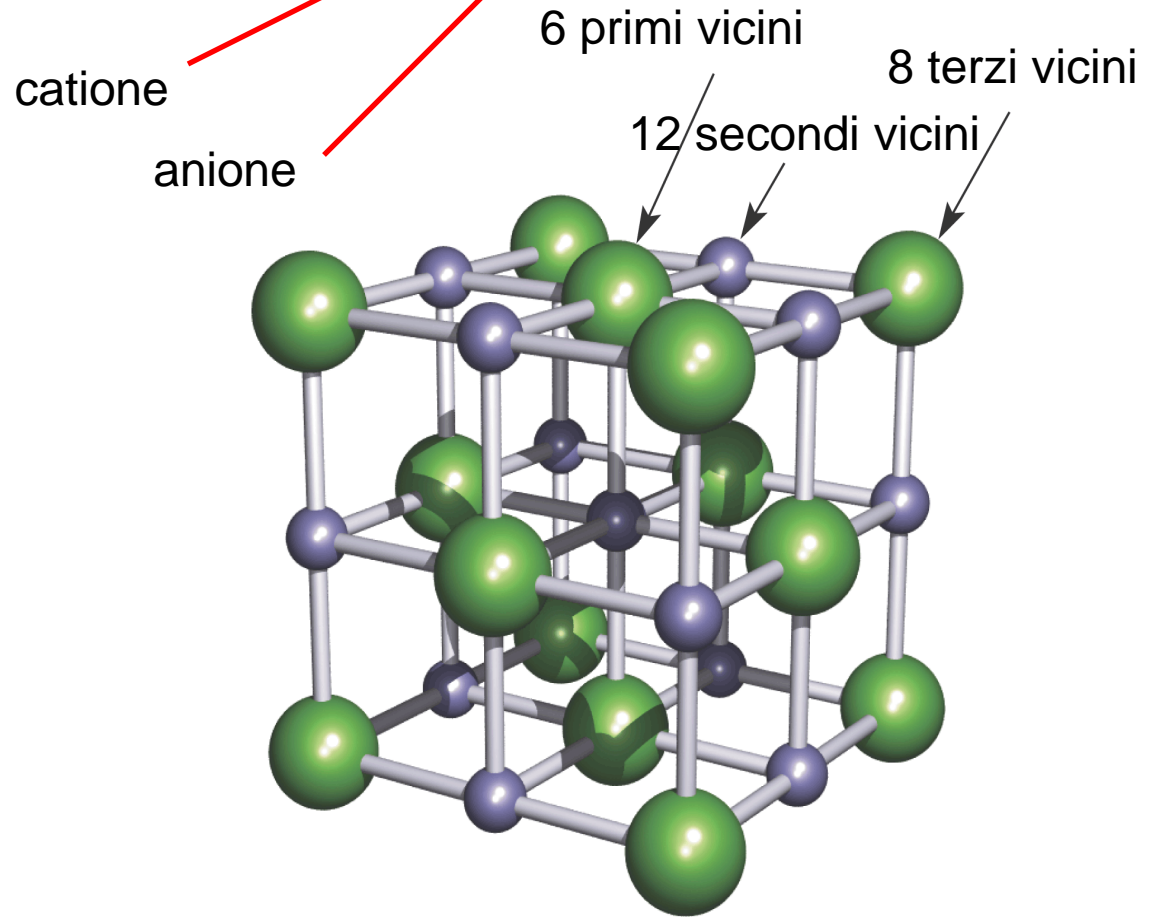
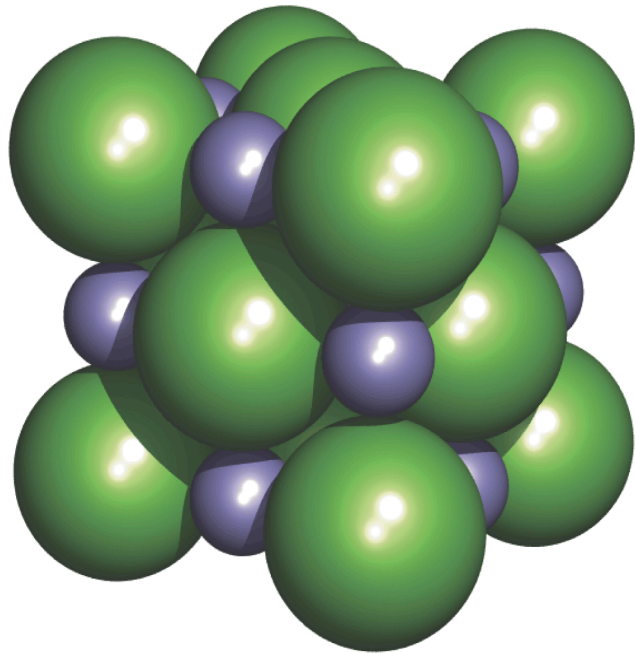


Solidi ionici

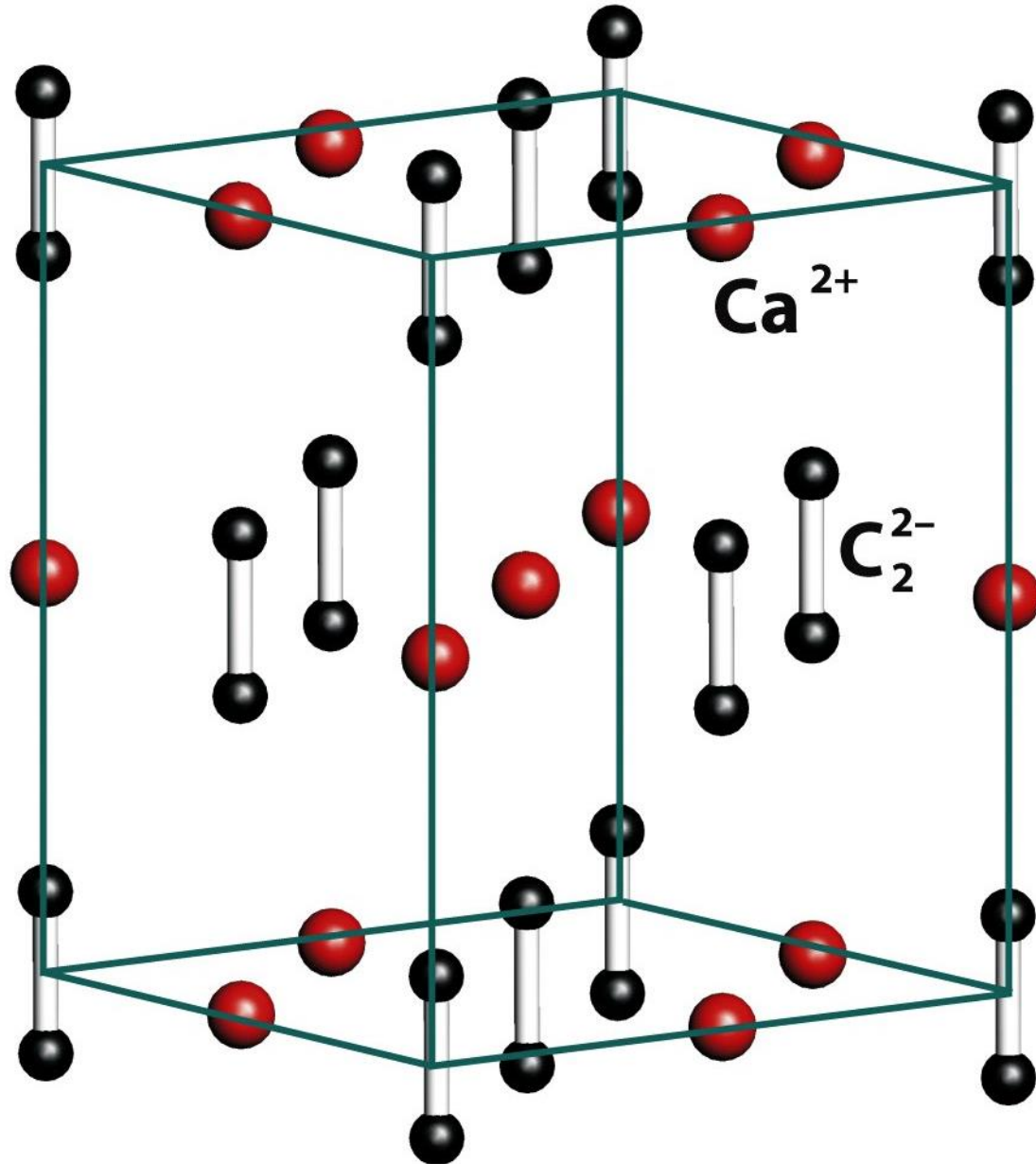
Molte delle strutture dei solidi ionici semplici possono essere considerate derivanti da reticoli nei quali gli ioni più grandi, usualmente gli anioni, si impaccano tra loro formando strutture ccp o hcp e i contro-ioni più piccoli, normalmente i cationi, occupano gli interstizi ottaedrici e/o tetraedrici nel reticolo

