Supporting Information

Improving the Optical and Thermoelectric Properties of $Cs_2InAgCl_6$ with Heavy Substitutional Doping: A DFT Insight

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SI 1. Structural details

The double-perovskite $Cs_2InAgCl_6$ crystallizes in a face-centered cubic structure with 40 atoms per unit cell. The unit cell contains two octahedra: one $InCl_6$ and the other $AgCl_6$. These two octahedra alternate along the different crystallographic planes: [100], [010], and [001].

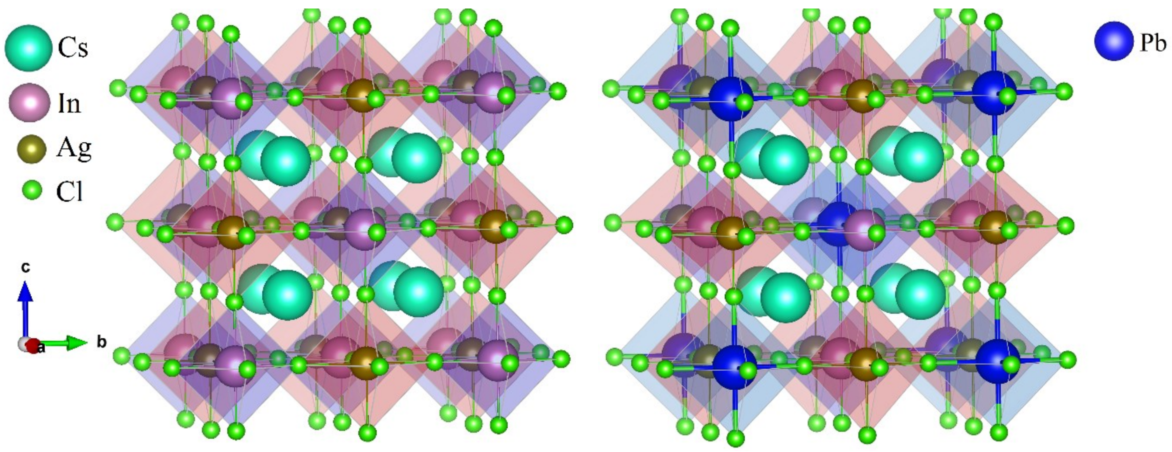

Fig. SI-1: Crystal structure of double perovskite$Cs_2InAgCl_6$ (left panel),and Pb-substituted-$Cs_2InAgCl_6$ (right panel).

The unit cell of $Cs_2InAgCl_6$ is shown in the left panel of Fig. SI-1. The K/Rb based structure is almost identical to the pristine $Cs_2InAgCl_6$ structure. The right panel shows the crystal structure of 25% Pb. We are not showing the crystal structure for other doped systems. This structure seems to be an octahedrally distorted antiperovskite type structure.

