Supplementary Materials

Stable Mixed Group II (Ca, Sr) and XIV (Ge, Sn) Lead-free Perovskite Solar Cells

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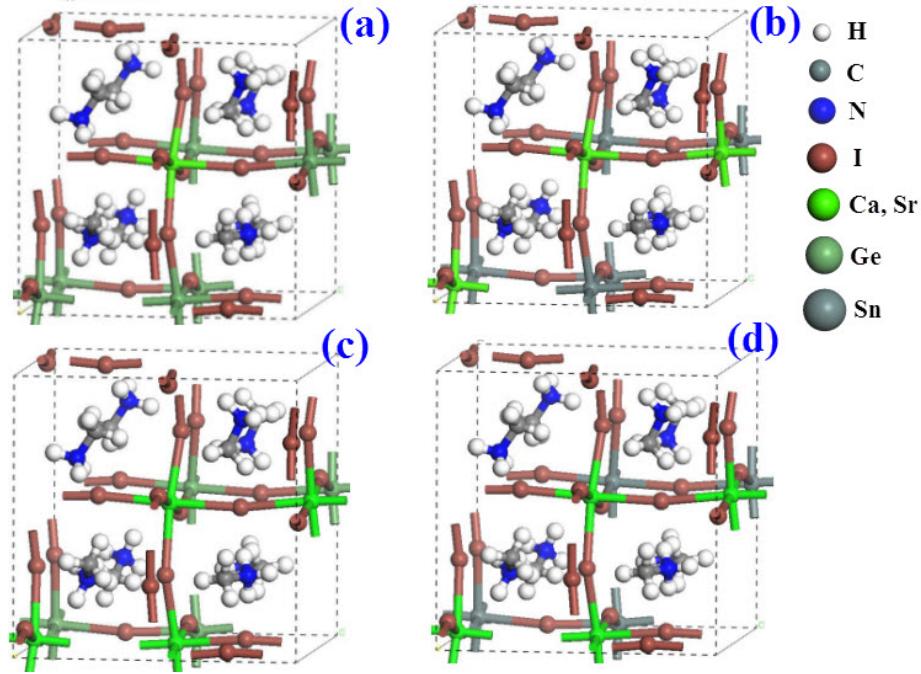
FIG. S1. The crystal structure for $MACa_{0.125}Ge_{0.875}I_3$ (a), $MACa_{0.375}Sn_{0.625}I_3$ (b), $MASr_{0.5}Ge_{0.5}I_3$ (c), and $MASr_{0.5}Sn_{0.5}I_3$ (d).

Material	$a/\mathring{A}$	$b/\mathring{A}$	$c/\mathring{A}$	Volume ($\mathring{A}^3$)	α°	β°	γ°
$MAPbI_3$	12.70	12.70	12.95	2088.7	90.0	89.0	90.0
$MACa_{0.125}Ge_{0.875}I_3$	12.17	12.26	12.38	1845.7	90.3	89.1	89.9
$MACa_{0.375}Ge_{0.625}I_3$	12.25	12.29	12.40	1868.2	90.1	89.2	90.0
$MACa_{0.5}Ge_{0.5}I_3$	12.29	12.35	12.44	1889.3	90.0	89.2	90.0
$MACa_{0.125}Sn_{0.875}I_3$	12.62	12.58	12.76	2026.3	89.9	89.2	89.9
$MACa_{0.375}Sn_{0.625}I_3$	12.56	12.52	12.74	2005.0	89.9	89.1	90.1
$MACa_{0.5}Sn_{0.5}I_3$	12.53	12.50	12.73	1993.8	89.9	89.2	90.1
$MASr_{0.125}Ge_{0.875}I_3$	12.59	12.50	12.65	1990.7	89.8	88.8	89.4
$MASr_{0.375}Ge_{0.625}I_3$	12.40	12.42	12.62	1943.7	89.7	89.1	90.2
$MASr_{0.5}Ge_{0.5}I_3$	12.48	12.54	12.71	1988.2	89.8	89.2	90.2
$MASr_{0.125}Sn_{0.875}I_3$	12.70	12.65	12.82	2060.1	90.0	89.1	89.9
$MASr_{0.375}Sn_{0.625}I_3$	12.74	12.68	12.94	2089.6	90.0	89.1	90.2
$MASr_{0.5}Sn_{0.5}I_3$	12.77	12.72	12.96	2104.2	89.9	89.1	89.9

TABLE S1. Lattice constants (a, b, c), lattice volume ($\mathring{A}^3$), and lattice angles (α, β, γ) are presented here for our mixed b-site perovskite materials, after successful relaxation of the structure in a comparison to $MAPbI_3$.

