a]GLLB-SC calculation [8]

Table S7. Fitting parameters (unit: eV) of band gaps calculated with HSE06 to quadratic function of $E_g(x) = E_g(0) + [E_g(1) - E_g(0) - b]x + bx^2$.

System	$E_g(0)$	$E_g(1)$	b
$KGe_{1-x}Mg_xI_3$			
I	1.172	3.050	−0.755
II	1.123	3.001	−2.056
$KSn_{1-x}Mg_xI_3$			
I	1.040	3.058	0.269
II	0.959	2.977	−1.898

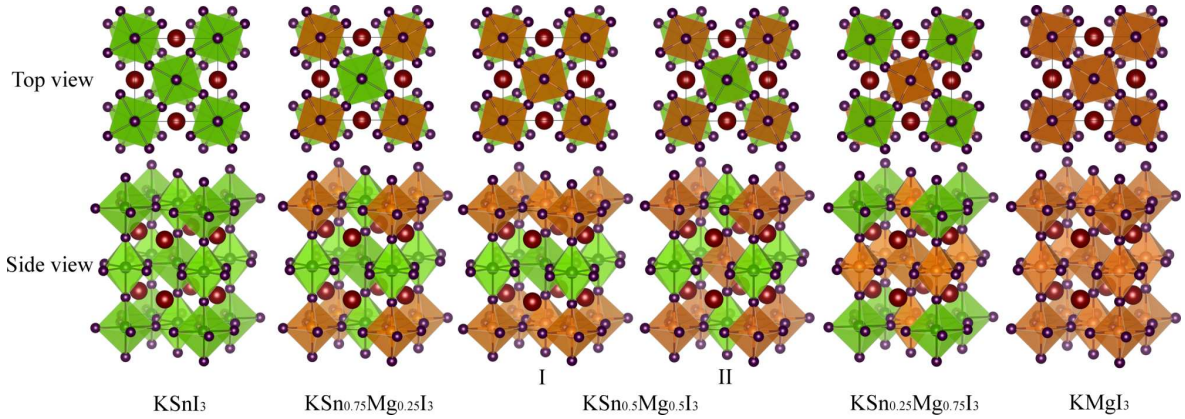

Figure S1. Crystalline structures of $KSn_{1-x}Mg_xI_3$ with x = 0, 0.25, 0.5 (I, II), 0.75, and 1, optimized with PBE functional.

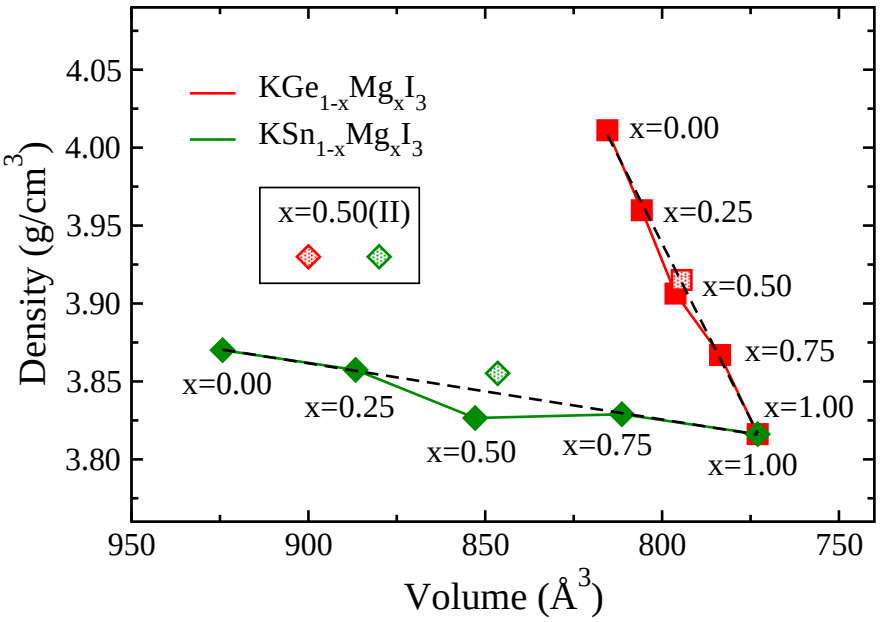

Figure S2. Linear relation of volume with density in $KB_{1-x}Mg_xI_3$ (B = Ge, Sn).

