Self-assembling Endohedrally Doped CdS Nanoclusters. New Porous Solid Phases of CdS

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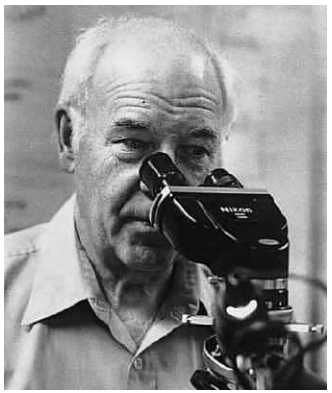
Outline

1. Introduction
2. Methods
3. Results
   - Monomers
   - Dimers
   - Solids
4. Conclusions
5. Acknowledgments

Introduction

Walter McCrone:

“Every compound has different polymorphic forms and, in general, the number of forms known for a given compound is proportional to the time and money spent in research on that compound”



McCrone et al. *Physics and Chemistry of the Organic Solid State*, **2**, 725-767 (1965)

- Dense spectrum of low-density polymorphs

Zwijnenburg et al. *Phys. Rev. Lett.* **104**, 175503 (2010)

Inorganic Solids

- Dense spectrum of low-density polymorphs
- Structure $\rightarrow$ Properties $\rightarrow$ Applications

Zwijnenburg et al. *Phys. Rev. Lett.* **104**, 175503 (2010)

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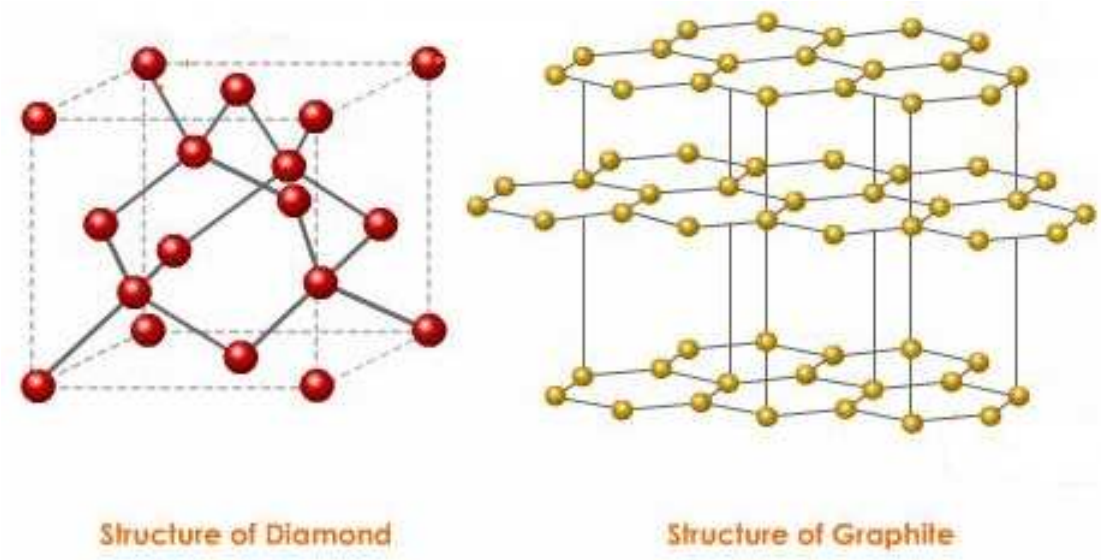
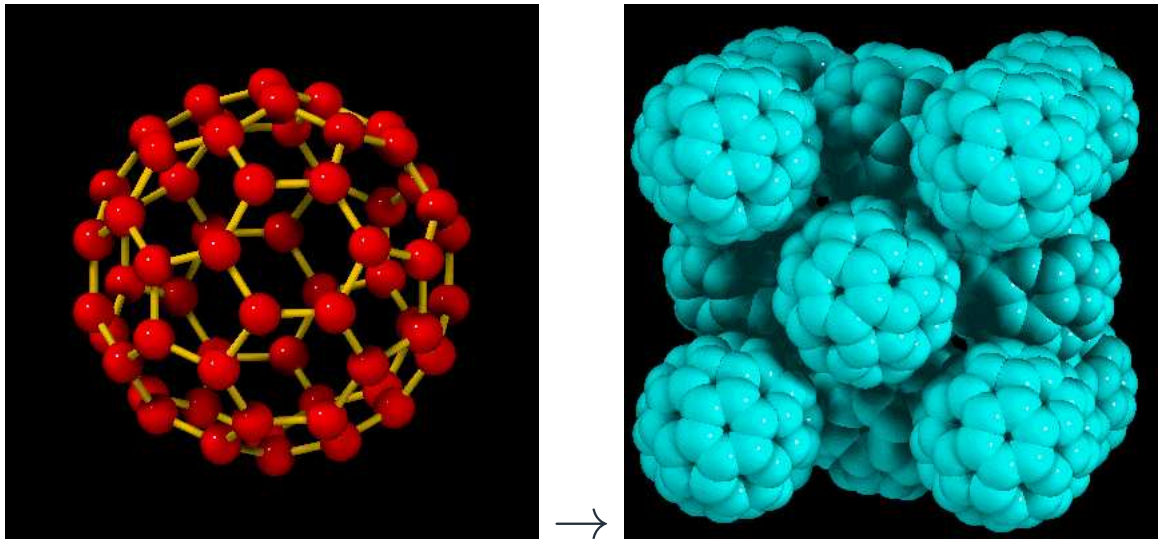


Zwijnenburg et al. *Phys. Rev. Lett.* **104**, 175503 (2010)