Fasi binarie AX: struttura del **salgemma** coordinazione-(6,6)

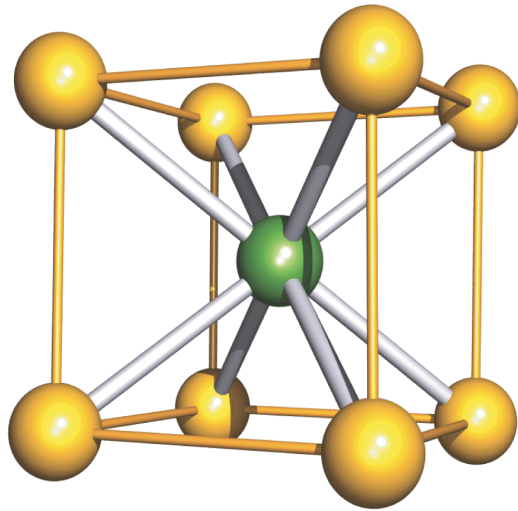


Reticolo ccp dei Cl^- , Na^+ in tutti i siti ottaedrici, $Z = 4$

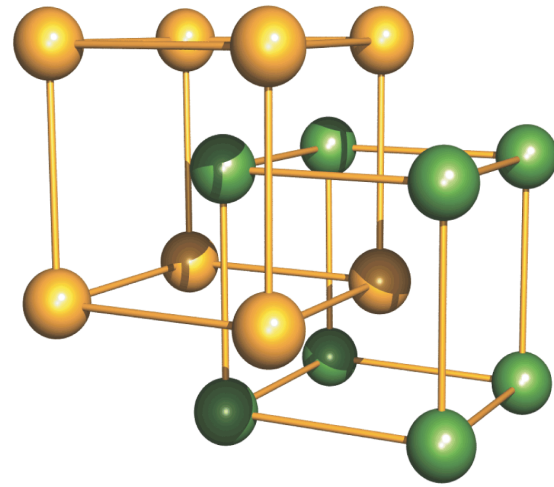
Struttura del salgemma in CaC_2



Fasi binarie AX: struttura del **cloruro di cesio** coordinazione-(8,8)



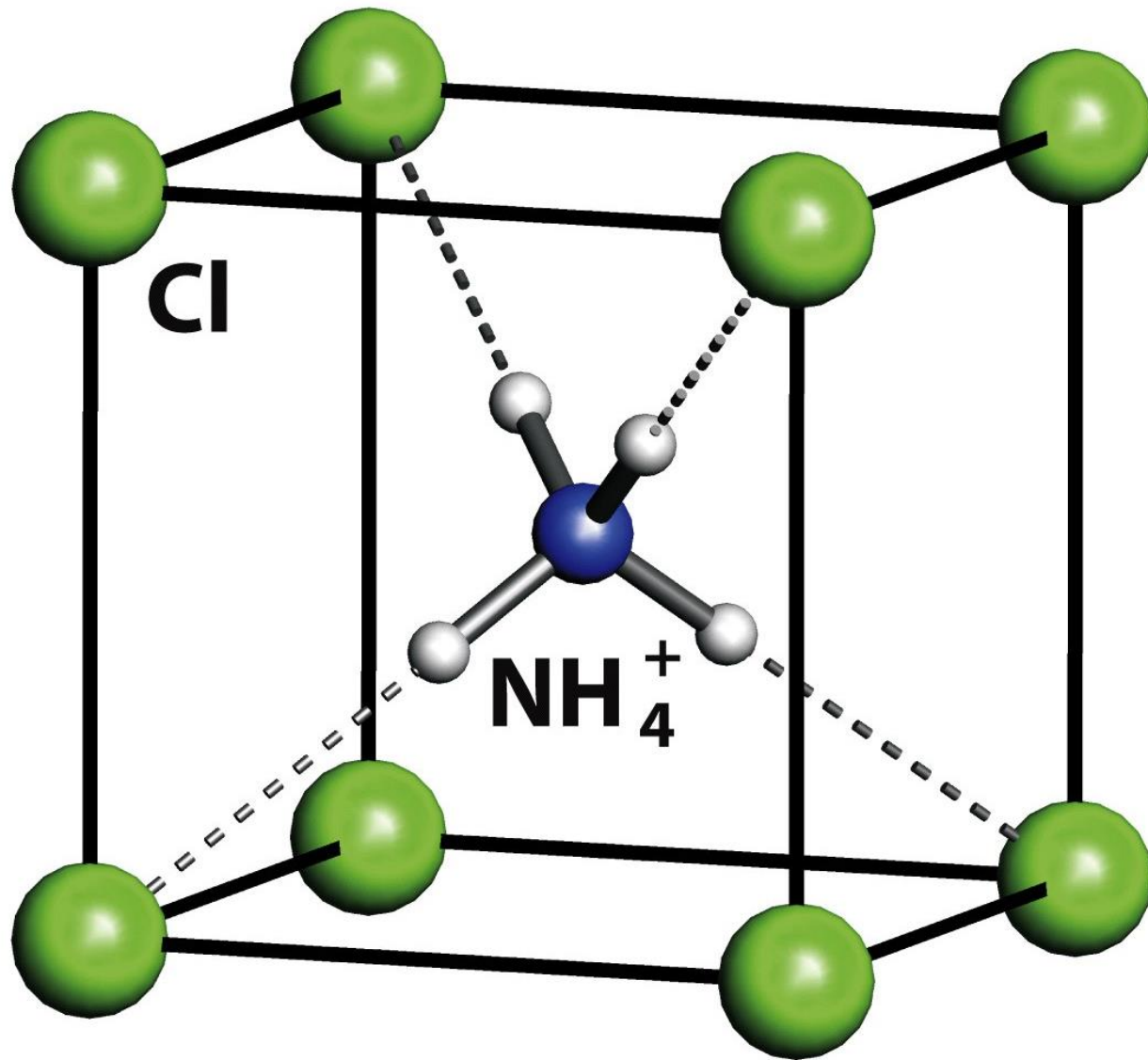
(a)



