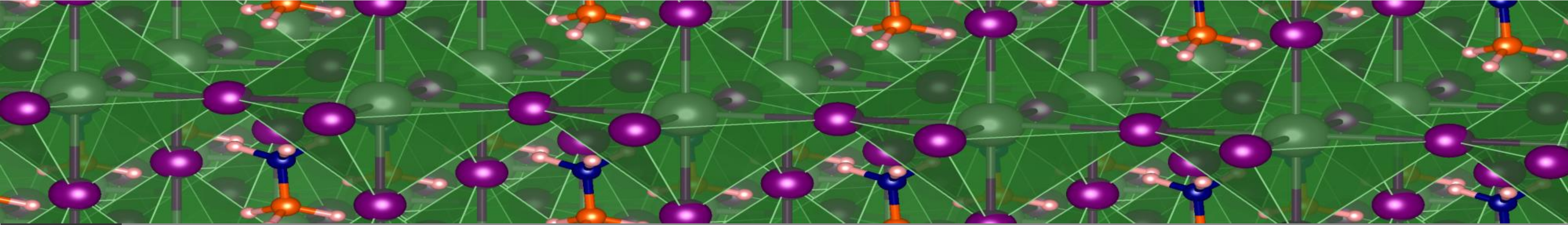


IX Congreso Nacional de Ciencias e Ingeniería de Materiales, Veracruz-2018

Universidad Autónoma Metropolitana
Casa abierta al tiempo
Azcapotzalco

Factores de estabilidad para perovskitas empleadas en celdas solares

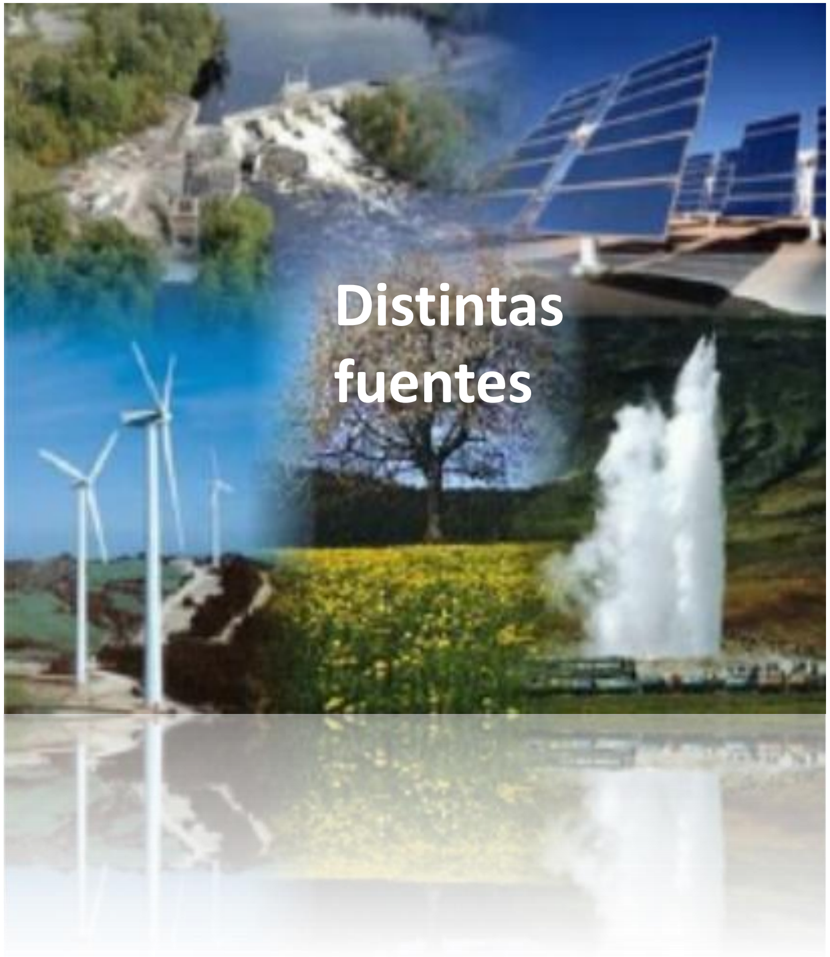
M. en C. e Ing. Arnulfo Montoya Moreno

Laboratorio de Física Atómica Molecular Aplicada

Asesor: Dr. Óscar Olvera Neria

Nuevos retos de la humanidad a satisfacer

- Retos globales
- **Energía y Medio Ambiente**
