Discovery of new crystal structures of iodide Perovskite $CsPbI_3$ and $RbPbI_3$ via density functional theory

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Owing to the polymorphism of $CsPbI_3$ and $RbPbI_3$, we employ first-principles density functional theory (DFT) to explore their low-energy crystal structures. We systematically evaluate 180 ABX_3 prototypes, along with an additional 740 candidate structures obtained by swapping the A and B positions. Each structure is associated with its corresponding space group number (e.g., $CsGeCl_3$-146).The ABX_3 stoichiometry structures we use include: $AgIO_3$-29, $AgNO_3$, $AgNO_3$-161, $AlHoO_3$, $AlInS_3$, $AlYO_3$, $AsLiO_3$-15, $BaBiSe_3$-19, $BaCO_3$-62, $BaCoO_3$, $BaGeO_3$-19, $BaLiD_3$-221, $BaNiO_3$-186, $BaPbO_3$, $BaSbTe_3$-19, $BaTbO_3$, $BaTeO_3$, $BaTeO_3$-62, $BaTeS_3$, $BaTiO_3$, $BaVSe_3$-194, $BeCsF_3$, $BiSe_3Sr$-19, Br_3CdRb-62, $BrNaO_3$, $BrNO_3$-19, $C_4P_4F_12$-137, $CaClO_3$, $CaCO_3$-167, $CaCO_3$-62, $CaIrO_3$-63, $CaSiO_3$-2, $CaSnO_3$, $CaTiO_3$-62, $CdCO_3$-167, $CdGeO_3$, $CdGeO_3$-88, $CdTiO_3$-148, $CdTiO_3$-33, $CeSiP_3$, $CoSeO_3$, $CrRbCl_3$-1, $CsBeF_3$-62, $CsCrI_3$-60, $CsCuBr_3$-20, $CsCuCl_3$-178, $CsGeCl_3$-146, $CsNbO_3$, $CsSnCl_3$-14, $CrRbCl_3$, $CsSnI_3$-62, $CsVO_3$, $CuGeO_3$-26, $CuGeO_3$-51, $CuKF_3$, $CuKF_3$-127, $CuKF_3$-19, $CuSeO_3$, $CuTeO_3$-62, $CuVO_3$, $Eu_3Ge_3S_9$, $Fe_2P_2S_6$-12, $Fe_2P_2Se_6$-146, FeS_3U, $FeTiO_3$, $GaGdO_3$-62, $GaNdO_3$-33, $GaYO_3$, $GdFeO_3$-62, $GdTiO_3$, $GePbS_3$, $GeRbCl_3$-11, $Hg_2P_2S_6$, $Hg_2P_2Se_6$, $HgTiO_3$-161, $HoNiO_3$-62, $HoVO_3$, $InYO_3$, $IrKO_3$, $KAgF_3$-62, $KClO_3$-62, $KClO_3$-1, $KFeBr_3$, $KFeCl_3$, $KFeF_3$-221, $KFeF_3$-62, $KMnF_3$, $KNbO_3$-38, $KNbO_3$-2, $KNiCl_3$-185, $KPbF_3$-62, KPO_3-62, $LaBO_3$-11, $LaCrO_3$, $LaErO_3$-62, $LaMnO_3$-62, $LaTiO_3$, $LaYbO_3$-33, $LiBaH_3$-221, $LiIO_3$-182, $LiIO_3$-1, $LiSbO_3$-52, $LiTaO_3$, $LiVO_3$, $LuBO_3$-167, $LuMnO_3$-185, $MgCO_3$-167, $MgRbCl_3$, $MgSeO_3$, $MgSiO_3$-14, $MgVO_3$, $MgVO_3$-65, $MnCsBr_3$-194, $MnCsCl_3$,