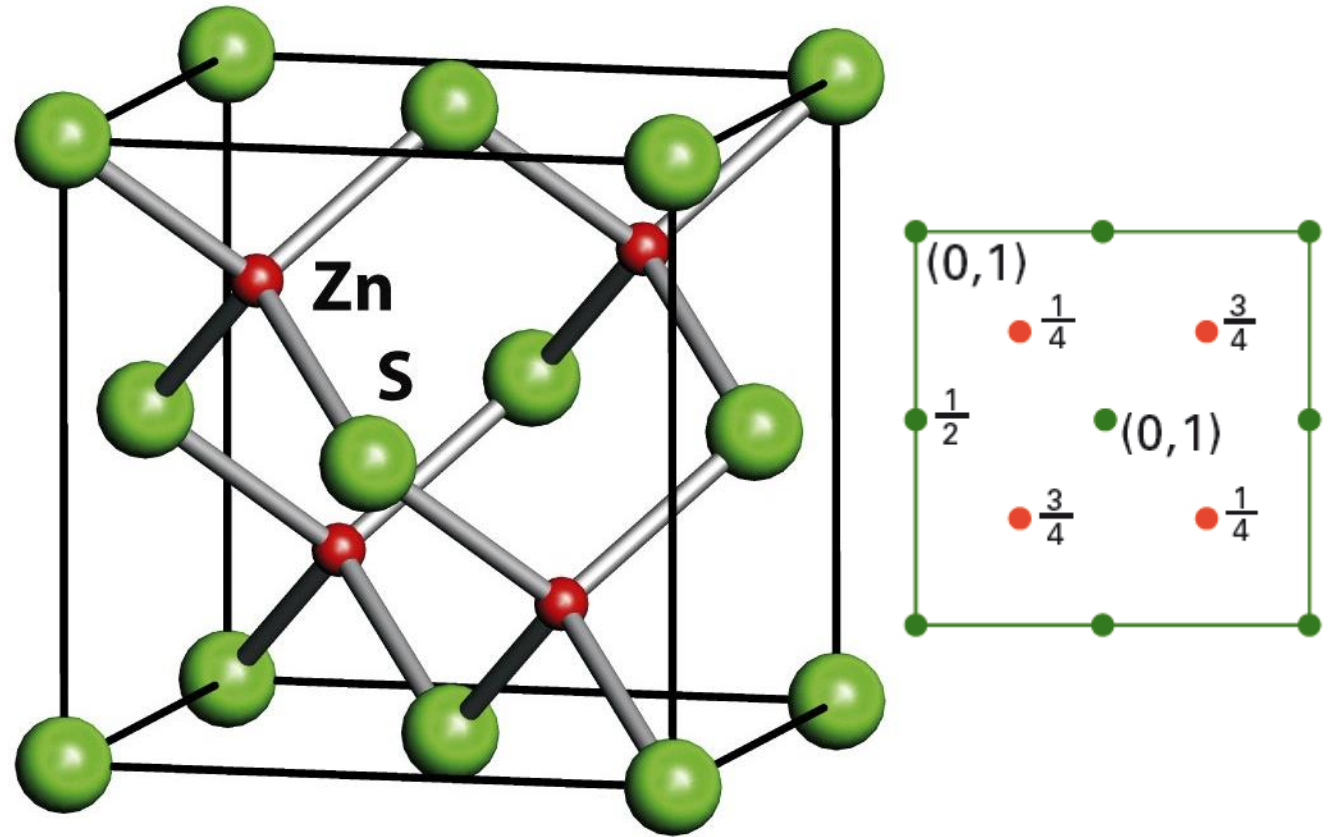
(b)

Per ioni con raggi simili, $Z = 1$

Struttura del cloruro di cesio in NH_4Cl

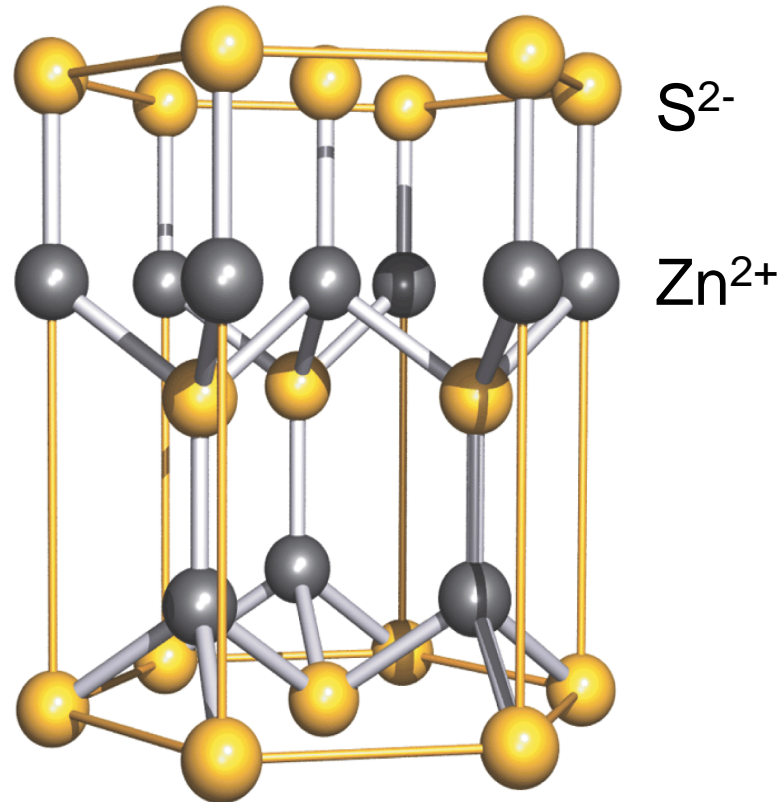


Fasi binarie AX: struttura della **sfalerite** (ZnS) coordinazione-(4,4)



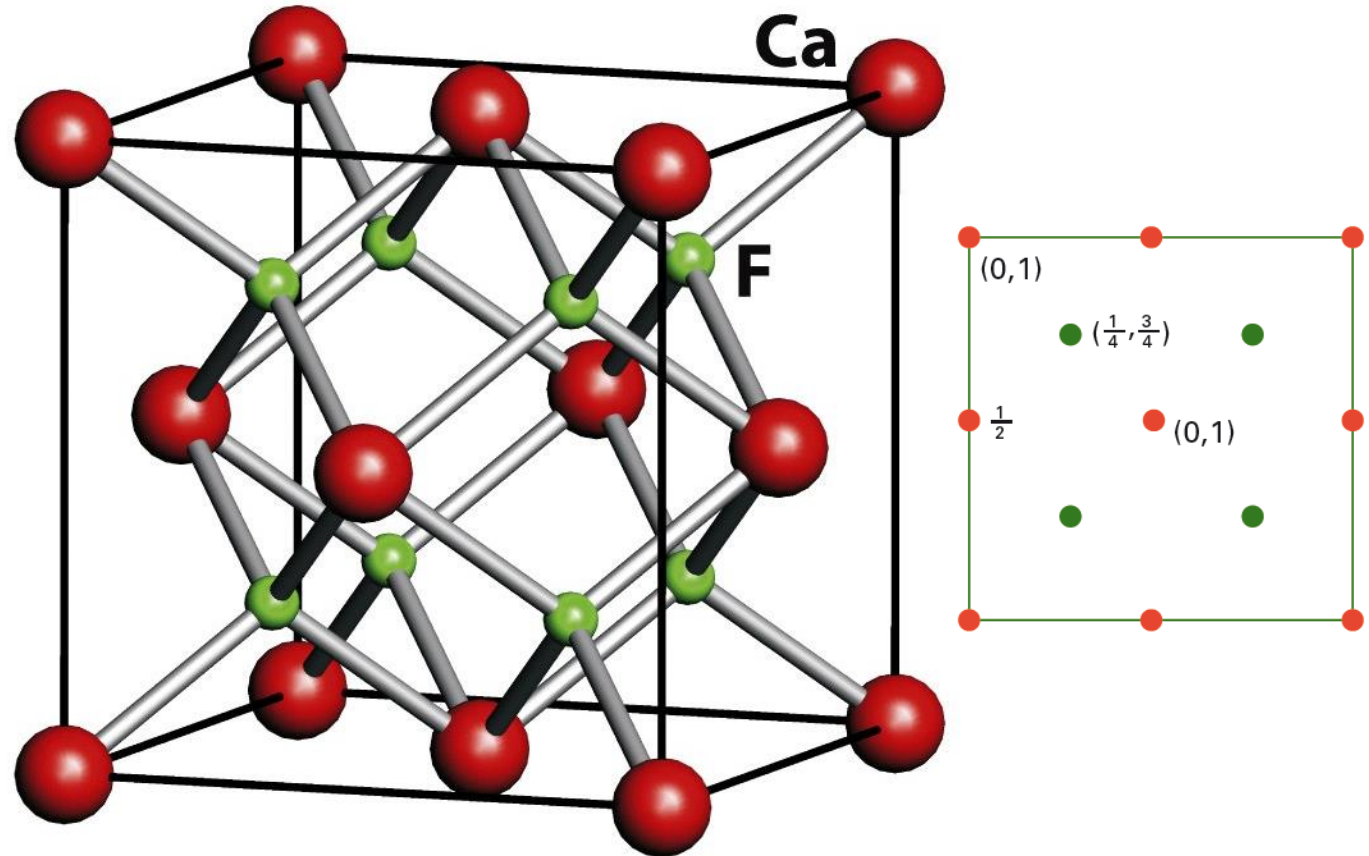
Reticolo ccp degli anioni, cationi in metà dei siti tetraedrici, $Z = 4$