- Salud global
- Los recursos hídricos
- Agricultura y Seguridad Alimentaria
- Seguridad internacional
- Población
- G Science / G8 Declaraciones
- Derechos humanos



The National Academies of Sciences, Engineering, and Medicine, National Academy of Sciences, 2017.

Nuevos retos por compensar

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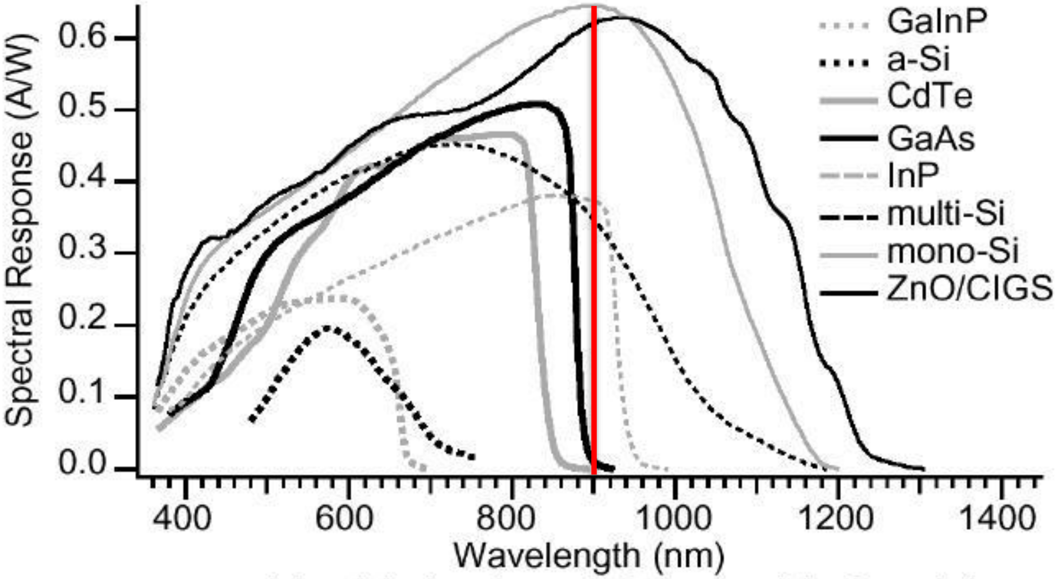
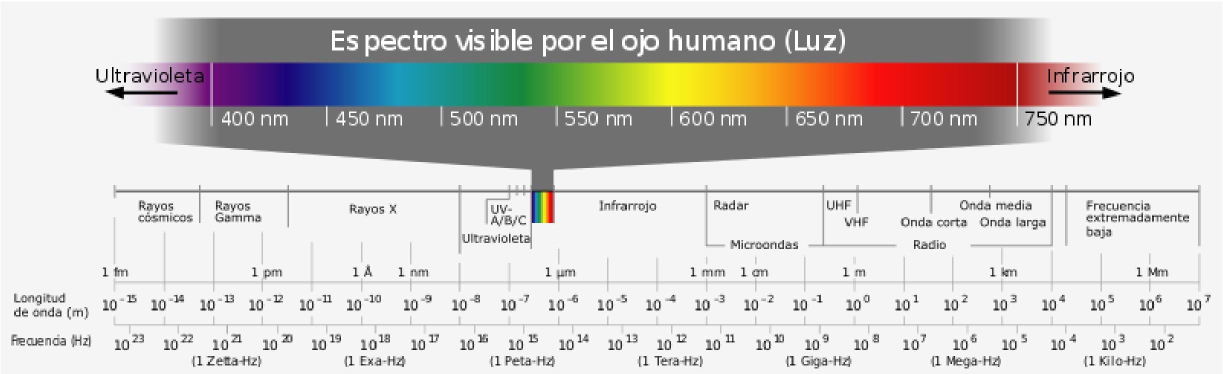
- **Estable**
- **Difícil fabricación**
- **Rígida**
- **PCE 26.5%**