$MnRbCl_3$, $MnRbSr_3$, $MnSeO_3$, $MnSO_3$-148, $NaAsO_3$-2, $NaClO_3$-14, $NaCoF_3$, $NaIO_3$-33, $NaMnCl_3$, $NaMnF_3$-62, $NaNbO_3$, $NaNbO_3$-57, $P_4Tl_4O_12$, $PbClO_3$, $PbRbI_3$, $PbSnS_3$-62, $PbTlI_3$, $PbZrS_3$, $PrMnO_3$-62, R_3MR-160, $RbAgF_3$-140, $RbCrI_3$, $RbCuCl_3$-5, $RbCuCl_3$-60, $RbGeI_3$-19, $RbHgF_3$-221, $RbMgCl_3$-194, $RbMnBr_3$-194, $RbNbO_3$-2, $RbNiCl_3$-194, $RbNO_3$-59, $RbPO_3$-14, $RbTaO_3$, $RbVO_3$, $SbTlO_3$, $ScUS_3$, $ScYS_3$-33, $SeZnO_3$-62, $SiZnO_3$-15, $SmAlO_3$-62, $SmBO_3$-1, $SmTiO_3$, $Sn_2P_2S_6$-7, $SrIrO_3$-15, $SrPbO_3$, $SrZrO_3$-62, $SrZrO_3$-63, $SrZrO_3$-1, $SrZrO_3$-2, $SrZrS_3$-62, $TaRbO_3$, $TbFeO_3$-62, $TbMnO_3$-62, $TiGdO_3$, $TiNdO_3$, $TiSmO_3$, $TiVO_3$, $TiYO_3$, $TlCdI_3$, $TlMnCl_3$-62, $TlNO_3$, $TlSbO_3$-163, $TlSbO_3$-182, $TmFeO_3$-62, $YFeO_3$-33, $ZnSeO_3$, $ZnSiO_3$, $ZnTeO_3$-61, $ZnTiO_3$-148, $ZrSrO_3$.

Table S1. The optimized crystal parameters of $CsPbI_3$ with relative energies below 10 kJ/mol.

Structures	Space group	Lattice Parameter
$TlCdI_3$	Pnma	a =10.889 Å
		b = 4.890 Å
		c =18.213 Å
		α = 90°
		β = 90°
		γ = 90°
$BaTeS_3$	Pnma	a =8.196Å
		b =8.749 Å
		c = 14.388 Å
		α = 90°
		β = 90°
		γ = 90°
$KNiCl_3$	P63cm	a =14.806Å
		b =14.806 Å
		c = 8.170 Å
		α = 90°
		β = 90°
		γ =120°
$LaErO_3$	Pbnm	a = 9.110 Å
		b = 8.324 Å
		c = 12.152 Å
		α = 90°
		β = 90°
		γ = 90°
$RbCrI_3$	C2	a =14.964 Å
		b = 8.6910 Å
		c =16.221 Å
		α = 90°
		β = 102.142°
		γ = 90°
$CrRbCl_3$	C2/m	a = 14.964 Å

		b = 8.692 Å c = 8.111Å α = 90° β = 102.146° γ = 90°
$PbTlI_3$	Cmcm	a = 4.834 Å b =16.223Å c = 12.424 Å α = 90° β = 90° γ = 90°
$CsCuBr_3$	C2221	a = 15.603 Å b = 8.850Å c = 15.071 Å α = 90° β = 90° γ = 90°
$CsNbO_3$	P21/c	a = 8.260Å b =20.243Å c = 12.811 Å α = 90° β = 93.358° γ = 90°
$SrZrO_3$	Cmcm	a = 12.537 Å b = 12.874 Å c = 12.612Å α = 90° β = 90° γ = 90°
$BaPbO_3$	Imma	a = 8.929 Å b = 12.583 Å c = 9.084 α = 90° β = 90° γ = 90°
$KMnF_3$	P4/mbm	a = 8.849 Å b = 8.849 Å c = 12.977 Å α = 89.967° β = 134.800° γ = 89.871°
$HgTiO_3$	R3c	a =8.251 Å b = 8.251 Å c = 20.104 Å α = 90° β = 90° γ = 120°
$RbHgF_3$	Pm-3m	a = 6.389 Å b = 6.389 Å c = 6.389 Å α = 90° β = 90° γ = 90°

Table S2. The optimized crystal parameters of $RbPbI_3$ with relative energies below 10 kJ/mol.

Structures	Space group	Lattice Parameter
$TlCdI_3$	Pnma	a = 10.780 Å
		b = 4.839 Å
		c = 17.679 Å
		α = 90°
		β = 90°
		γ = 90°
$PbTlI_3$	Cmcm	a =4.778 Å
		b = 15.906 Å
		c = 12.190 Å
		α = 90°
		β = 90°
		γ = 90°

Table S3. Band gap changes of $CsPbI_3$ candidate structures.

Structures	Band gap value (eV)	Band character
$TlCdI_3$	2.5215	Inirect
$BaTeS_3$	2.9132	Inirect
$KNiCl_3$	2.8261	Inirect
$LaErO_3$	1.8246	Direct
$RbCrI_3$	2.8218	Inirect
$CrRbCl_3$	2.7667	Inirect
$PbTlI_3$	2.4677	Inirect
$CsCuBr_3$	2.5663	Inirect
$CsNbO_3$	2.8080	Inirect
$SrZrO_3$	1.6710	Direct
$BaPbO_3$	1.7257	Direct
$KMnF_3$	1.6013	Direct
$RbHgF_3$	1.4831	Direct

Table S4. Band gap changes of $RbPbI_3$ candidate structures.