Fasi binarie AX: struttura della **wurtzite** (ZnS) coordinazione-(4,4)



Reticolo hcp degli anioni, cationi in metà dei siti tetraedrici

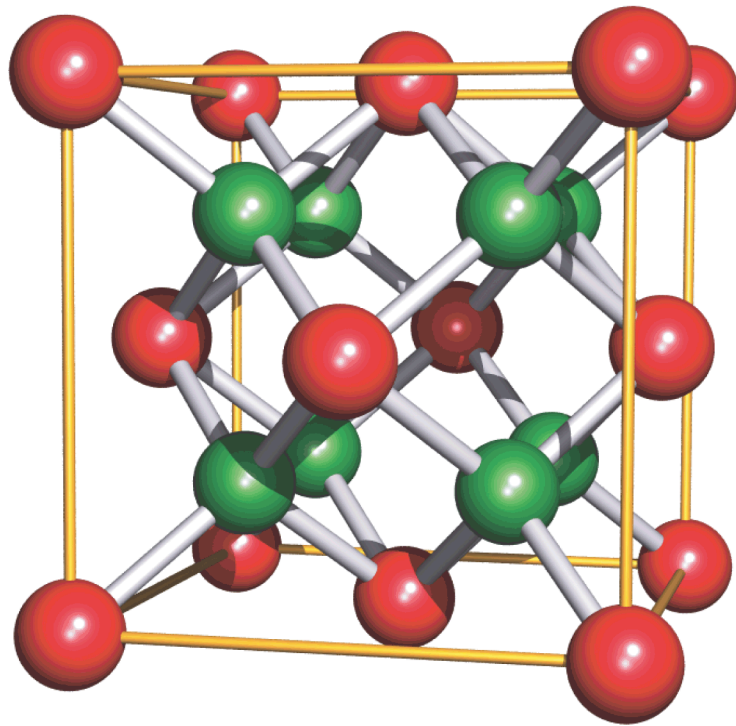
Fasi binarie AX_2 : struttura della **fluorite** (CaF_2) coordinazione-(8,4)



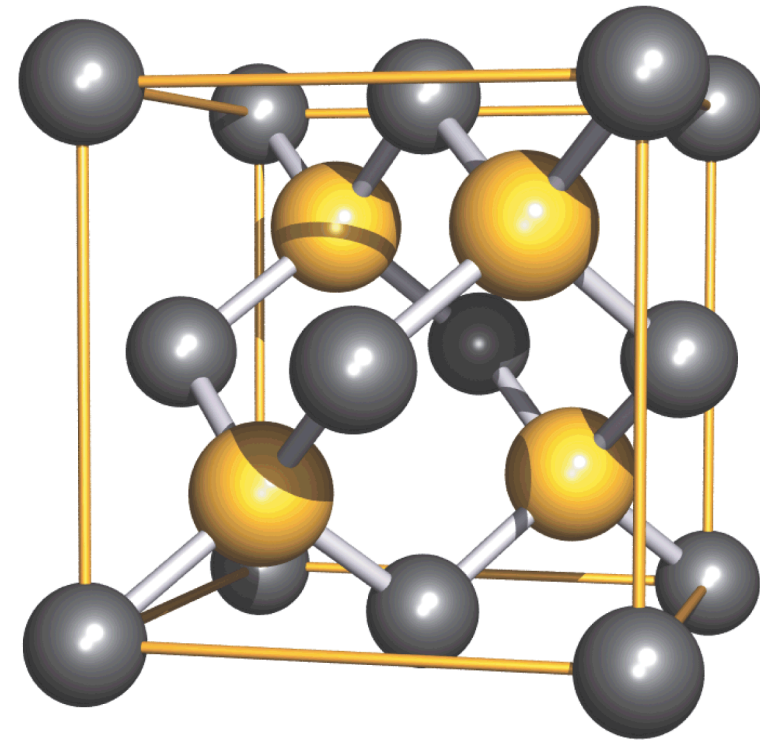
Reticolo ccp dei cationi, anioni in tutti i siti tetraedrici

Struttura della **antifluorite**, e.g. Li_2O , coordinazione-(4,8)

Strutture della fluorite e della blenda di zinco a confronto



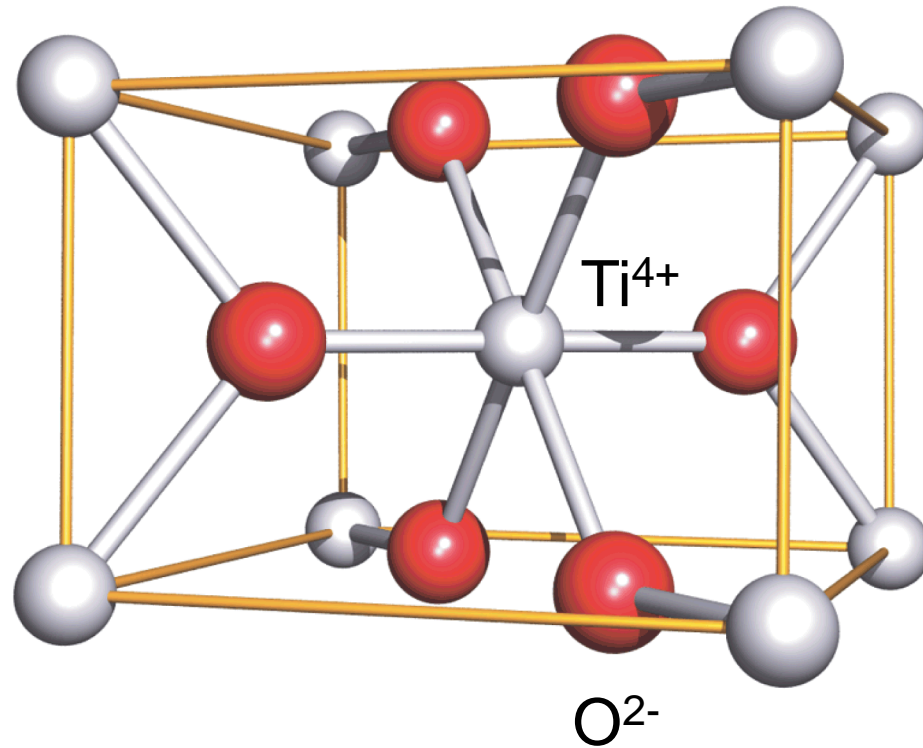
(a)



(b)

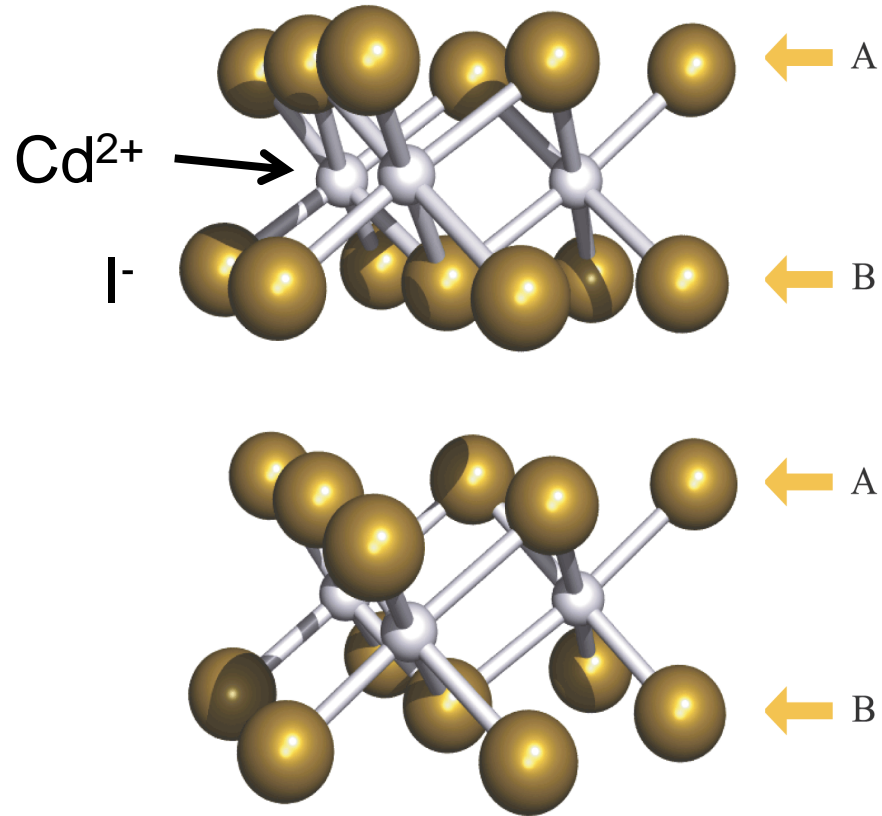


Fasi binarie AX_2 : struttura del **rutilo** (TiO_2)
coordinazione-(6,3) o (4+2,3)