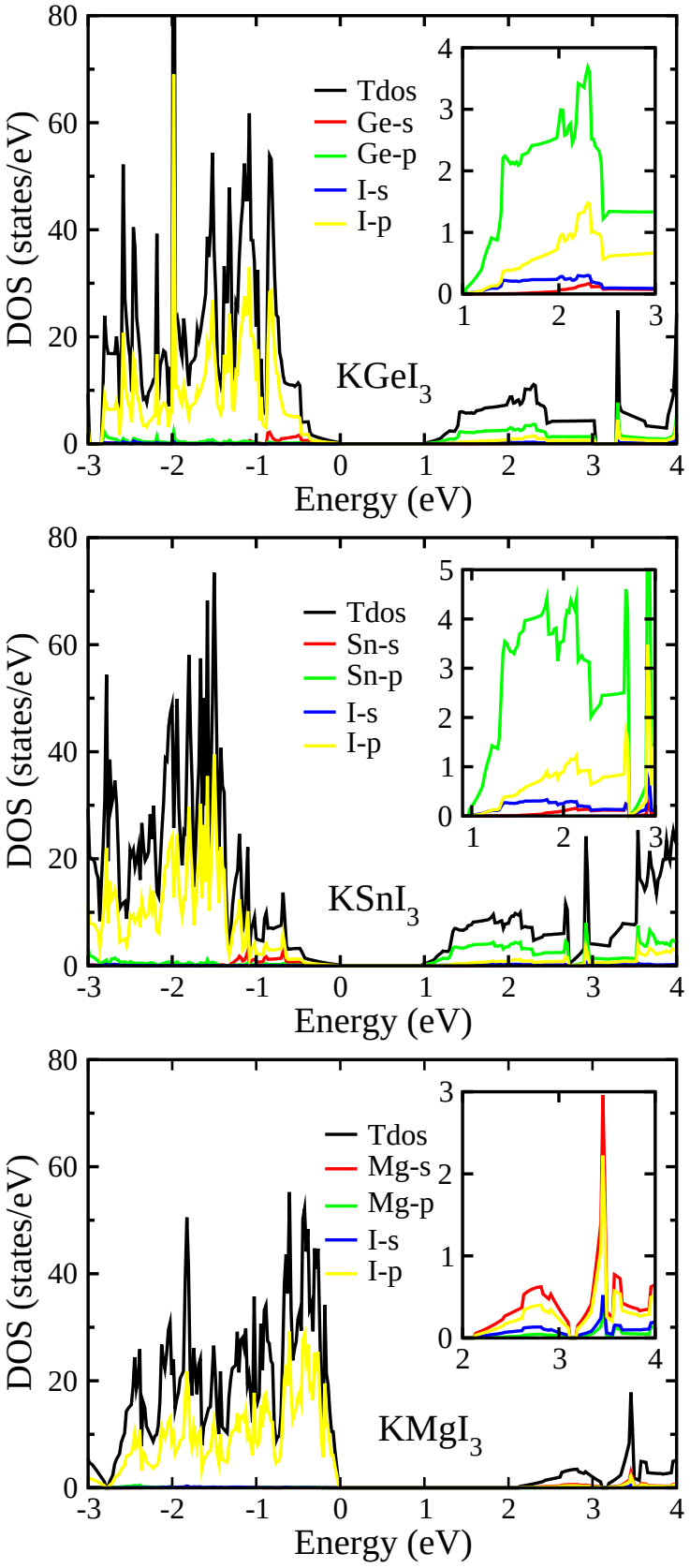

Figure S3. Partial density of states (DOS) of $KGeI_3$, $KSnI_3$ and $KMgI_3$.