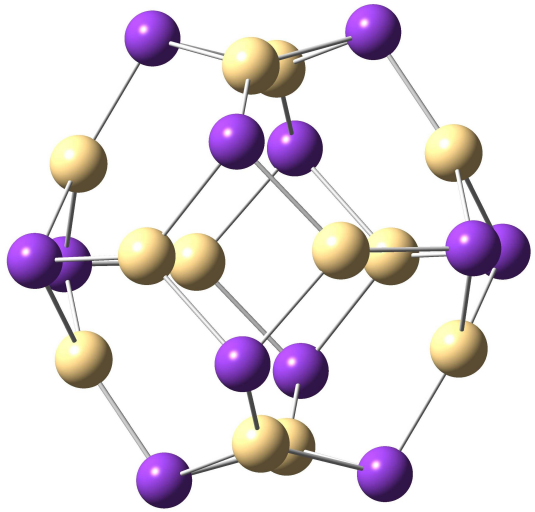
Nanoclusters as building blocks

Buckminsterfullerene → Fullerite



Nanoclusters must retain their structure

Nanoclusters as building blocks

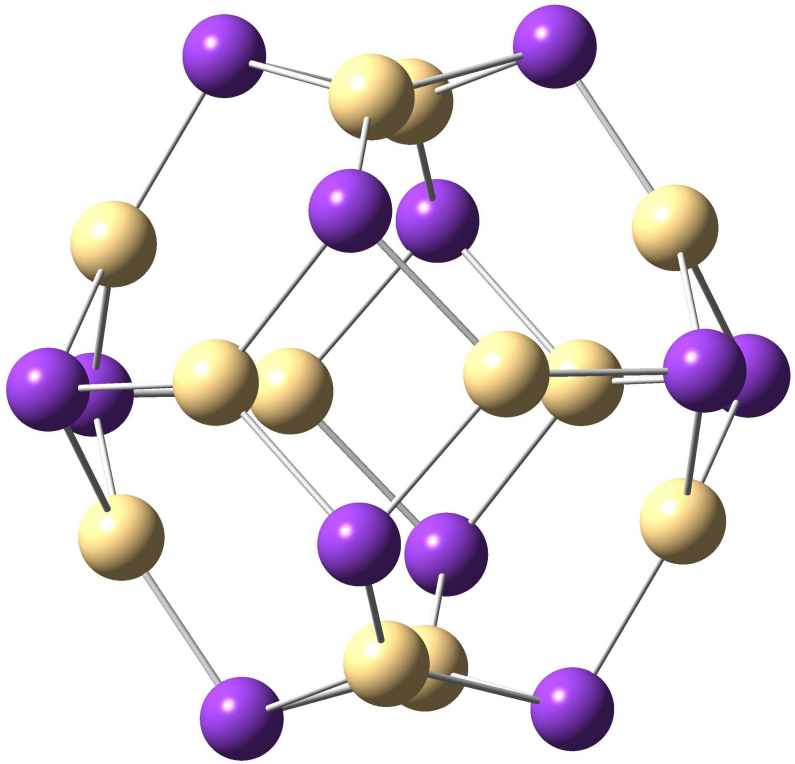


$M_{12}X_{12}$

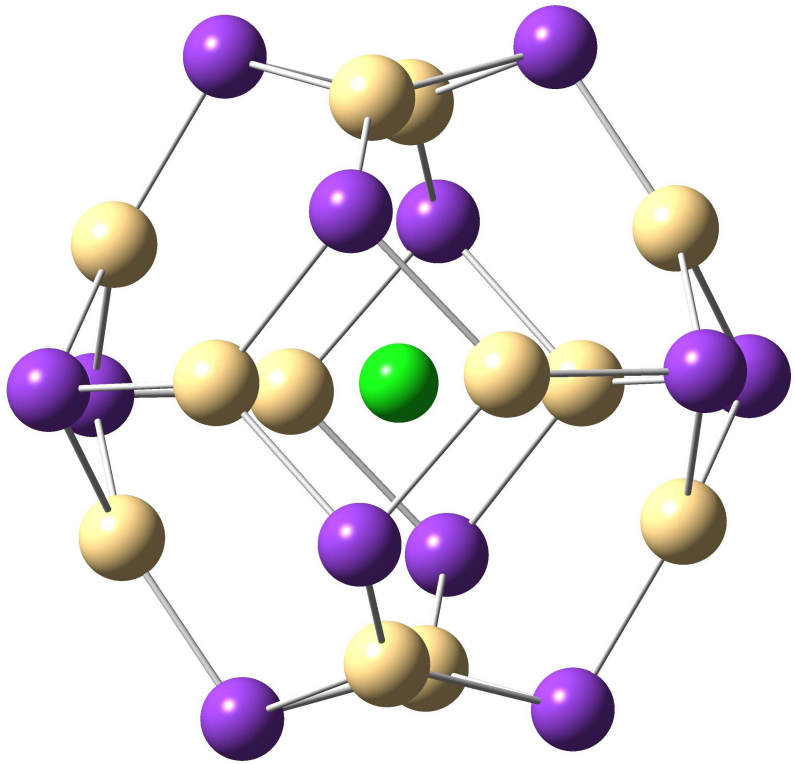
$(BN)_{12}$, $(MgO)_{12}$, $(ZnO)_{12}$, $(AlN)_{12}$, $(GaN)_{12}$

Matxain et al. *J. Phys. Chem. C* **111**, 13354 (2007)
Carrasco et al. *Phys. Rev. Lett.* **99**, 235502 (2007)
Yong et al. *Phys. Chem. Chem. Phys.* **13**, 16182 (2011)
Yong et al. *J. Phys. Chem. C* **115**, 6455 (2011)