Respuesta espectral de células basadas en distintos materiales fotovoltaicos.



Celda solar de perovskita

- **Delgado**
- **Transparente**
- **Fabricación a temperatura ambiente**
- **Ligero**
- **PCE 21.2%**

$CH_3NH_3PbI_3$

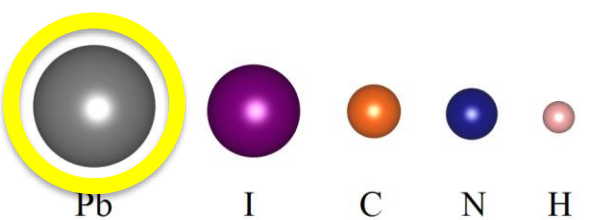
Estructura de perovskita

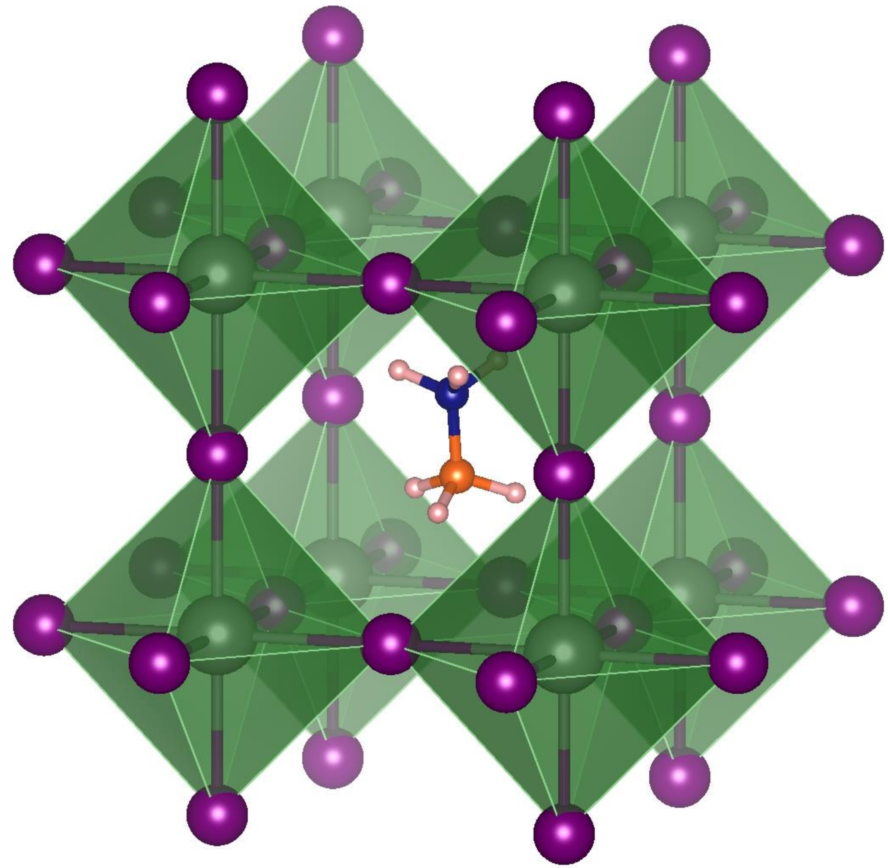
ABX_3

A: MA

B: Plomo

X: Yodo





$CH_3NH_3PbI_3$

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Año versus PCE de la celda solar de perovskita