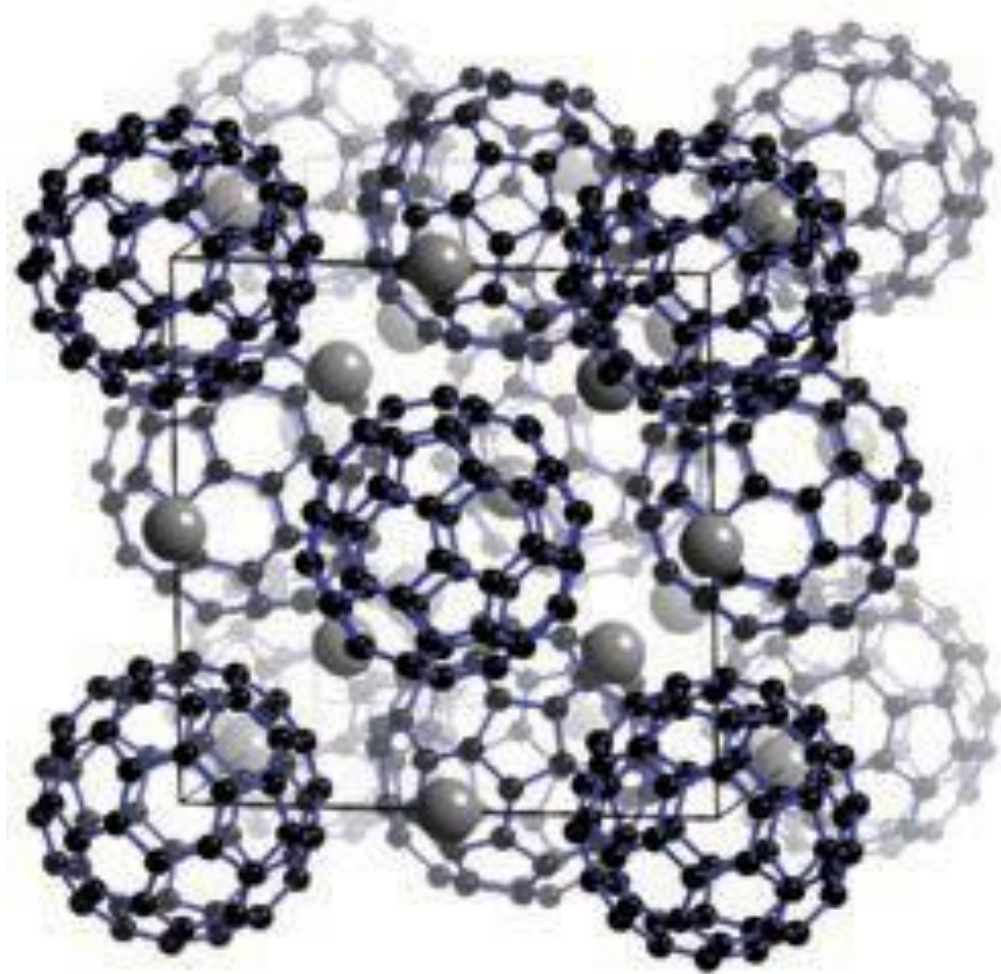
Reticolo hcp degli anioni, cationi in metà dei siti ottaedrici

Fasi binarie AX_2 : struttura a strati del CdI_2 coordinazione-(6,3)



Reticolo hcp degli anioni, cationi in metà dei siti ottaedrici

Esempio di fase binaria AX_3 : struttura di K_3C_{60}



Reticolo ccp di ioni C_{60}^{3-} e tutti gli interstizi ottaedrici e tetraedrici riempiti dagli ioni K^+

Relazione fra struttura dei solidi ionici e riempimento degli interstizi

Close-packing type	Hole filling	Structure type (exemplar)
Cubic (ccp)	All octahedral	Rock salt (NaCl)
	All tetrahedral	Fluorite (CaF ₂)
	Half tetrahedral	Sphalerite (ZnS)
Hexagonal (hcp)	All octahedral	Nickel arsenide (NiAs); with some distortion from perfect hcp
	Half octahedral	Rutile (TiO ₂); with some distortion from perfect hcp
	All tetrahedral	No structure exists: tetrahedral holes share faces
	Half tetrahedral	Wurtzite (ZnS)

Relazione fra tipo di struttura e rapporto dei raggi

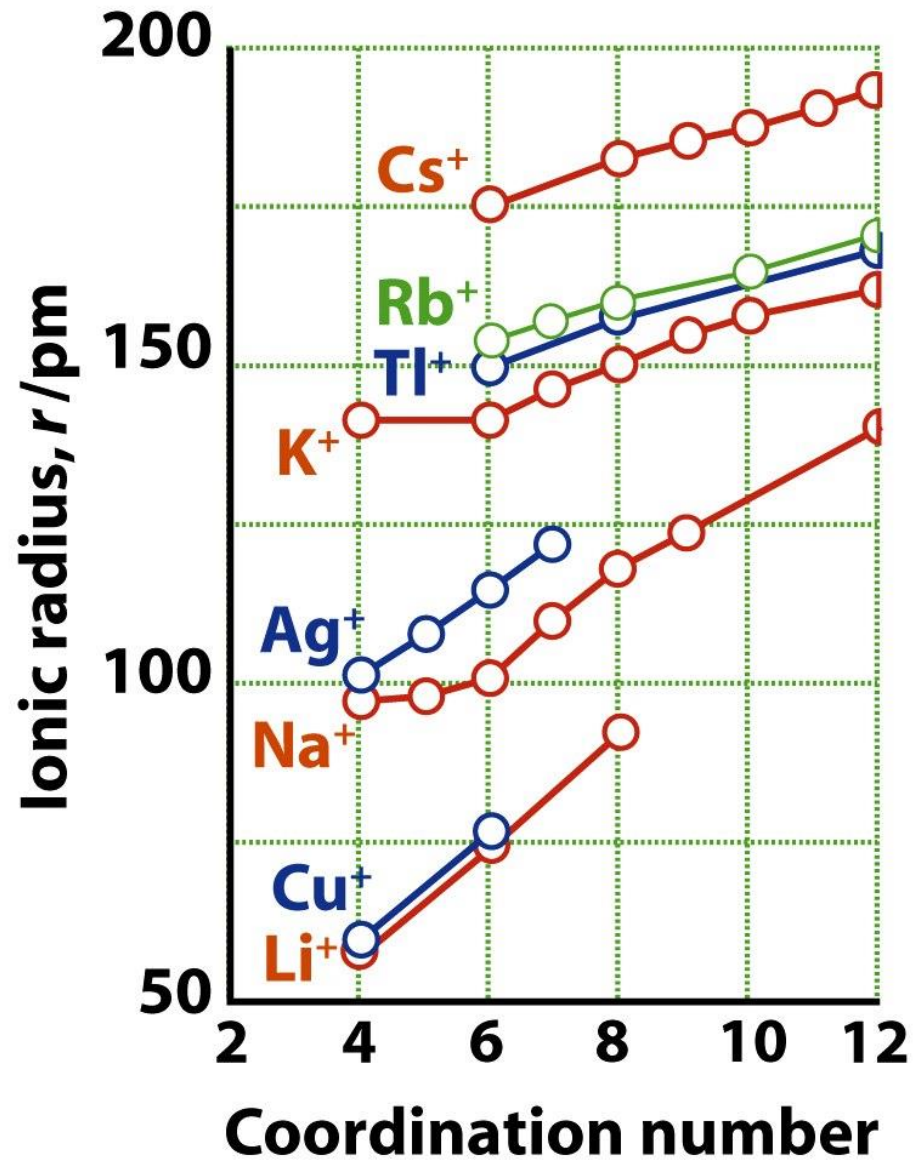
$$\gamma = \frac{r_{\text{small}}}{r_{\text{large}}}$$