Remarks on PDOS.- We divided the PDOS (Fig. S6) plot into three main parts (MA, (Ca,Sr)/(Ge,Sn), and I). It is clear that the lowest unoccupied molecular orbital (LUMO) is dominated by Sn-p (or Ge-p) orbitals; while the highest occupied molecular orbital (HOMO) is dominated by I-p orbitals. At LUMO there is no contribution at VB and CB, but large contribution (Ca-d, Sr-d states) after Sn-p (or Ge-p) orbitals at CB. We did not find any effective influence of the MA cation in the electronic properties, but could expect some influence on octahedral tilting and bond lengths. Futhremore we expect that in our mixed cations study (Ca/(Sn,Ge), Sr/(Sn,Ge)) the oxidation of Ge and Sn from oxidation state 2^+ to 4^+ will decrease due to the chemical interaction of these mixed cations with each
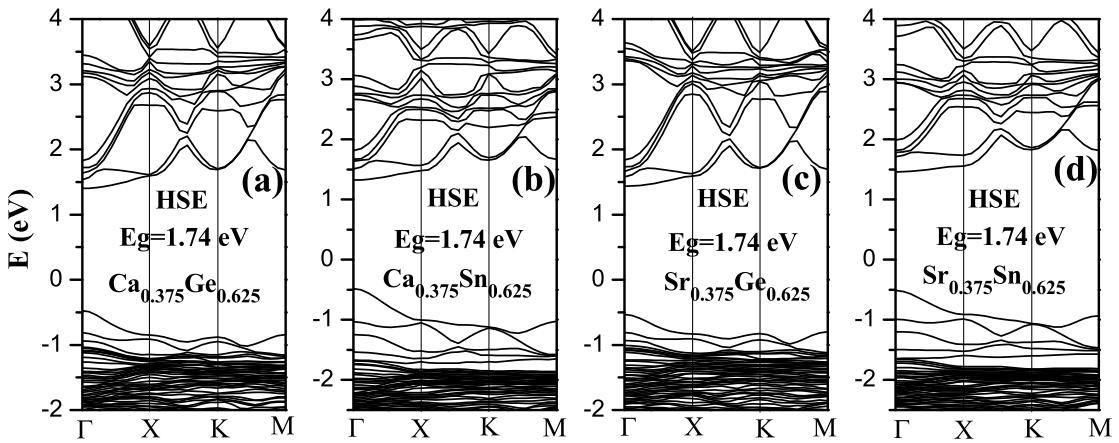
FIG. S2. HSE06-Bandgap values for $MACa_{0.375}Ge_{0.625}I_3$ (a), $MACa_{0.375}Sn_{0.625}I_3$ (b), $MASr_{0.375}Ge_{0.625}I_3$ (c), and $MASr_{0.375}Sn_{0.625}I_3$ (d).

other.

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[1] K. Wang, Z. Liang, X. Wang, X. Cui, Adv. electron. Mater., 2015, **1**, 1500089.

[2] P. Umari, E. Mosconi and F. De Angelis, Sci. Rep., 2014, **4**, 4467.