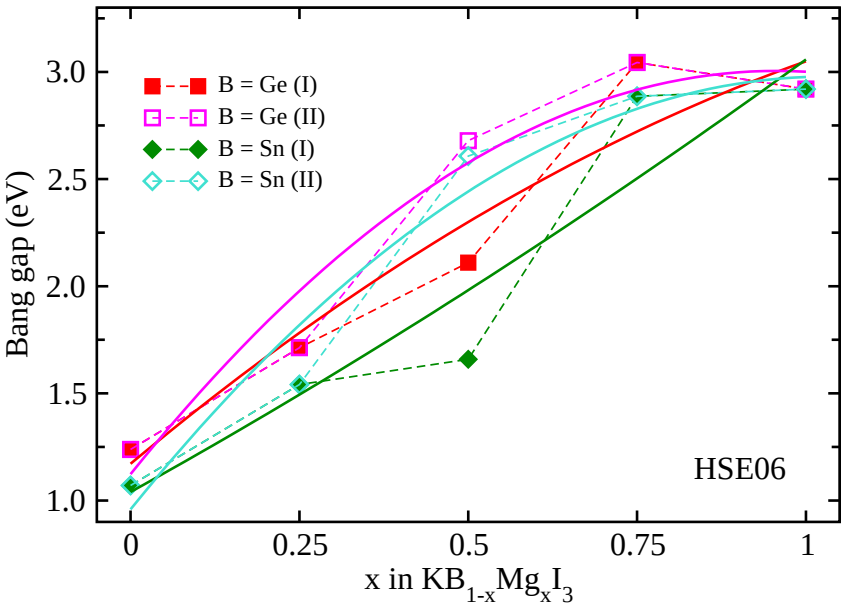

Figure S4. Fitting the band gaps calculated with HSE06 to the quadratic function for $KB_{1-x}Mg_xI_3$ (B = Ge, Sn) with x = 0, 0.25, 0.5 (I, II), 0.75, and 1. Dashed lines show the calculated values, and solid lines show the quadratic fitting functions.

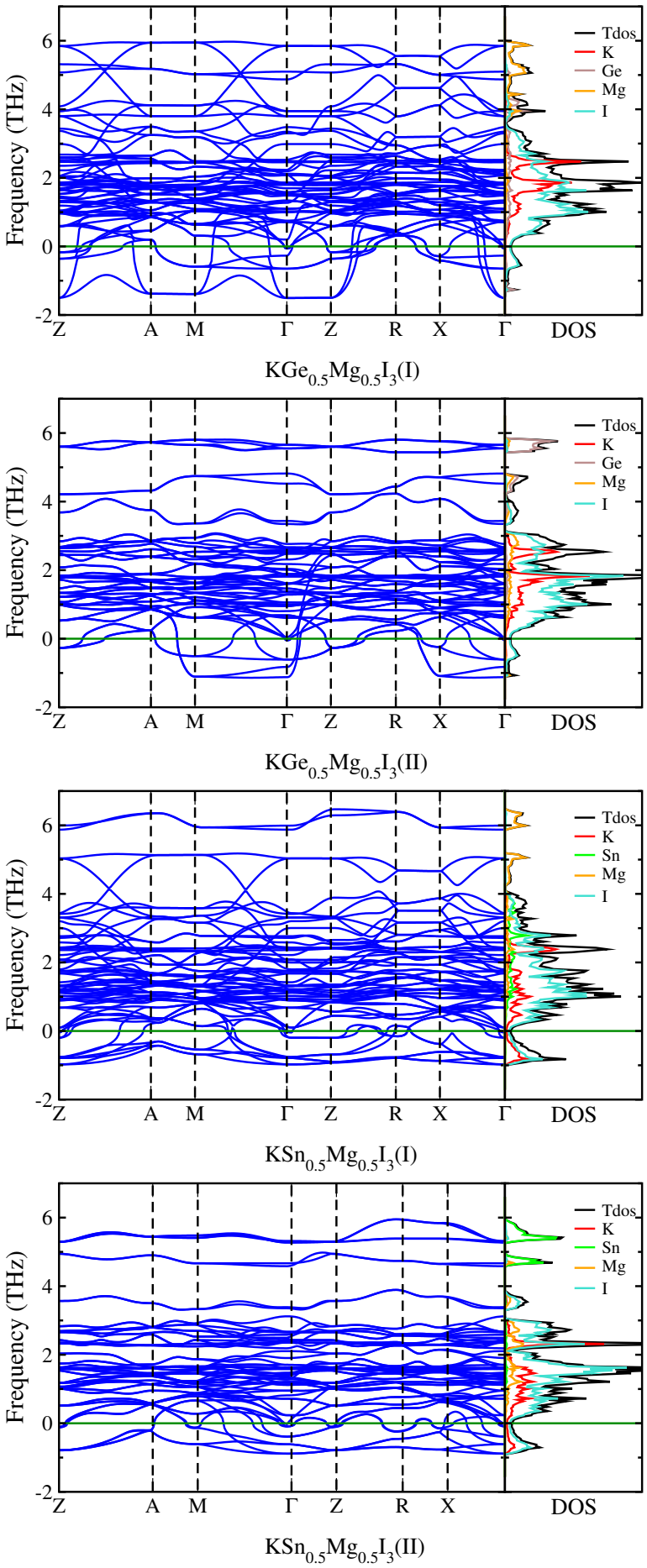

Figure S5. Phonon dispersion curves and the atom-resolved phonon DOS for (a) $KGe_{0.5}Mg_{0.5}I_3$ (I), (b) $KGe_{0.5}Mg_{0.5}I_3$ (II), (c) $KSn_{0.5}Mg_{0.5}I_3$ (I), (d) $KSn_{0.5}Mg_{0.5}I_3$ (II).