Rapporto dei raggi (γ)	NC per stechiometrie 1:1 e 1:2	Tipo di struttura binaria AB	Tipo di struttura binaria AB ₂
1	12	Nessuna conosciuta	Nessuna conosciuta
0,732–1	8:8 e 8:4	CsCl	CaF ₂
0,414–0,732	6:6 e 6:3	NaCl (ccp), NiAs (hcp)	TiO ₂
0,225–0,414	4:4	ZnS (ccp e hcp)	

NC sta per numero di coordinazione.

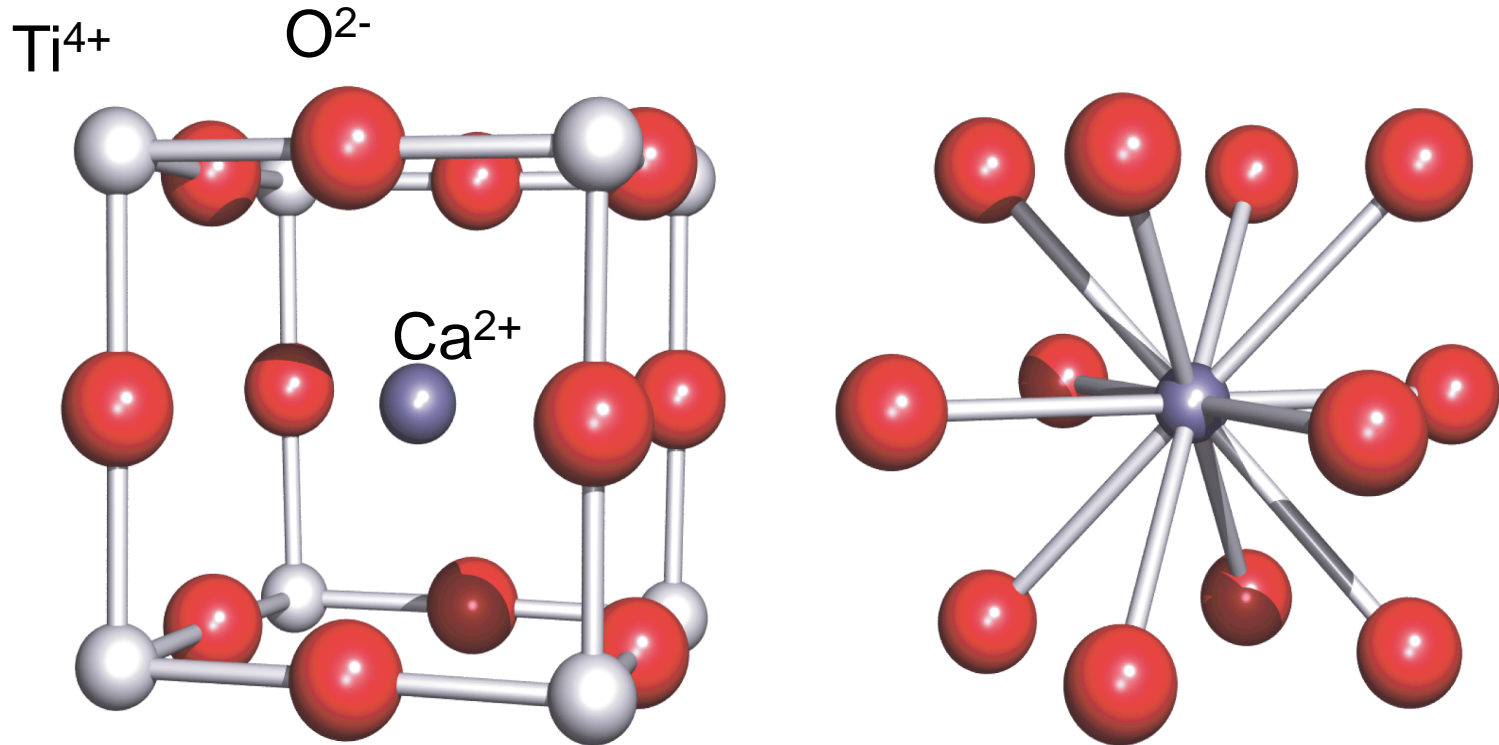
$$r(\text{Tl}^+) = 159 \text{ pm}, r(\text{Cl}^-) = 181 \text{ pm} \quad \gamma = 0.88$$

Raggi ionici e numero di coordinazione



Fasi ternarie ABX_3 : struttura della **perovskite** $CaTiO_3$

(dal mineralogista Russo Lev Perovski)

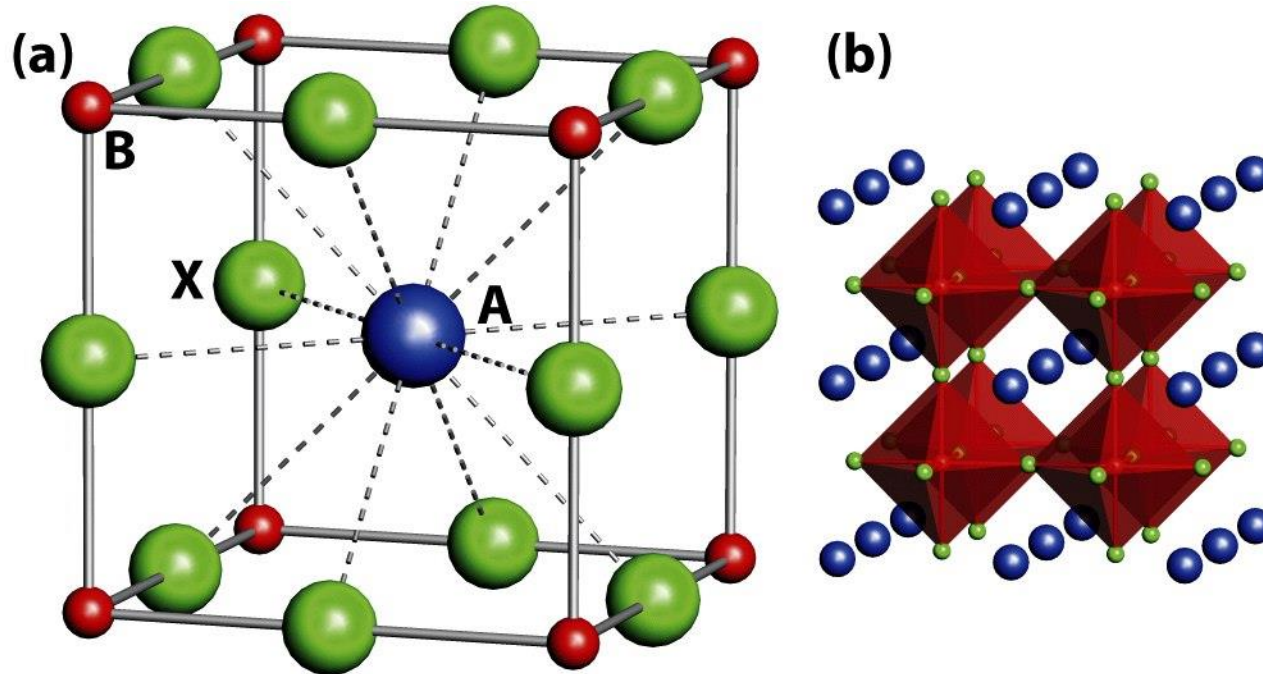


Struttura cubica

Lo ione Ca^{2+} (A) è circondato da 12 O^{2-} (X)