SI 2. Electronic structure

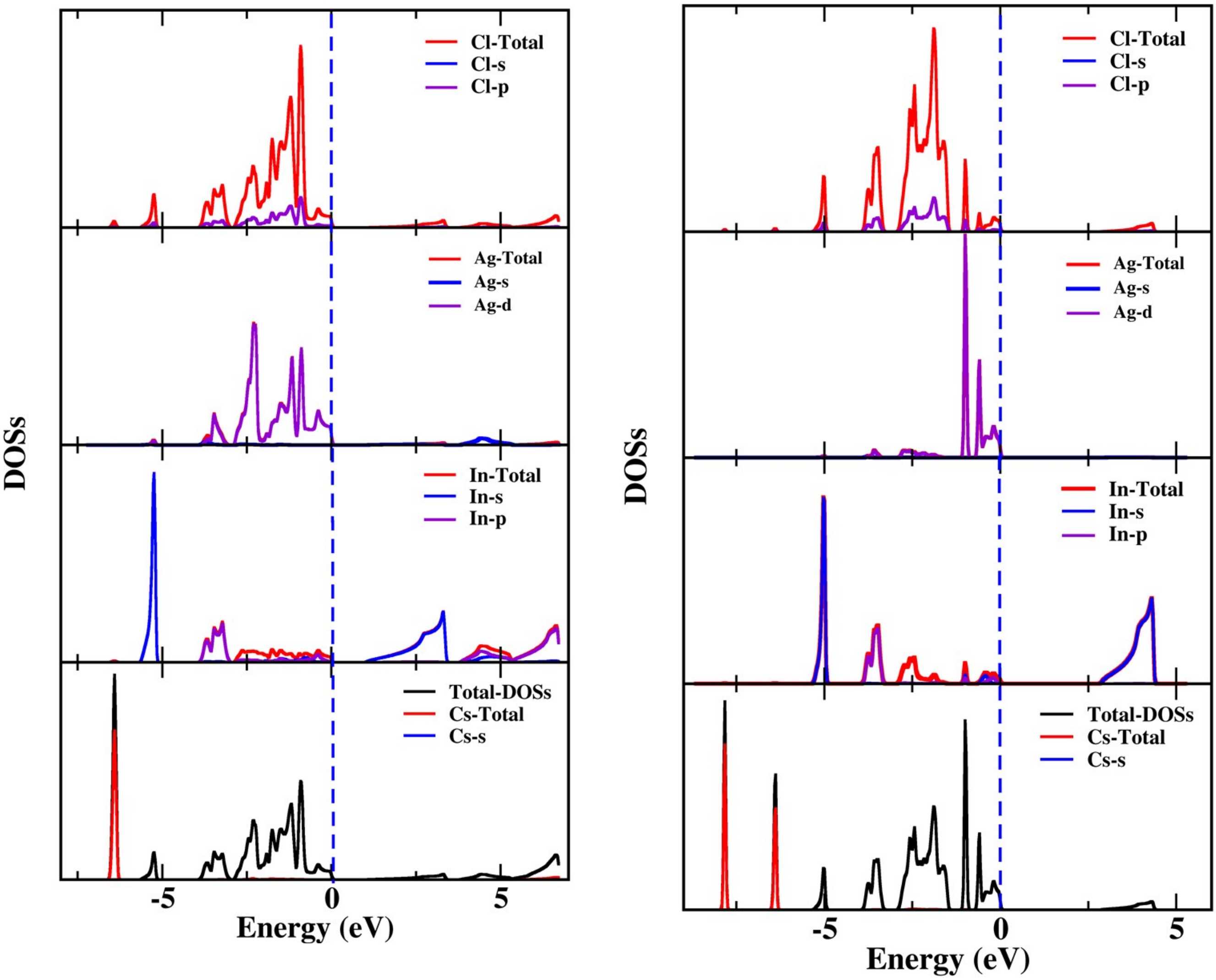

Fig. SI-2: Calculated total, atom, and orbital decomposed density of states of pristine $Cs_2InAgCl_6$ by using PBE functional (left panel) and with KTB-mBJ+SO potential (right panel).

We see from DOSs that in the pristine case the valence band maximum (VBM) is composed of Ag-*d* and Cl-*p* states while conduction band minimum is originated from In-*s* and Ag-*s* (minor contribution) states. Assuming a similar trend for PBE and KTB-mBJ+SO for doped materials as we observe for pristine, we report only KTB-mBJ+SOC band structure only for the doped case.