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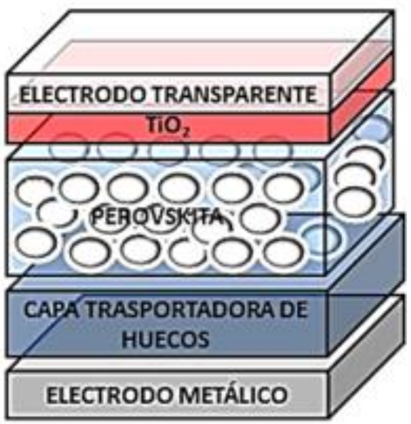
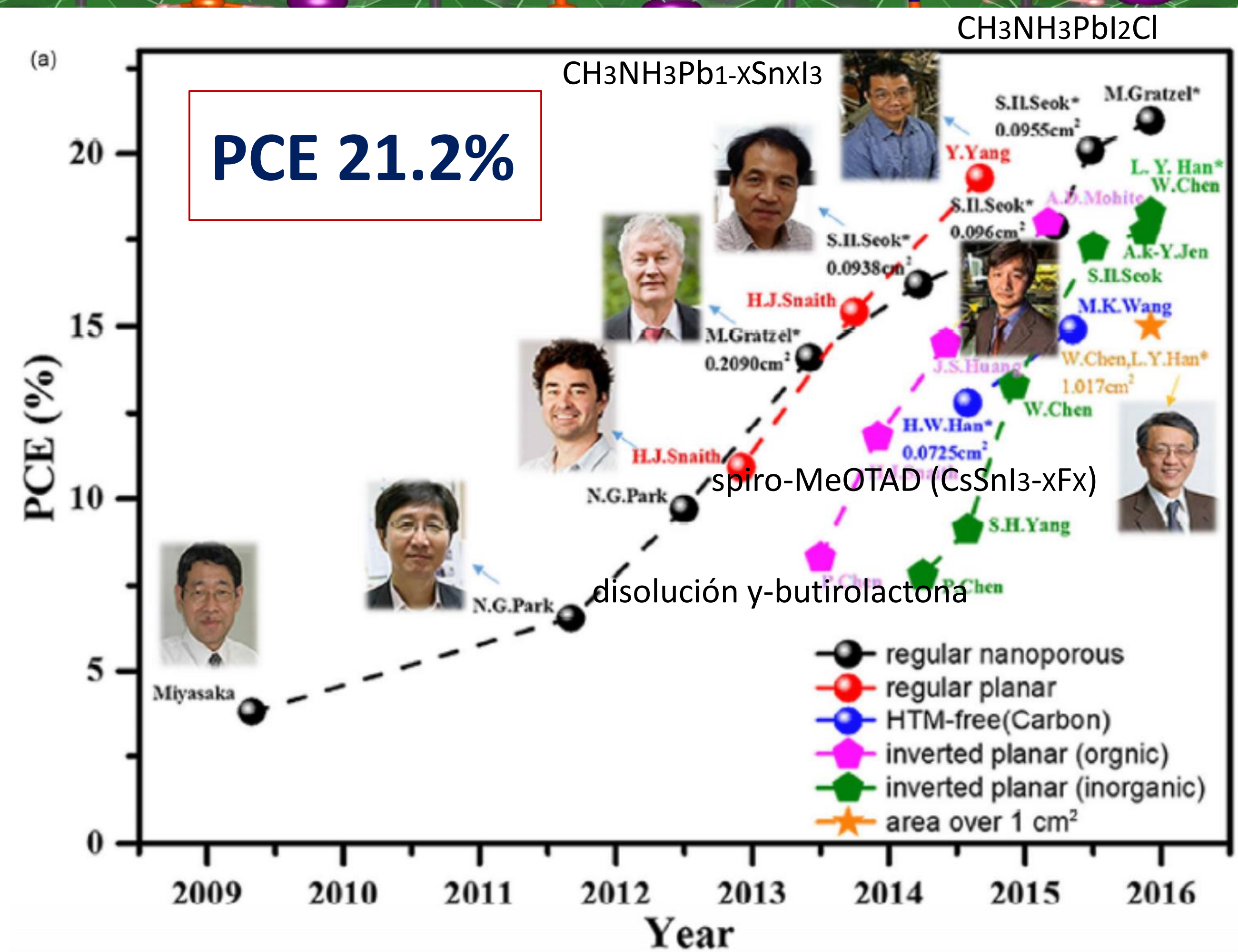
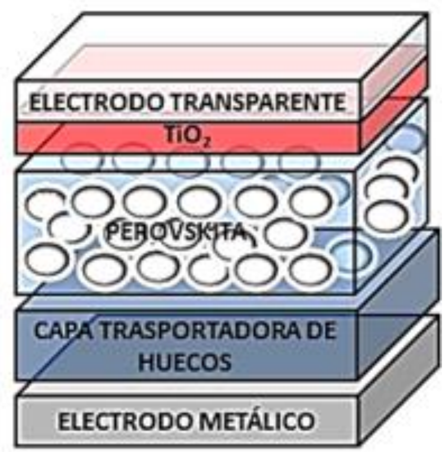
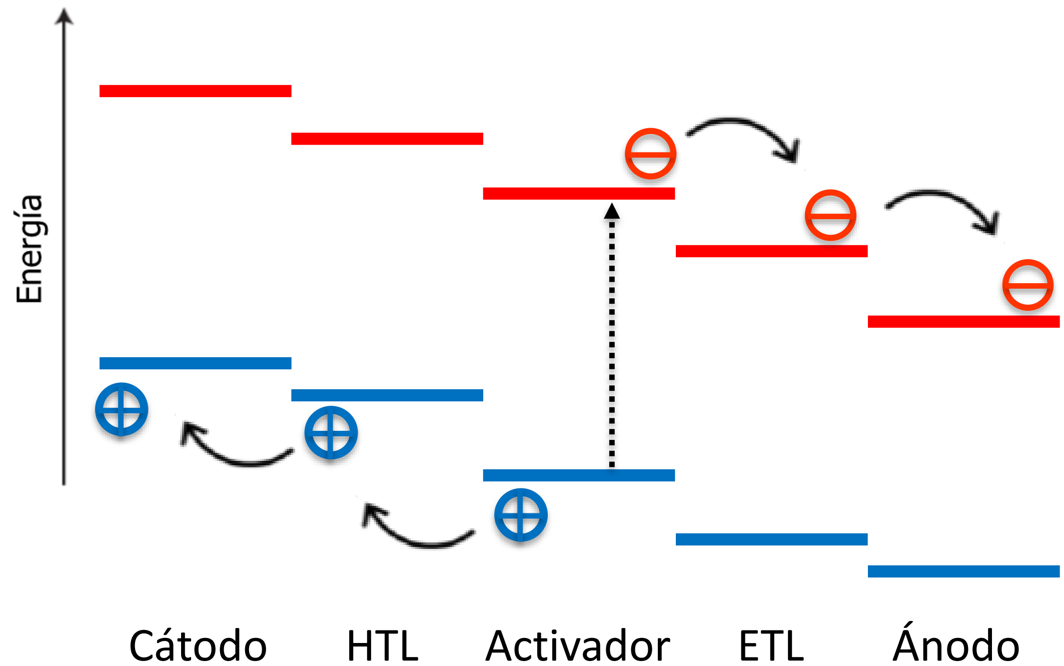