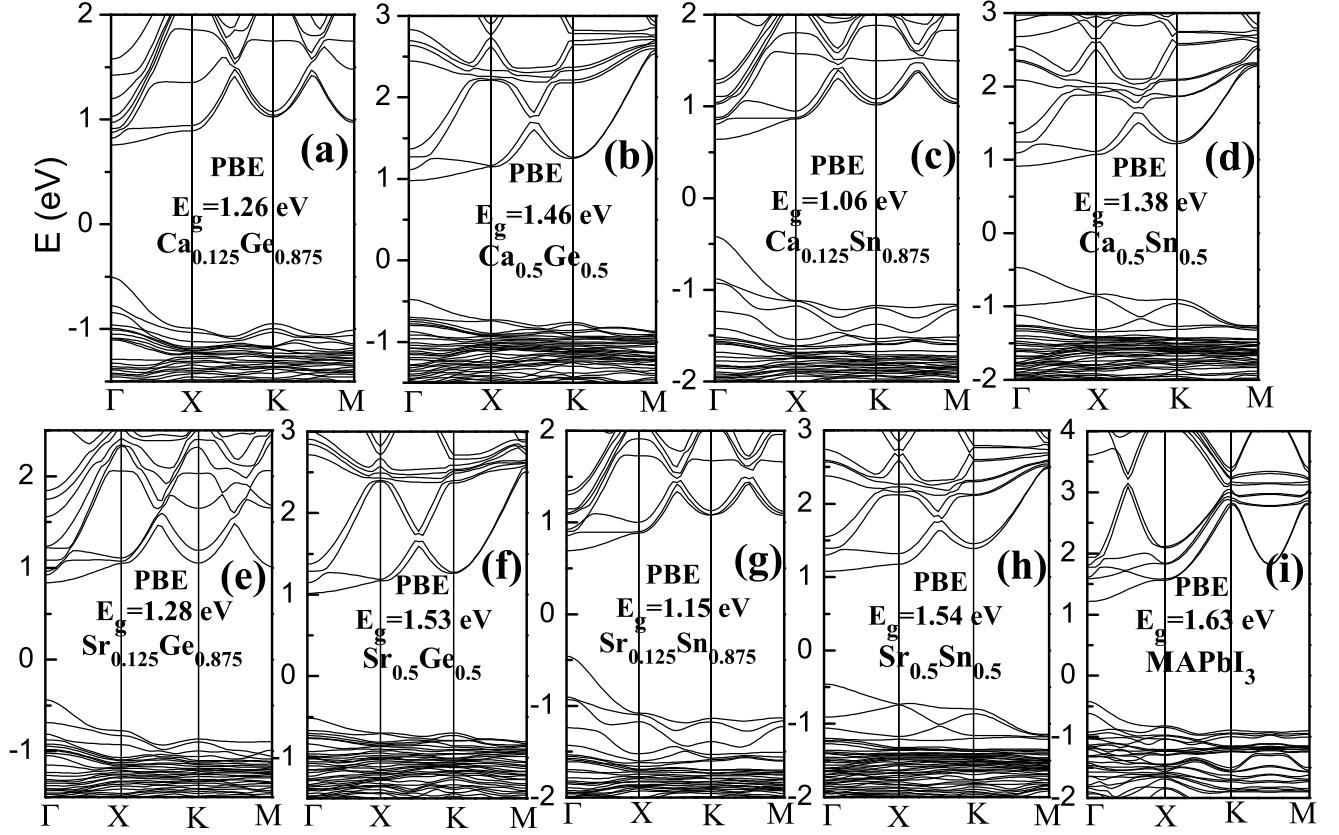
FIG. S3. Band structures for our explored mixed Pb-free perovskite materials with PBE calculations for $MACa_{0.125}Ge_{0.875}I_3$ (a), $MACa_{0.5}Ge_{0.5}I_3$ (b), $MACa_{0.125}Sn_{0.875}I_3$ (c), $MACa_{0.5}Sn_{0.5}I_3$ (d), $MASr_{0.125}Ge_{0.875}I_3$ (e), $MASr_{0.5}Ge_{0.5}I_3$ (f), $MASr_{0.125}Sn_{0.875}I_3$ (g), $MASra_{0.5}Sn_{0.5}I_3$ (h), in a comparison to PBE $MAPbI_3$ (i).