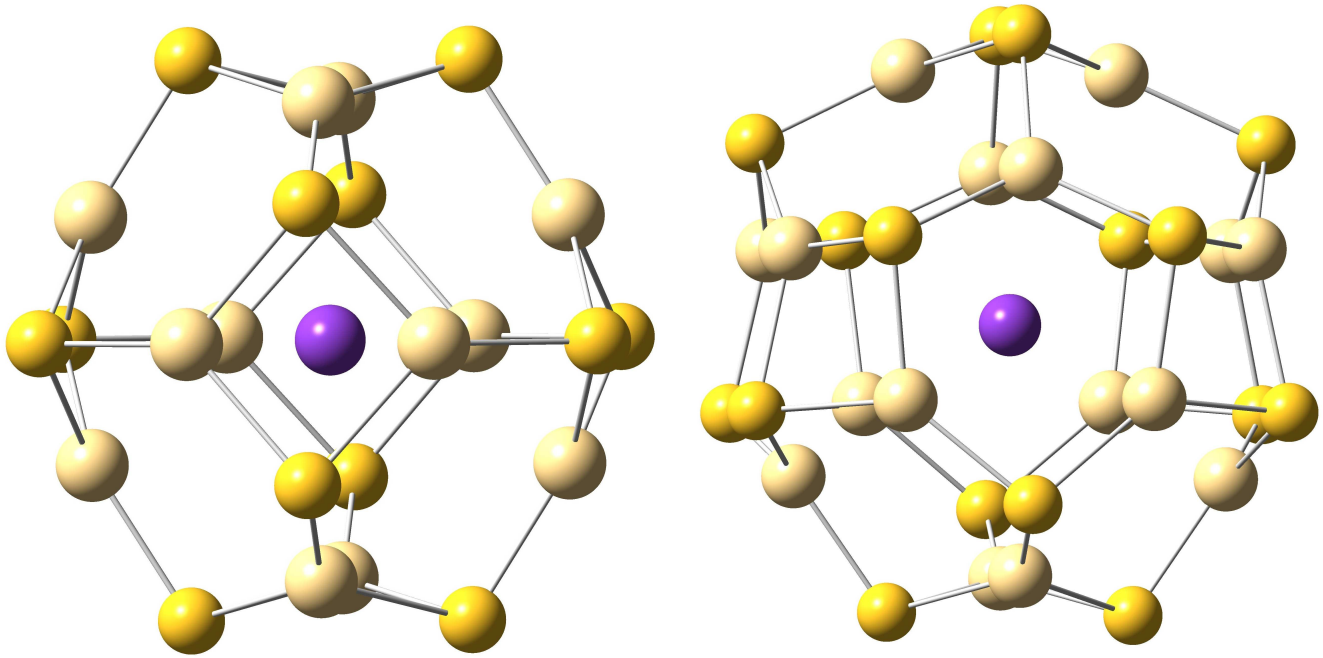
Endohedral Doping



Endohedral Doping



Present Work



$X@Cd_iS_i$, X= K, Cl, Br; i= 12, 16

Methods

Gas phase

- Monomers and dimers in gas phase
  - Geometry Optimization and Frequency Calculations
  - Gaussian09 code
  - All calculations within DFT$\rightarrow$ gradient corrected hybrid B3LYP functional
  - 6-311+G(d) for alkali and halogen dopant atoms
  - SKBJ(d) core potentials and basis set for nanoparticle atoms
  - APT charges

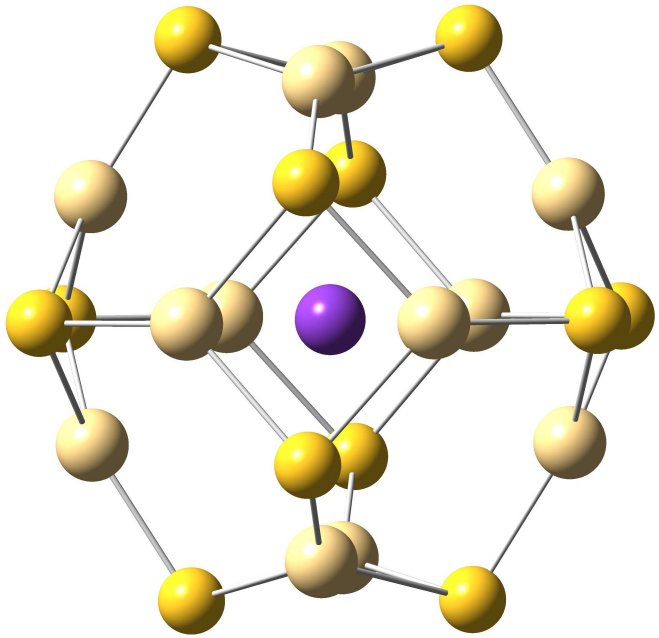
- Solid state
  - Intra- and inter-cell parameters optimized
  - SIESTA 2.0 code
  - All calculations within DFT$\rightarrow$ GGA, rPBE functional
  - DZP basis set
  - Troullier-Martins norm-conserving pseudopotentials
  - $\triangle$E$_{PAO}$=50 meV ; E$_{cutoff}$= 300 Ry ; 18 K points

Matxain et al. *J. Phys. Chem. C* **111**, 13354 (2007)
Matxain et al. *Chem. Eur. J.* **15**, 5138 (2009)