- *F. Yang, K. Sun, and S. R. Forrest. Ecient Solar Cells Using All-Organic Nanocrystalline Networks. Advanced Materials, 19:41664171, 2007.*
- *K. Suemori, T. Miyata, M. Yokoyama, and M. Hiramoto. Three-layered organic solar cells incorporating a nanostructure-optimized phthalocyanine: fullerene codeposited interlayer. Applied Physics Letters, 86:063509, 2005.*

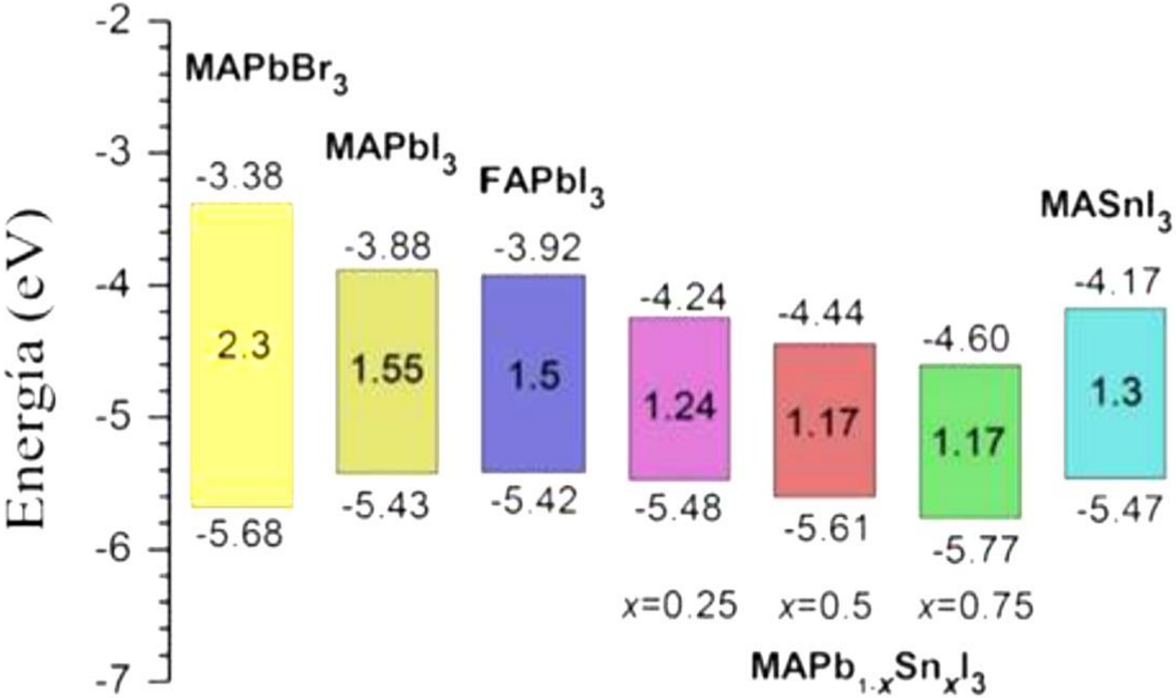
Recombinación y efecto multitúnel en perovskita



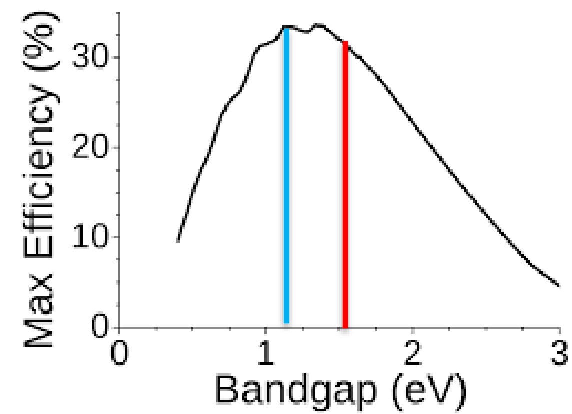


- *Sims, L., Egelhaaf, H.-J., Hauch, J. A., Kogler, F. R. & Steim, R. in Comprehensive Renewable Energy (ed. Sayigh, A.) 439–480 (Elsevier, 2012). at <http://www.sciencedirect.com/science/article/pii/B9780080878720001207>*
- *7. Chapin, D. M., Fuller, C. S. & Pearson, G. L. A New Silicon p-n Junction Photocell for Converting Solar Radiation into Electrical Power. J. Appl. Phys.* ***25,*** *676–677 (1954).*