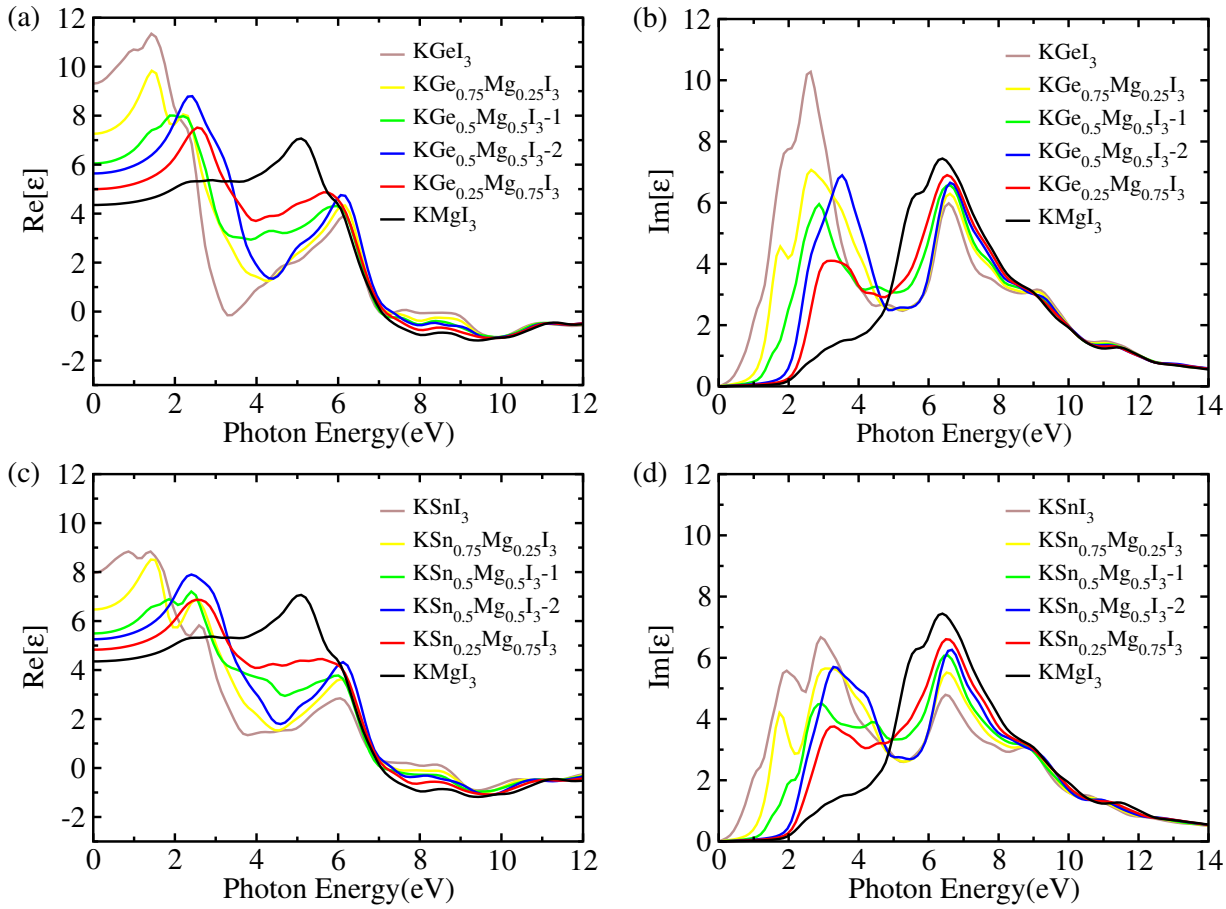

Figure S6. (a), (c) Real parts and (b), (d) imaginary parts of frequency-dependent dielectric constants of $KB_xMg_{1-x}I_3$ (B = Ge, Sn) with x = 0, 0.25, 0.5 (I, II), 0.75 and 1, calculated with PBE functional.

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