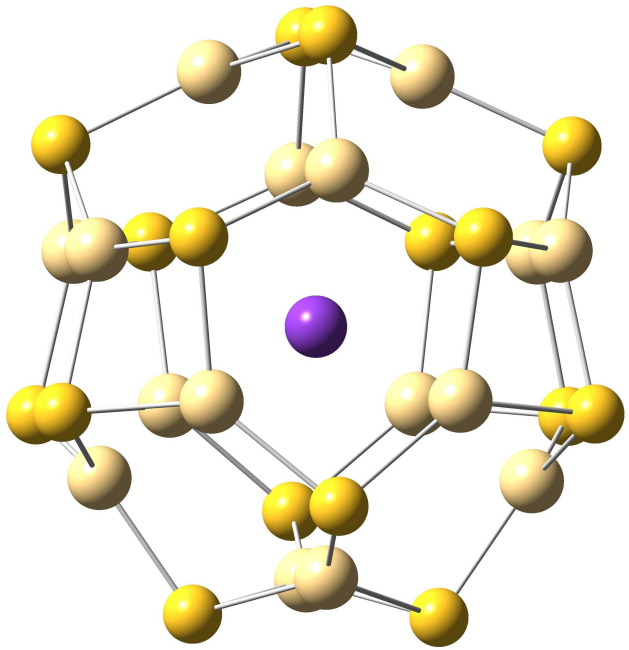
Results

X@Cd_iS_i Monomers

$X@Cd_iS_i$; i= 12, 16; X= K, Cl, Br



$X@Cd_{12}S_{12}$



$X@Cd_{16}S_{16}$

light yellow = Cd; dark yellow = S; violet = dopant atom

- X@Cd_iS_i ; i= 12, 16; X= K, Cl, Br

Jimenez-Izal et al. *J. Phys. Chem. C* **114**, 2476 (2010)

- $X@Cd_iS_i$; i= 12, 16; X= K, Cl, Br

- $Na@Cd_iS_i$: QMD calculations:$\rightarrow$ thermally unstable

Jimenez-Izal et al. *J. Phys. Chem. C* **114**, 2476 (2010)

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- IE (K) $\sim$ IE(K@Cd_iS_i) $<$ IE (Cd_iS_i)

Jimenez-Izal et al. *J. Phys. Chem. C* **114**, 2476 (2010)

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- Na@Cd_iS_i: QMD calculations:$\rightarrow$ thermally unstable
- IE (K) $\sim$ IE(K@Cd_iS_i) $<$ IE (Cd_iS_i)
- EA (Cd_iS_i) $<$ EA (X) $<$ EA (X@Cd_iS_i)

Jimenez-Izal et al. *J. Phys. Chem. C* **114**, 2476 (2010)

- $X@Cd_iS_i$; i= 12, 16; X= K, Cl, Br

- $Na@Cd_iS_i$: QMD calculations:$\rightarrow$ thermally unstable
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- EA (Cd_iS_i) $<$ EA (X) $<$ EA ($X@Cd_iS_i$)
- EA ($X@Cd_iS_i$) $\sim$ IE($K@Cd_iS_i$)

Jimenez-Izal et al. *J. Phys. Chem. C* **114**, 2476 (2010)

- X@Cd_iS_i ; i= 12, 16; X= K, Cl, Br

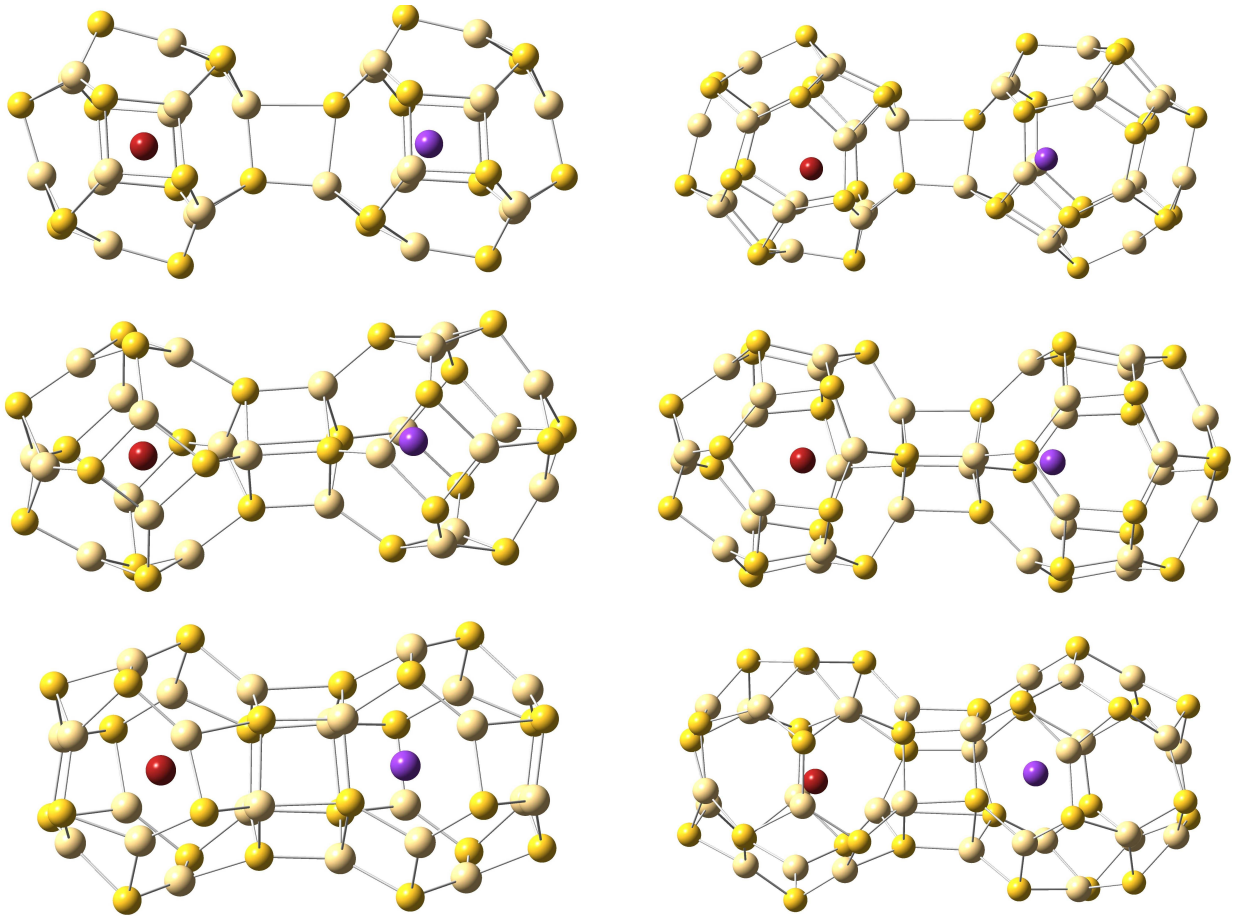
- Na@Cd_iS_i: QMD calculations:$\rightarrow$ thermally unstable
- IE (K) $\sim$ IE(K@Cd_iS_i) $<$ IE (Cd_iS_i)
- EA (Cd_iS_i) $<$ EA (X) $<$ EA (X@Cd_iS_i)
- EA (X@Cd_iS_i) $\sim$ IE(K@Cd_iS_i)
- $q_K \sim$ 0.4; $q_{Cl,Br} \sim$ -0.6