Structures	Band gap value (eV)	Band character
$TlCdI_3$	2.4912	Inirect
$PbTlI_3$	2.4265	Inirect

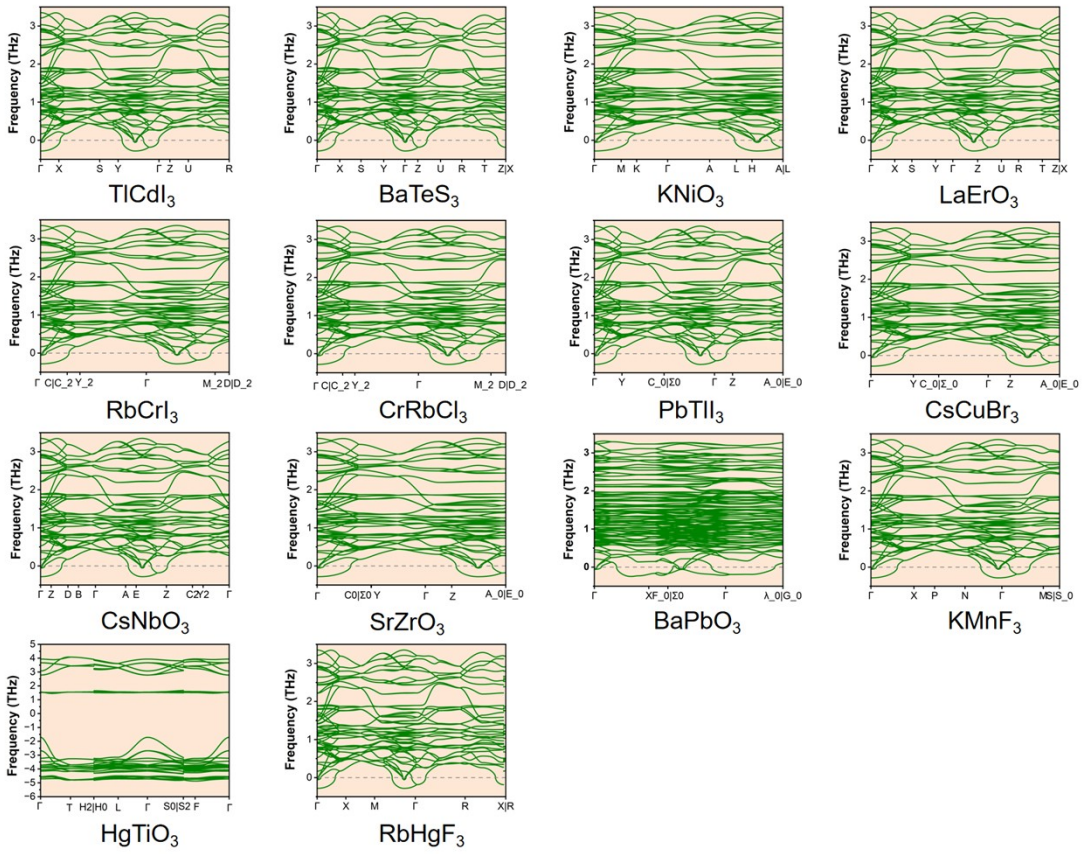

Fig. S1 The phonon spectra of the 14 candidate structures of $CsPbI_3$.

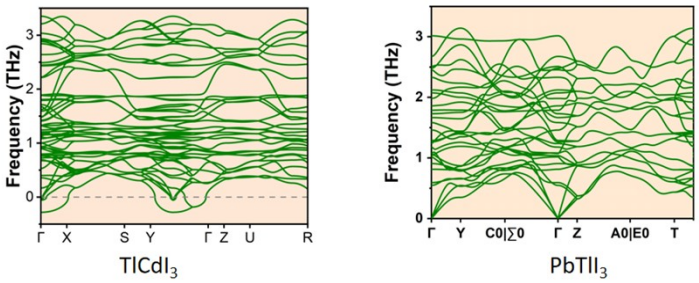

Fig. S2 The phonon spectra of the 2 candidate structures of $RbPbI_3$.