Lo ione Ti^{4+} (B) è circondato da 6 O^{2-} (X)

Fasi ternarie ABX_3 : struttura della **perovskite** $CaTiO_3$



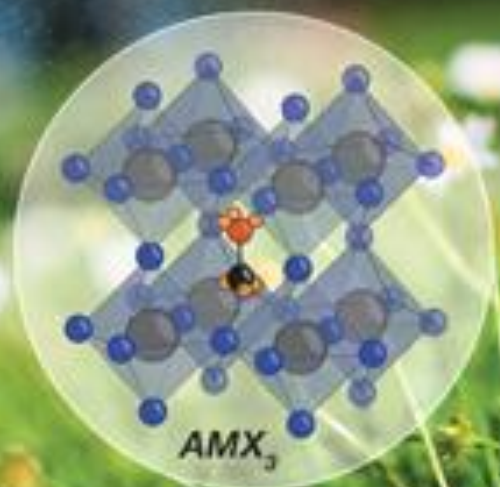
Coordinazione ottaedrica di B (Ti⁴⁺)

$$r_A > 110 \text{ pm}, r_B < 100 \text{ pm}$$

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CHEMICAL REVIEWS

PEROVSKITES



2019

Applicazioni di perovskiti

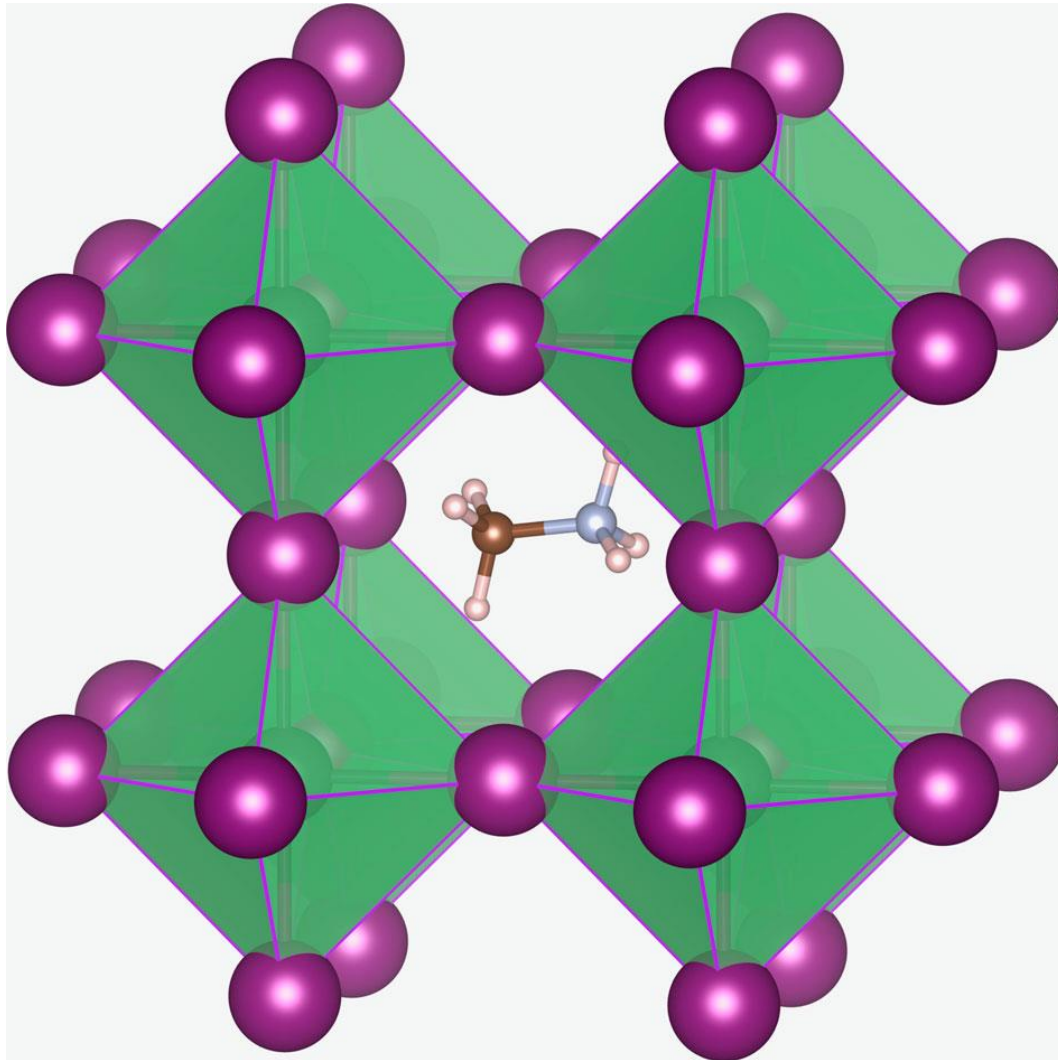
Mixed metal oxide	Properties of the material	Electronic applications
BaTiO ₃	Dielectric	Sensors; dielectric amplifiers; memory devices
Pb(Zr,Ti)O ₃	Dielectric; pyroelectric; piezoelectric	Memory devices; acoustic devices
La-doped Pb(Zr,Ti)O ₃	Electrooptic	Optical memory displays
LiNbO ₃	Piezoelectric; electrooptic	Optical memory displays; acoustic devices; wave guides; lasers; holography
K(Ta,Nb)O ₃	Pyroelectric; electrooptic	Pyrodetector; wave guides; frequency doubling