Jimenez-Izal et al. *J. Phys. Chem. C* **114**, 2476 (2010)

K@Cd_iS_i-X@Cd_iS_i Dimers

Resulting Structures

(K-Br)@Cd_iS_i



light yellow = Cd; dark yellow = S; violet = K; red = Br

	R (Å)	q_K	q_X	E_{dim} (kcal/mol)	$\triangle\varepsilon_{HL}$(eV)
$Cd_{12}S_{12}$ **(H-H)**	8.77	-	-	-38.28	3.32
$Cd_{12}S_{12}$ **(S-S)**	9.82	-	-	-29.06	3.43
$Cd_{12}S_{12}$ **(E-E)**	10.26	-	-	-21.22	3.45
(K-Cl)@$Cd_{12}S_{12}$ **(H-H)**	7.75	0.49	-0.76	-102.39	2.74
(K-Br)@$Cd_{12}S_{12}$ **(H-H)**	7.67	0.49	-0.78	-103.54	2.76
(K-Cl)@$Cd_{12}S_{12}$ **(S-S)**	8.78	0.51	-0.79	-85.09	2.44
(K-Br)@$Cd_{12}S_{12}$ **(S-S)**	8.86	0.51	-0.81	-85.55	2.42
(K-Cl)@$Cd_{12}S_{12}$ **(E-E)**	9.65	0.52	-0.80	-67.80	2.00
(K-Br)@$Cd_{12}S_{12}$ **(E-E)**	9.58	0.52	-0.82	-68.49	1.98

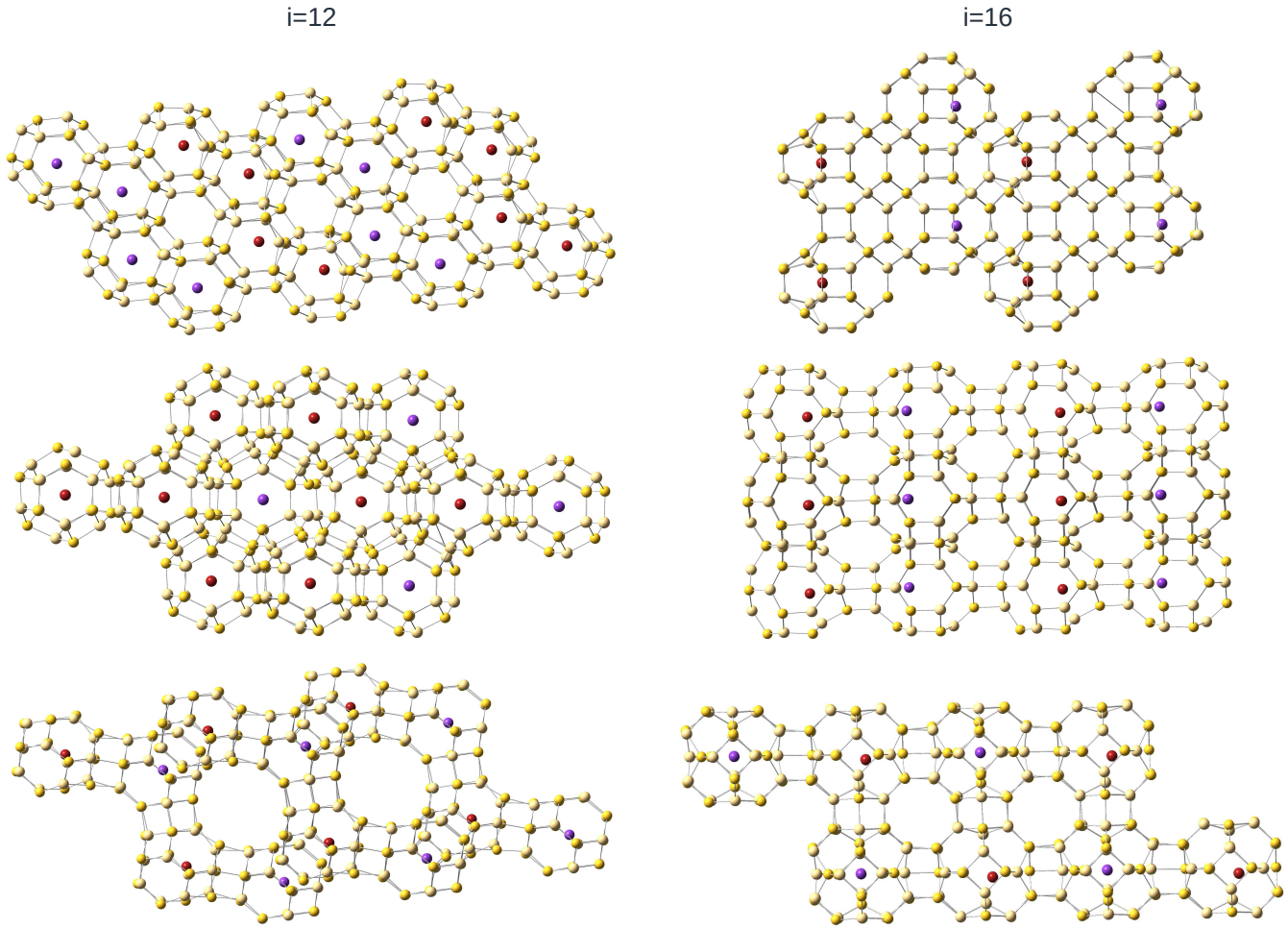
$\triangle E_{dim} < 0 \rightarrow$ thermodynamically stable