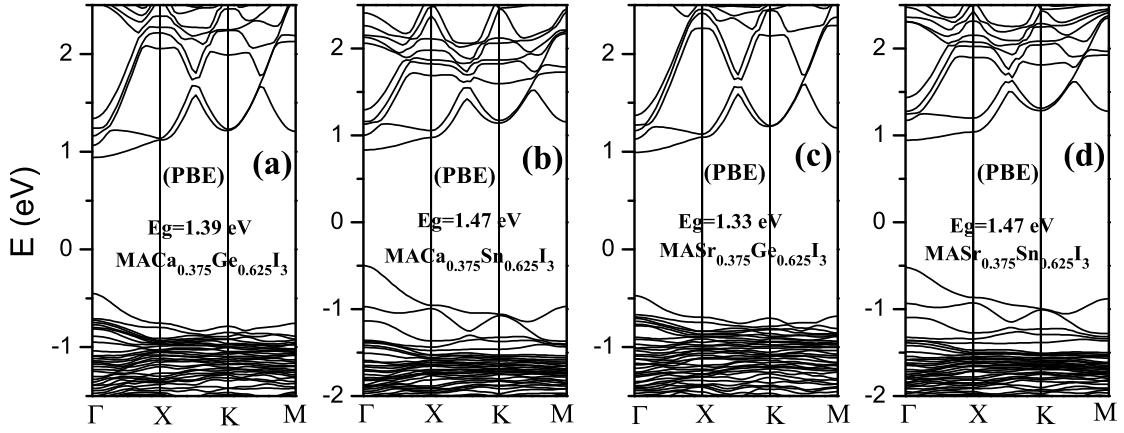
FIG. S4. PBE-structure for $MACa_{0.375}Ge_{0.625}I_3$ (a), $MACa_{0.375}Sn_{0.625}I_3$ (b), $MASr_{0.375}Ge_{0.625}I_3$ (c), and $MASr_{0.375}Sn_{0.625}I_3$ (d)..
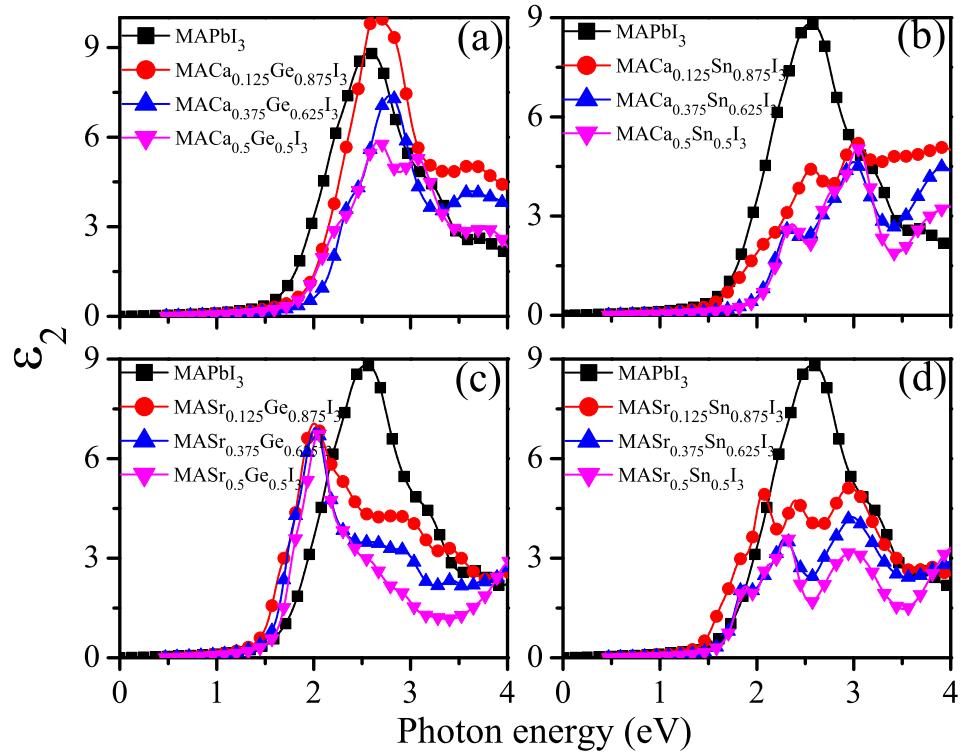
FIG. S5. Imaginary part of dielectric function (ε_2) is calculated for $MA(Ca/Ge)I_3$ in (a), $MA(Ca/Sn)I_3$ in (b), $MA(Sr/Ge)I_3$ in (c) and $MA(Sr/Sn)I_3$ in (d).