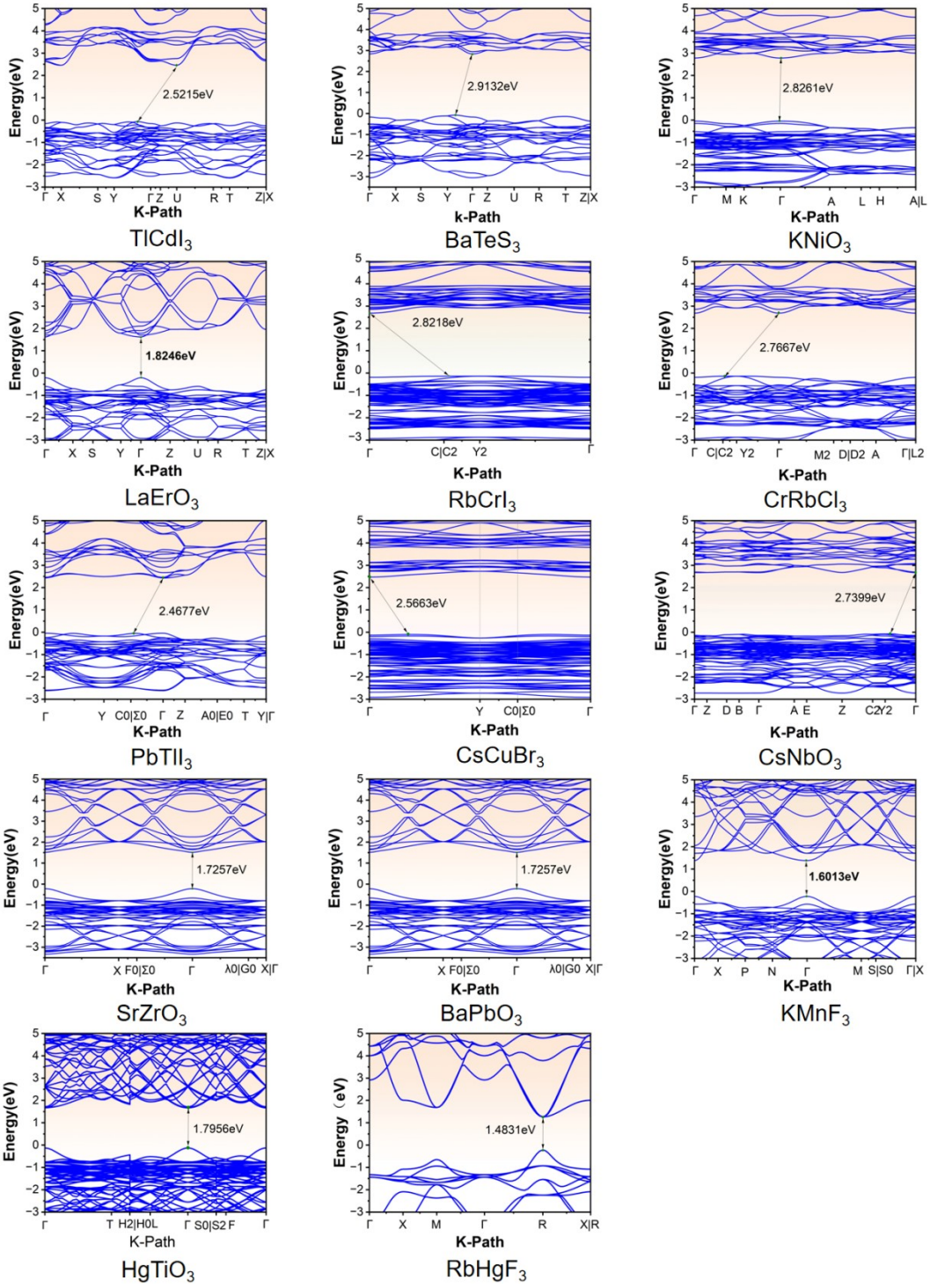

Fig. S3 The band structures of the 14 candidate structures of $CsPbI_3$.

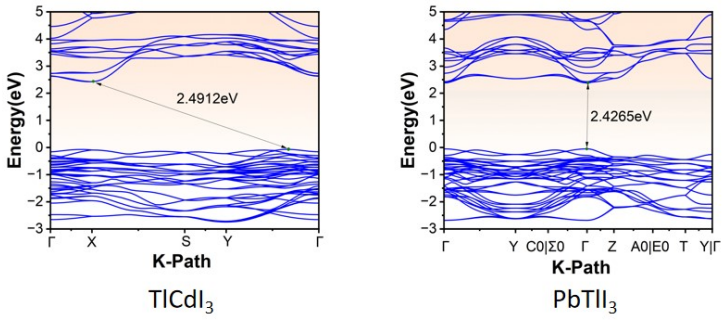

Fig. S4 The band structures of the 2 candidate structures of $RbPbI_3$.