After doping: R, $\triangle\varepsilon_{HL} \downarrow$, Stability $\uparrow$

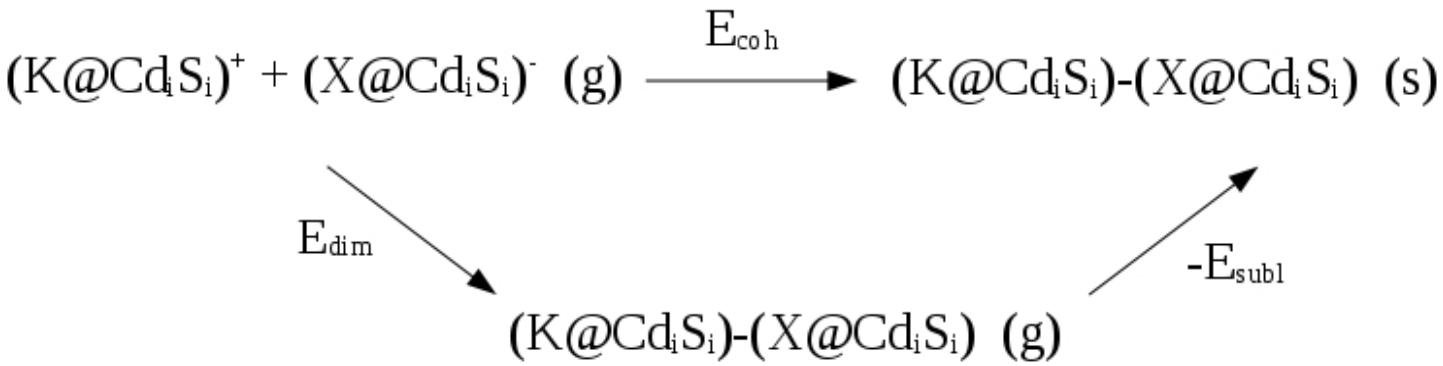
Solids

Resulting Structures

(K-Br)@Cd_iS_i



E-E $\longrightarrow$SOD ; S-S $\longrightarrow$ LTA ; H-H $\longrightarrow$ FAU



Jimenez-Izal et al. *Phys. Chem. Chem. Phys.* **14**, 9676 (2012)

$Cd_{12}S_{12}$ Solids

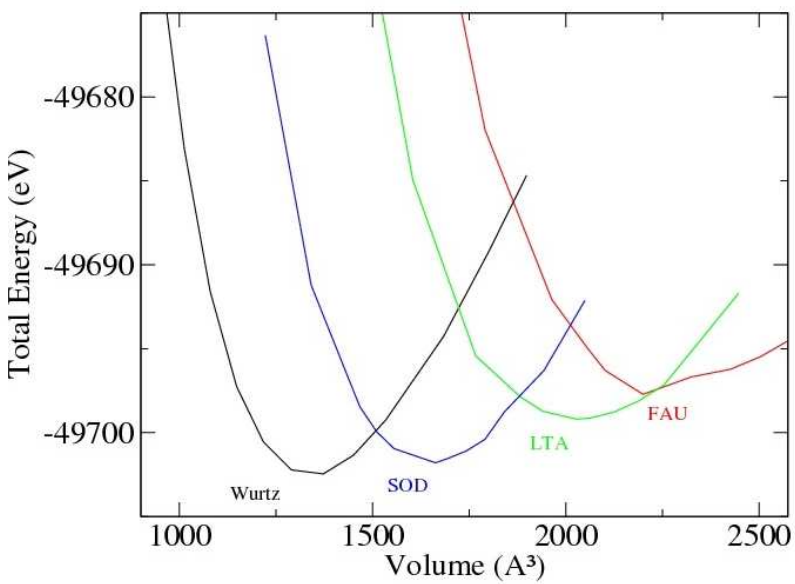
Unit Cell	V (Å^3)	E_{coh}(eV)	$\triangle_\Gamma$(eV)
FAU-$Cd_{12}S_{12}$	2324.90	-1.13	1.67
LTA-$Cd_{12}S_{12}$	2028.18	-1.55	1.66
SOD-$Cd_{12}S_{12}$	1662.51	-1.63	1.31
FAU (K-Cl)@$Cd_{12}S_{12}$	2272.52	-1.65	1.63
FAU (K-Br)@$Cd_{12}S_{12}$	2325.56	-1.64	1.65
LTA (K-Cl)@$Cd_{12}S_{12}$	2031.61	-2.00	1.22
LTA (K-Br)@$Cd_{12}S_{12}$	2030.51	-2.02	1.33
SOD (K-Cl)@$Cd_{12}S_{12}$	1664.62	-2.42	1.22
SOD (K-Br)@$Cd_{12}S_{12}$	1661.02	-2.43	1.28