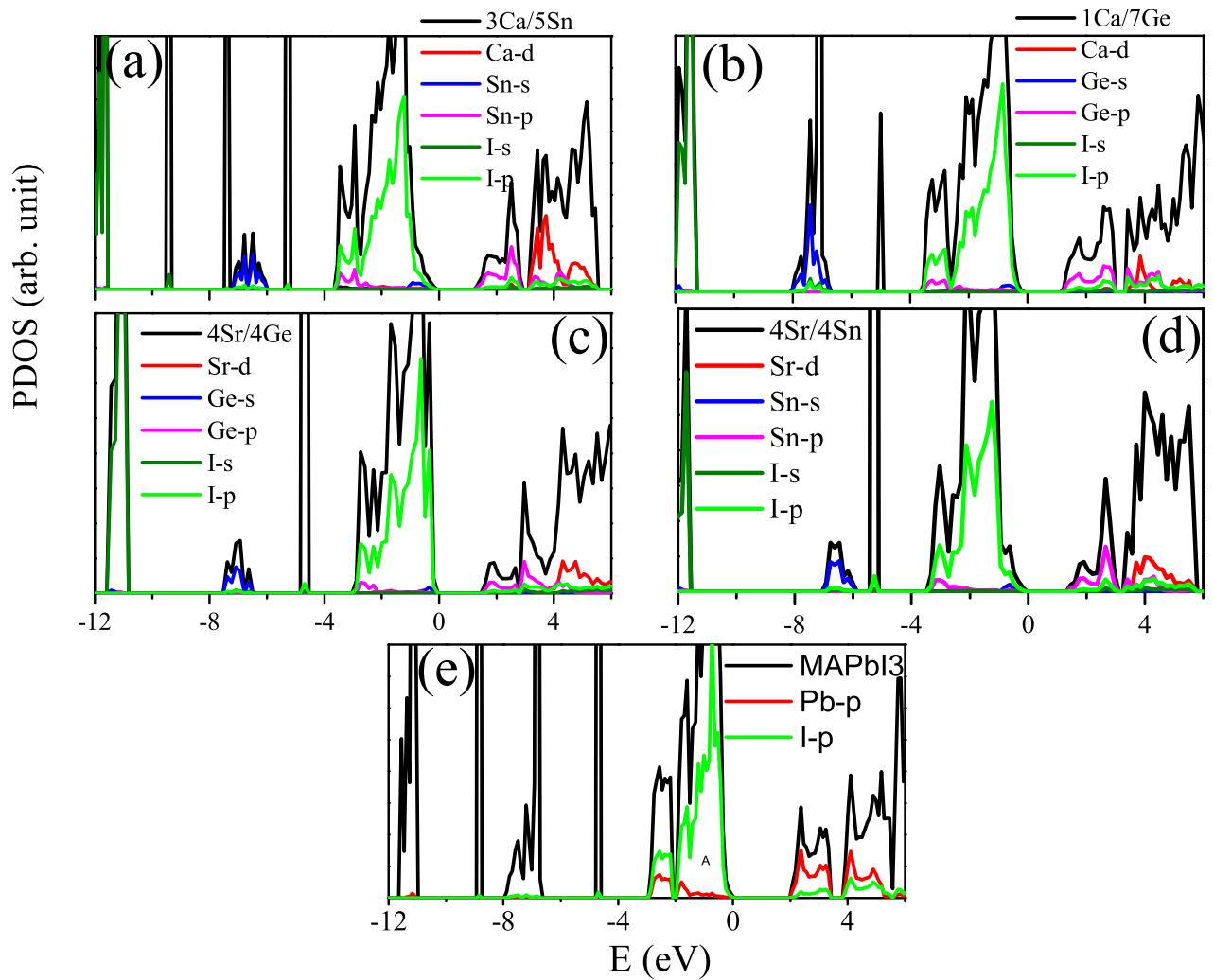
FIG. S6. PDOS plots for selected $MACa_{0.375}Sn_{0.625}I_3$ (a), $MACa_{0.125}Ge_{0.875}I_3$ (b), $MASr_{0.5}Ge_{0.5}I_3$ (c), and $MASr_{0.5}Sn_{0.5}I_3$ (d), mixed perovskite materials in a comparison to $MAPbI_3$ (e) with PBE calculations.