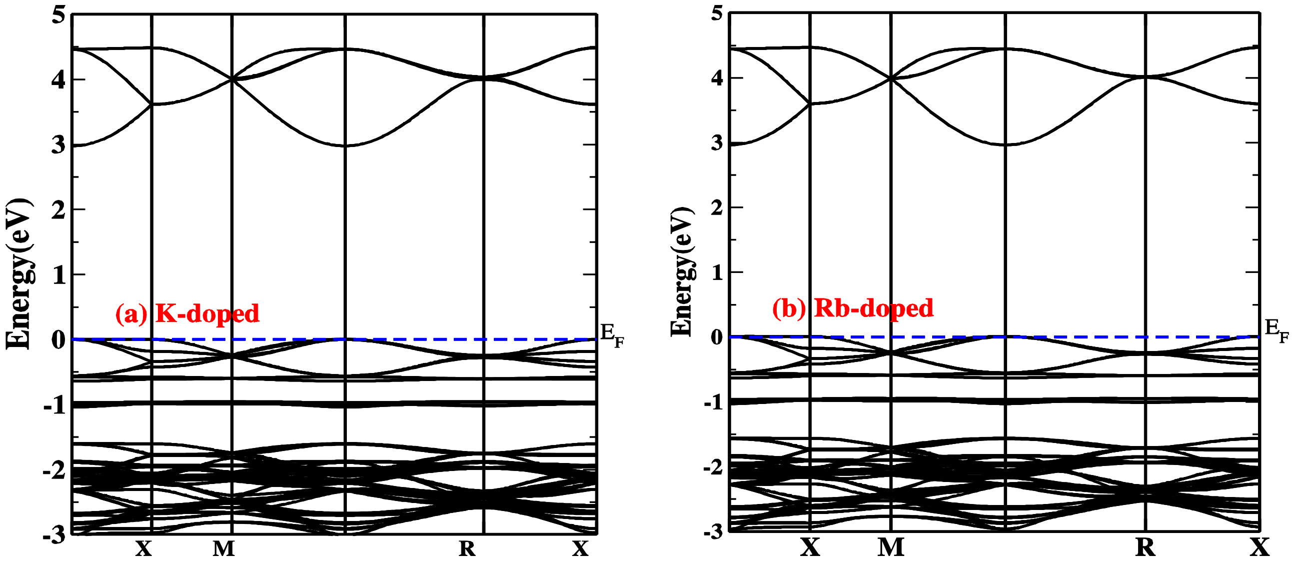

Fig. SI-3: Electronic dispersion relations of: (a) K- doped and (b) Rb-doped $Cs_2InAgCl_6$ by using PBE functional with KTB-mBJ potential including SO effect. The blue dash line represents the Fermi level.