$E_{coh} < 0 \rightarrow$ thermodynamically stable

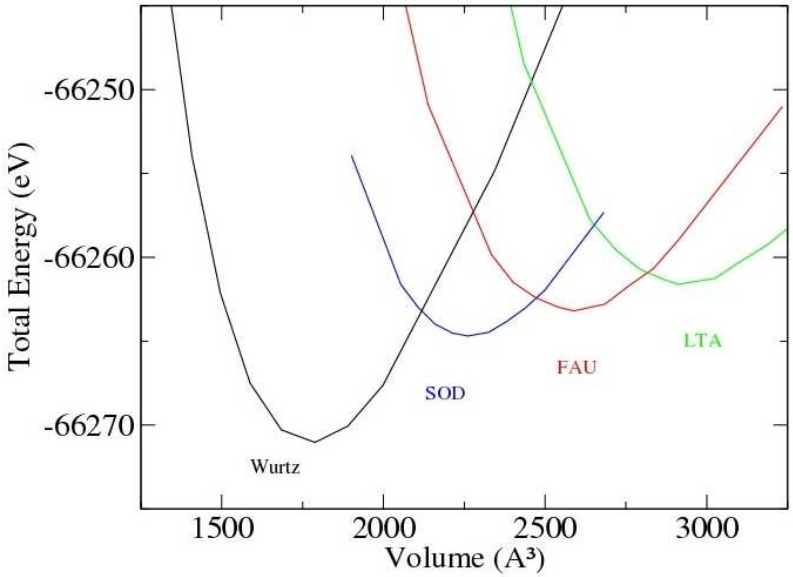
After doping: Stability $\uparrow$, $\triangle_\Gamma \downarrow$

E_{coh}(wurtzite)= -2.65 eV ; Datta et al. *J. Phys. Chem. C* **112**, 8206 (2008)