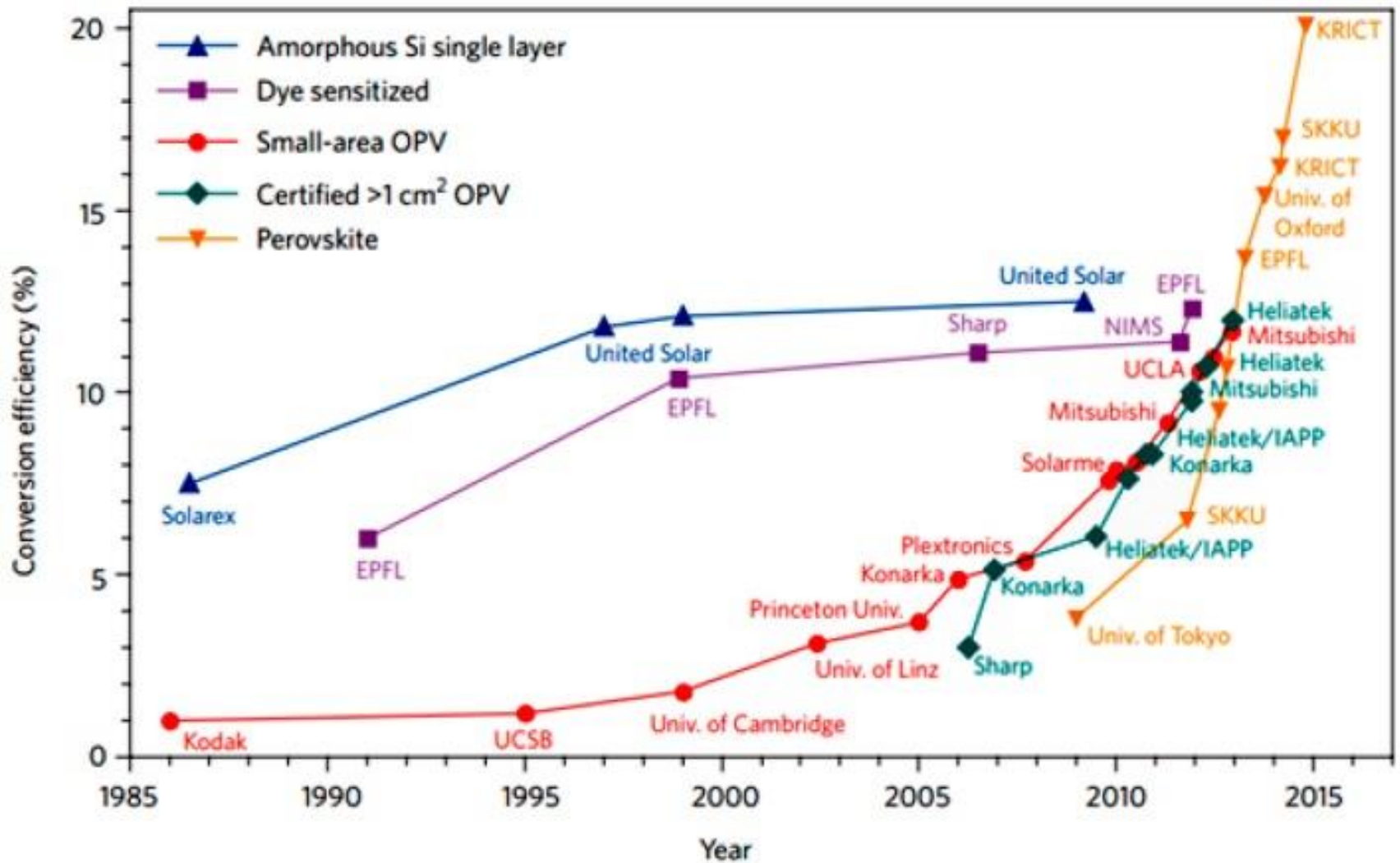
CsPbX₃ (X=Cl, Br, I) nanocrystals



Alogeno Perovskiti: $(\text{CH}_3\text{NH}_3)\text{PbI}_3$

Nelle alogeno-perovskiti, quando $X = \text{I}$ e $B = \text{Pb}$, il sito del catione A è molto grande





A comparison of perovskite efficiency progress with other kinds of photovoltaic (PV) devices

Al-Ashouri et al., *Science* **2020**, 370, 1300–1309.

RESEARCH

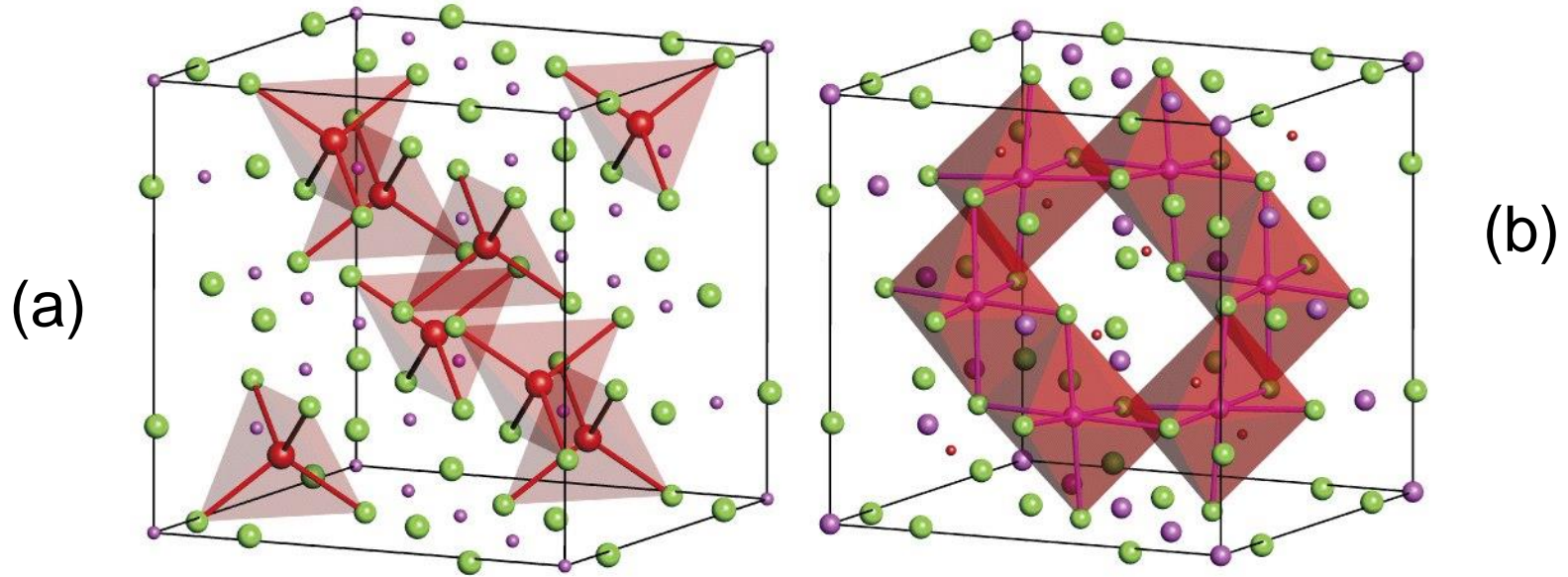
SOLAR CELLS

Monolithic perovskite/silicon tandem solar cell with >29% efficiency by enhanced hole extraction

Amran Al-Ashouri^{1*}, Eike Köhnen^{1*}, Bor Li¹, Artiom Magomedov², Hannes Hempel³, Pietro Caprioglio^{1,4}, José A. Márquez³, Anna Belen Morales Vilches⁵, Ernestas Kasparavicius², Joel A. Smith^{6,7}, Nga Phung⁶, Dorothee Menzel¹, Max Grischek^{1,4}, Lukas Kegelmann¹, Dieter Skroblin⁸, Christian Gollwitzer⁸, Tadas Malinauskas², Marko Jošt^{1,9}, Gašper Matic⁹, Bernd Rech^{10,11}, Rutger Schlatmann^{5,12}, Marko Topič⁹, Lars Korte¹, Antonio Abate⁶, Bernd Stannowski^{5,13}, Dieter Neher⁴, Martin Stollerfoht⁴, Thomas Unold³, Vytautas Getautis², Steve Albrecht^{1,11†}

Tandem solar cells that pair silicon with a metal halide perovskite are a promising option for surpassing the single-cell efficiency limit. We report a monolithic perovskite/silicon tandem with a certified power conversion efficiency of 29.15%. The perovskite absorber, with a bandgap of 1.68 electron volts, remained phase-stable under illumination through a combination of fast hole extraction and minimized nonradiative recombination at the hole-selective interface. These features were made possible by a self-assembled, methyl-substituted carbazole monolayer as the hole-selective layer in the perovskite cell. The accelerated hole extraction was linked to a low ideality factor of 1.26 and single-junction fill factors of up to 84%, while enabling a tandem open-circuit voltage of as high as 1.92 volts. In air, without encapsulation, a tandem retained 95% of its initial efficiency after 300 hours of operation.

Fasi ternarie AB_2X_4 : struttura dello **spinello** $MgAl_2O_4$ (e.g. $NiCr_2O_4$, $ZnFe_2O_4$, Fe_3O_4 , Mn_3O_4)



Reticolo ccp di ioni O^{2-}

I cationi A occupano 1/8 dei siti tetraedrici (a)

I cationi B occupano 1/2 dei siti ottaedrici (b)

Normalmente i siti ottaedrici sono occupati del catione a carica più alta (e più piccolo): $A[B_2]O_4$

Spinelli inversi: $B[AB]O_4$

Composti ionici non-stechiometrici: composizione variabile, stessa struttura Il parametro reticolare varia in modo continuo

Blocco d		Blocco f		
<i>Idruri</i>				
TiH _x	1–2		Tipo fluorite	Esagonale
ZrH _x	1,5–1,6	GdH _x	1,9–2,3	2,85–3,0
HfH _x	1,7–1,8	ErH _x	1,95–2,31	2,82–3,0
NbH _x	0,64–1,0	LuH _x	1,85–2,23	1,74–3,0
<i>Ossidi</i>				
	Tipo salgemma	Tipo rutilo		
TiO _x	0,7–1,25	1,9–2,0		
VO _x	0,9–1,20	1,8–2,0		
NbO _x	0,9–1,04			
<i>Solfuri</i>				
ZrS _x	0,9–1,0			
YS _x	0,9–1,0			

* Espresso come l'intervallo di valori che x può assumere.

Soluzioni solide ioniche
(La_{1-x}Sr_x)FeO₃ per 0 ≤ x ≤ 1