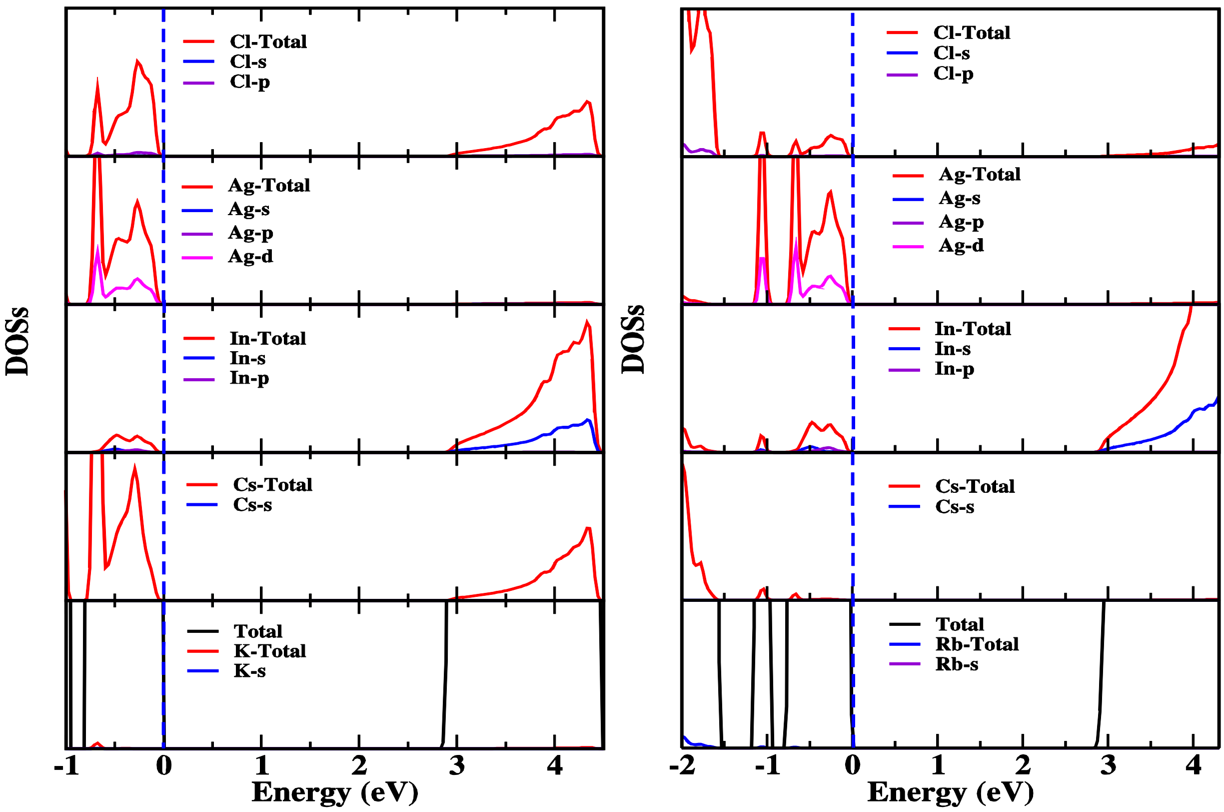

Fig. SI-4: Calculated total, atom, and orbital decomposed density of states of 25% K- (Left panel) and Rb-doped (Right panel).

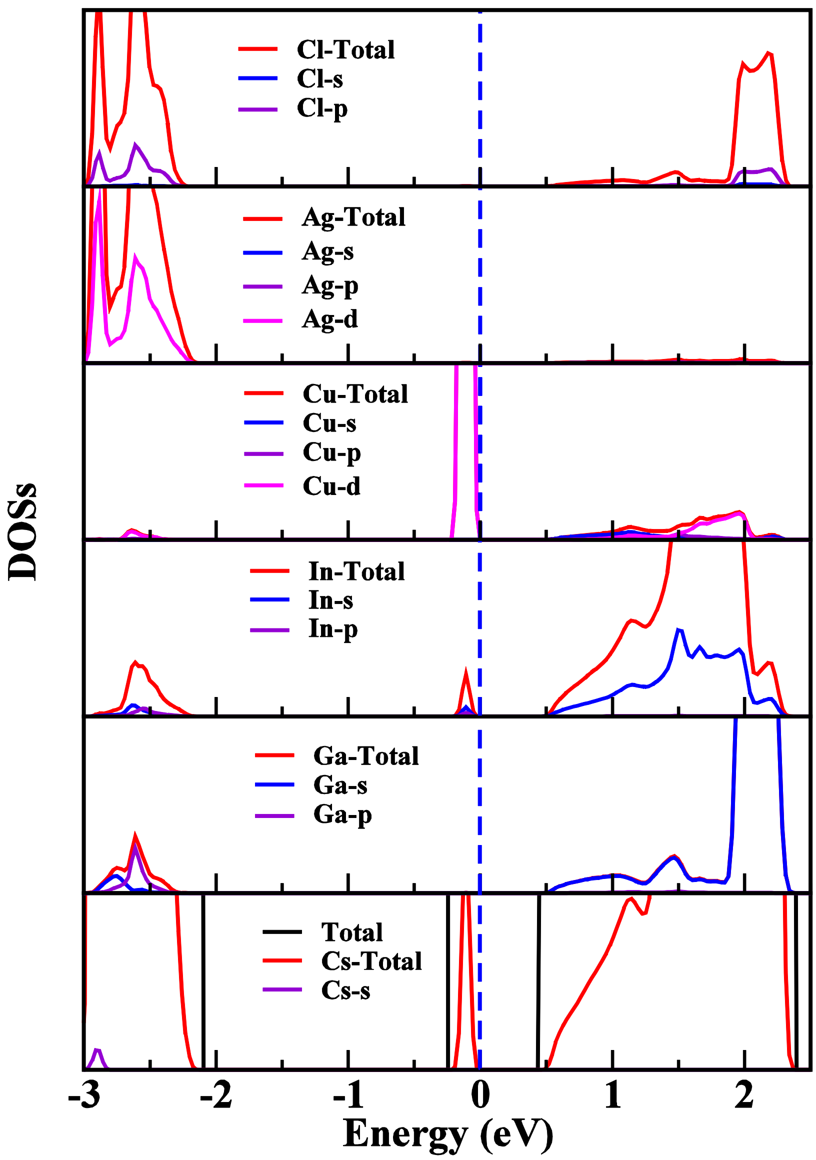

Fig. SI-5: Calculated total, atom, and orbital decomposed density of states of 12.5% Cu & 12.5% Ga-co-doped $Cs_2InAgCl_6$.