$Cd_{12}S_{12}$

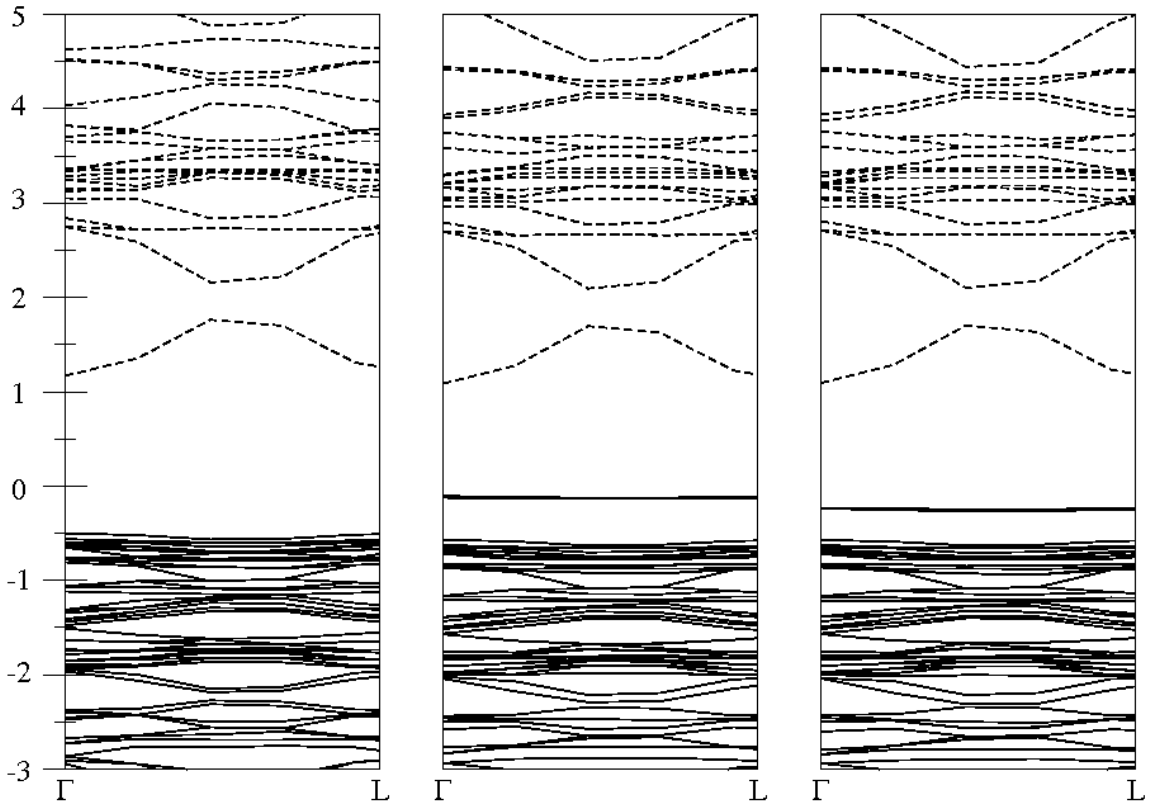


$Cd_{16}S_{16}$



Bands

LTA $Cd_{12}S_{12}$ | LTA (K-Cl)$Cd_{12}S_{12}$ | LTA (K-Br)$Cd_{12}S_{12}$

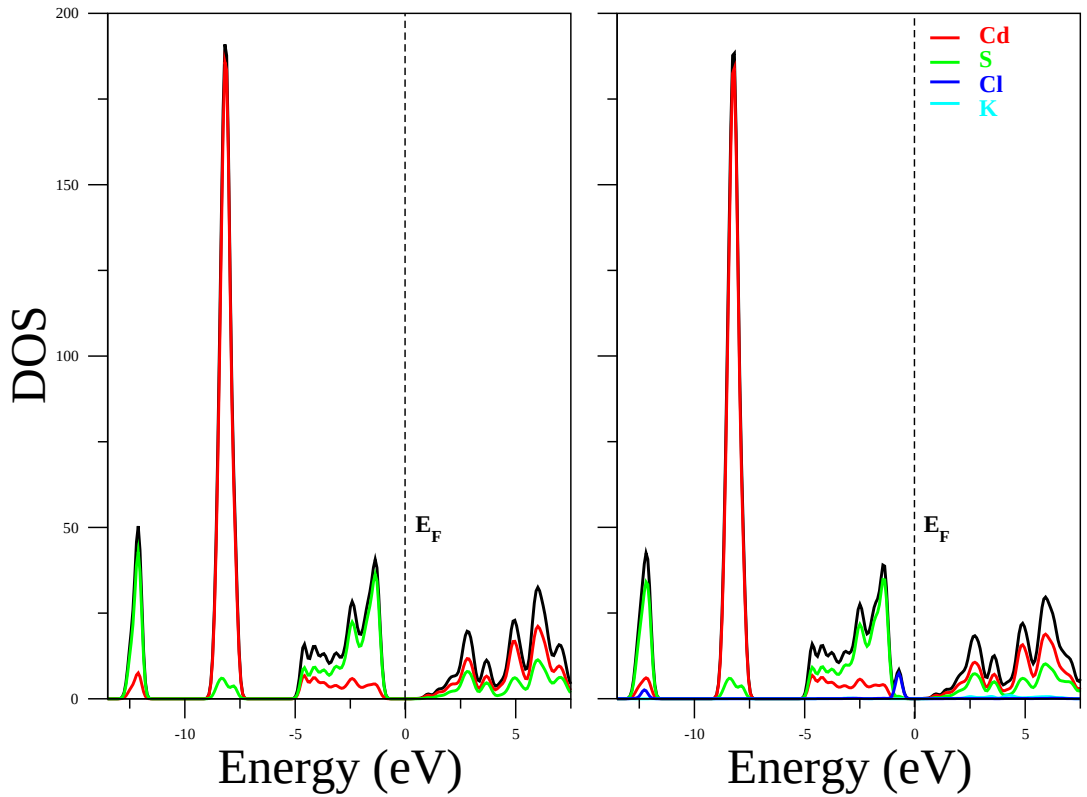


$\triangle_\Gamma$= 1.66 | $\triangle_\Gamma$= 1.22 | $\triangle_\Gamma$= 1.33

Projected Density of States

LTA $Cd_{12}S_{12}$

LTA (K-Cl)$Cd_{12}S_{12}$



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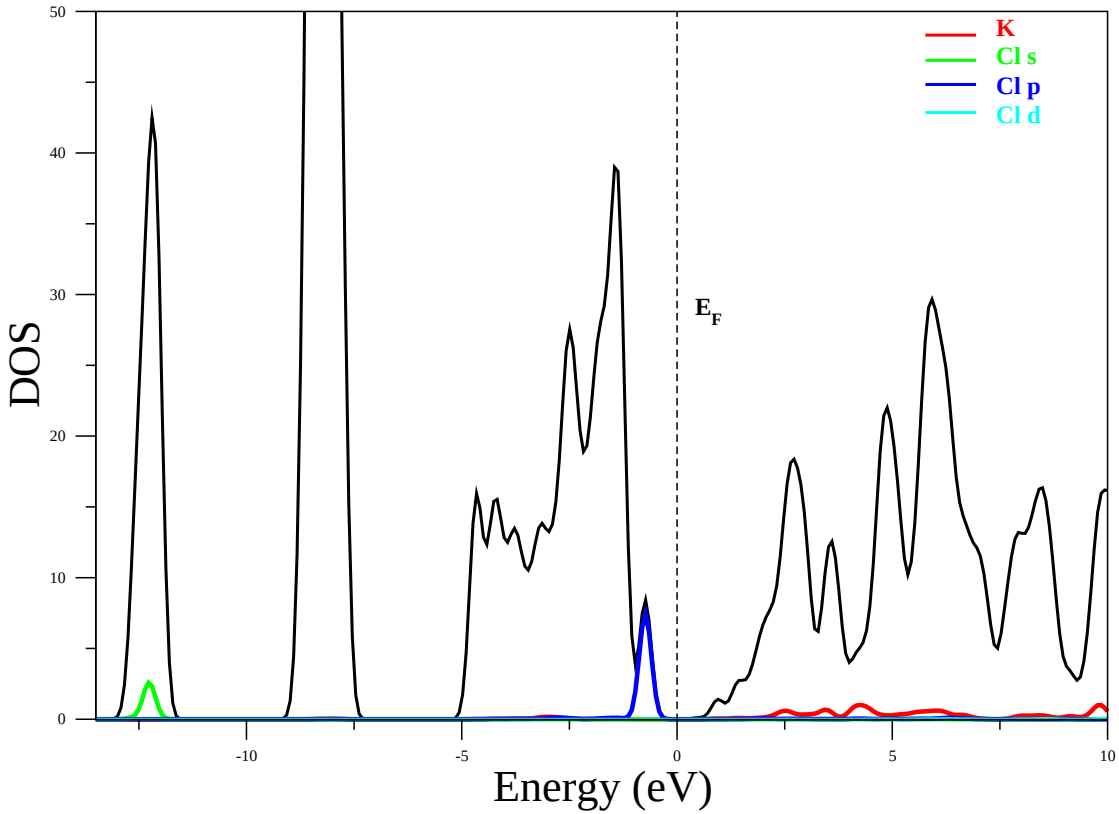

Conclusions

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  - Increases the stability
  - Decreases the band-gap
- Low-density and nanoporous
- Applications in hetereogeneous catalysis, atomic sieves, ...

Acknowledgments

All the group at the University of the Basque Country