Table-SI-1: Equilibrium lattice parameters of pristine $Cs_2InAgCl_6$ along with its doped derivatives with experimental and other available data (symbols have their usual meaning).

Material	Space group	a (Å) (PBE)	(Δa/a)%	Exp. [17]	Cal. (Others)
$Cs_2InAgCl_6$	225 (Fm-3m)	10.676	-	10.467	10.20 (LDA) [17], 10.23 (LDA) [36], 10.62 (HSE) [17]
Cu-Ga co-doped	221 (Pm-3m)	10.545	1.23	-	-
K-0.25	224 (Pn-3m)	10.629	0.28	-	-
Rb-0.25	224 (Pn-3m)	10.646	0.44	-	-
Sn-0.25	221 (Pm-3m)	10.854	1.67	-	-
Pb-0.25	221 (Pm-3m)	10.916	2.25	-	-

Pb/Rb/K/Cs/Sn/In/Ag*/Cl*: 2.5/2.5/2.5/2.5/2.5/2.37/2.4/1.85
*R_{mt} for Ag/Cl for pristine case is 2.5/2.04.

Table-SI-2: Calculated bandgap of $Cs_2InAgCl_6$ by using different approaches of functional along with other theoretical and experimental values. The bandgap of the studied alloys is listed for PBE functional and KTB-mBJ potential only.

Compound	PBE		TB-mBJ		nKTB-mBJ		KTB-mBJ		HSE	PBE0	EXP.
	PBE	+SOC	mBJ	+SOC	mBJ	+SOC	mBJ	+SOC			
$Cs_2InAgCl_6$	1.03	1.004	2.57	2.46	2.68	2.56	2.91	2.85 (d)	2.6[1]	2.7[1]	3.3[1]
Cu &Ga	0.12	0.09	-	-	-	-	-	0.65 (I)	-	-	-
K-0.25	1.11	1.08	-	-	-	-	-	3.03 (d)	-	-	-
Rb-0.25	1.11	1.09	-	-	-	-	-	3.01 (d)	-	-	-
Pb-0.25	2.13	1.85	-	-	-	-	-	2.40 (I)	-	-	-
Sn-0.25	1.66	1.59	-	-	-	-	-	2.08 (I)	-	-	-

Formation energy:

To check the chemical and mechanical stability of the studied compounds, we have computed the formation energy (using Eq.-1) and elastic constants. Negative formation energies confirmation that these systems are chemically stable. The calculated the elastic constants satisfies the necessary mechanical stability condition (Eq.-8) for cubic case which predicts the mechanical stability of pristine $Cs_2AgInCl_6$ and its doped derivatives.

Computational Details:

To calculate the formation energy, we performed a series of calculations by using plane wave (PW) method as implemented in Quantum Espresso[1]. We used 100(1000) Ry kinetic cut-off energy for wavefunction(charge density). convergence threshold on forces (a.u) for ionic minimization was 10^{-3} and convergence threshold on total energy (a.u) for ionic minimization was $10^{-4.}$ Structre was visualised using XcrySDen software[2].

Formation Energy:

The chemical stability of the pristine and doped systems was checked using below equation:

$$E_{formation} = E_{product} - E_{reactant} \quad (1)$$

The calculated values are:

E(Pristine) = -8.17306 Ry (2)

E(Cu & Ga co-doping) = -8.21226 Ry (3)

E (K-25% doped) = -8.24138 Ry (4)

E (Rb-25% doped) = -8.25616 Ry (5)

E (Pb-25% doped) = -8.35351 Ry (6)

E (Sn-25% doped) = -8.33529 Ry (7)

From above equations (2-7), we can see that the energy difference between the product and the reactant is negative, which confirms the chemical stability of the studied systems. In the **Table-SI3**, we give ground state energy of the calculated systems.

Table-SI-3: Calculated formation energy of $Cs_2InAgCl_6$ and its doped derivatives. Unit is in Ry.

$Cs_2AgInCl_6$	**$Cs_2Ag(Cu)In(Ga)Cl_6$**	**$Cs(K)_2AgInCl_6$**	**$Cs(Rb)_2AgInCl_6$**	**$Cs_2Ag(Pb)In(Pb)Cl_6$**
-3067.83703430	-3278.685788	-3167.676406	-3039.52761796	-4376.87914
$Cs_2Ag(Sn)In(Sn)Cl_6$	**-**	**-**	**-**	**-**
-2962.20007834	-	-	-	-
Cs	**Ag**	**In**	**Cl**	**K**
-63.065709720	-287.14287239	-144.67274095	-34.494826600	-112.951240
Rb	**Sn**	**Pb**	**Cu**	**Ga**
-48.869451860	-163.00821624	-870.33864204	-364.89183305	-277.733337

Optical Properties:

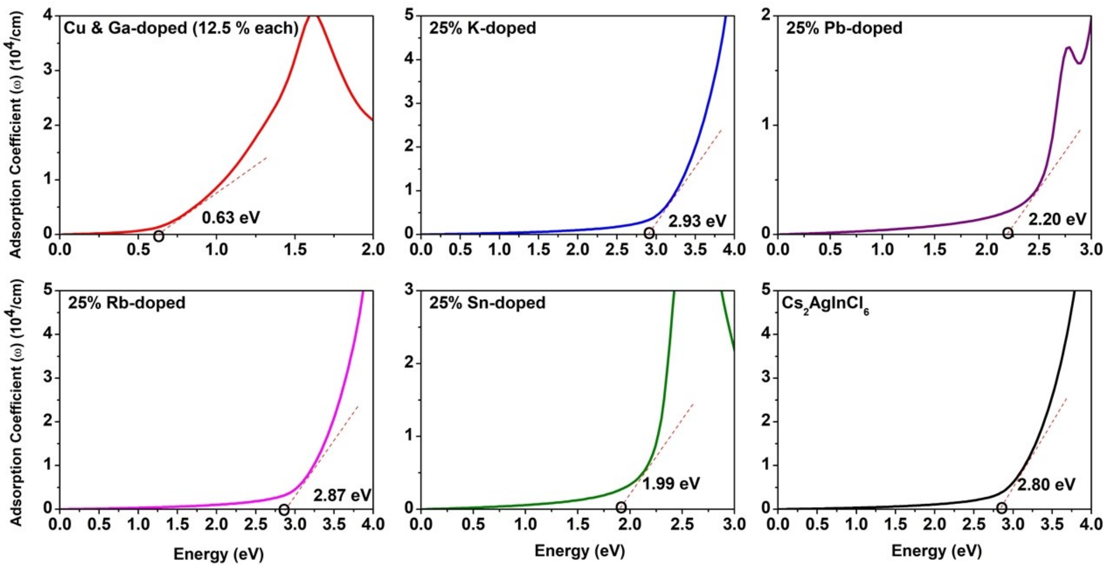

Fig. SI-6: Extraplotted band gap of pristine and its doped derivatives.

From the Table-SI2 and Fig. SI-6, we see that the optical band gap is slightly underestimated.

Mixing Energy:

To understand the stability of the studied doped systems we have calculated the mixing energies as follows,

E_{mixing} = E_{doped system} + E_{replaced} - E_{printine} - E{subsituent}

Where all the terms in the right side are the total energy of the respective bulk system. A positive value of E_{mixing} means the substitutional doping is endergonic in comparison to the pristine Cs2InAgCl6 and a negative value of E_{mixing} means the substitutional doping is exergonic and more stable than pristine system. The calculated values of E_{mixing} for all the doped systems are presented in Table-SI-4.

Table-SI-4: Calculated mixing energies of the doped systems studied in this work.

System	E_{mixing} (eV)
$Cs(K)_2AgInCl_6$	0.70
$Cs(Rb)_2AgInCl_6$	0.38
$Cs_2Ag(Pb)In(Pb)Cl_6$	-1.40
$Cs_2Ag(Sn)In(Sn)Cl_6$	-0.79
$Cs_2Ag(Cu)In(Au)Cl_6$	0.88

References:

1. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo and others, *J. Phys. Condens. Matter*, 2009, **21**, 395502.

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