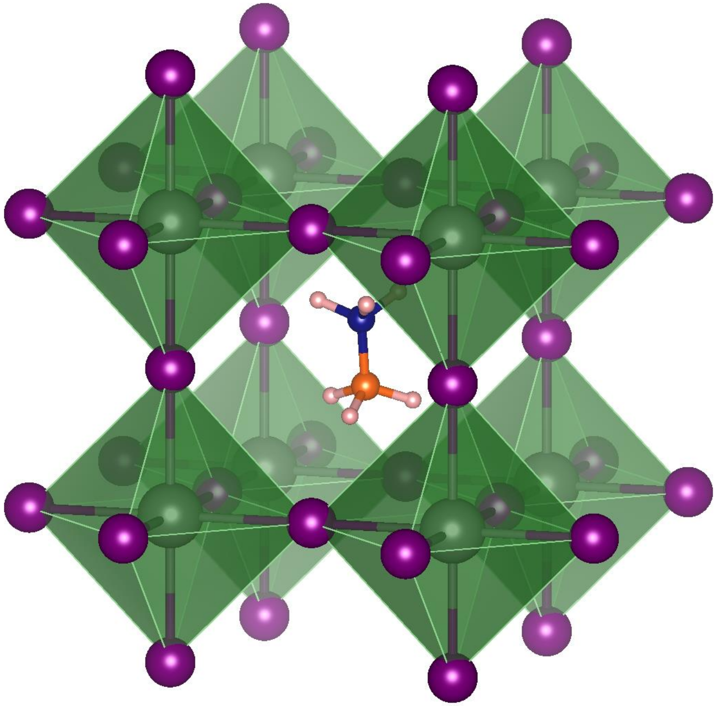
Propiedades optoelectrónicas



gap 1.18 eV (Si)

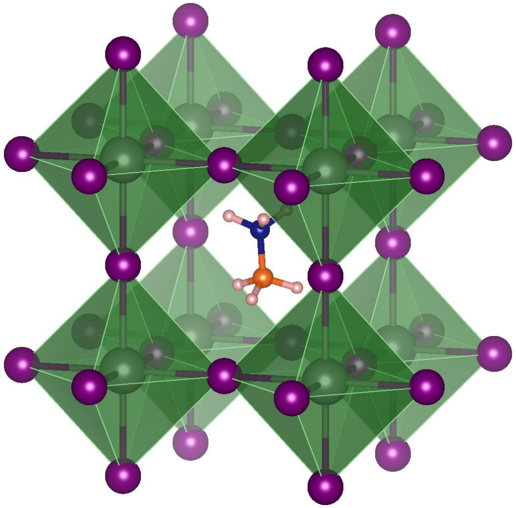


- *M. Pagliaro, G. Palmisano and R. Ciriminna, Flexible solar Cells, WILEY-VCH Verlag GmbH & Co. KGaA, (2009).*
- *S. Liu, F. Zheng, N. Koocher, H. Takenaka, F. Wang, and A, Rappe. Ferroelectric Domain Wall Induced Band Gap Reduction and Charge Separation in Organometal Halide Perovskitas, J. Phys. Chem. Lett, (2015), 6, 693−699.*



La estabilidad del sistema está relacionada con la estabilidad intrínseca del catión orgánico A y con la magnitud de las interacciones electrostáticas del catión A con los BX_3 vecinos

Metodología



- **Sustituir del Pb por cationes metálicos**
- **Sustituir al MA por cationes orgánicos**
- **Estudiar la estabilidad energética**
- **Estudiar la estabilidad en presencia de agua y temperatura**

Radios de Shannon y el teorema de Pitágoras

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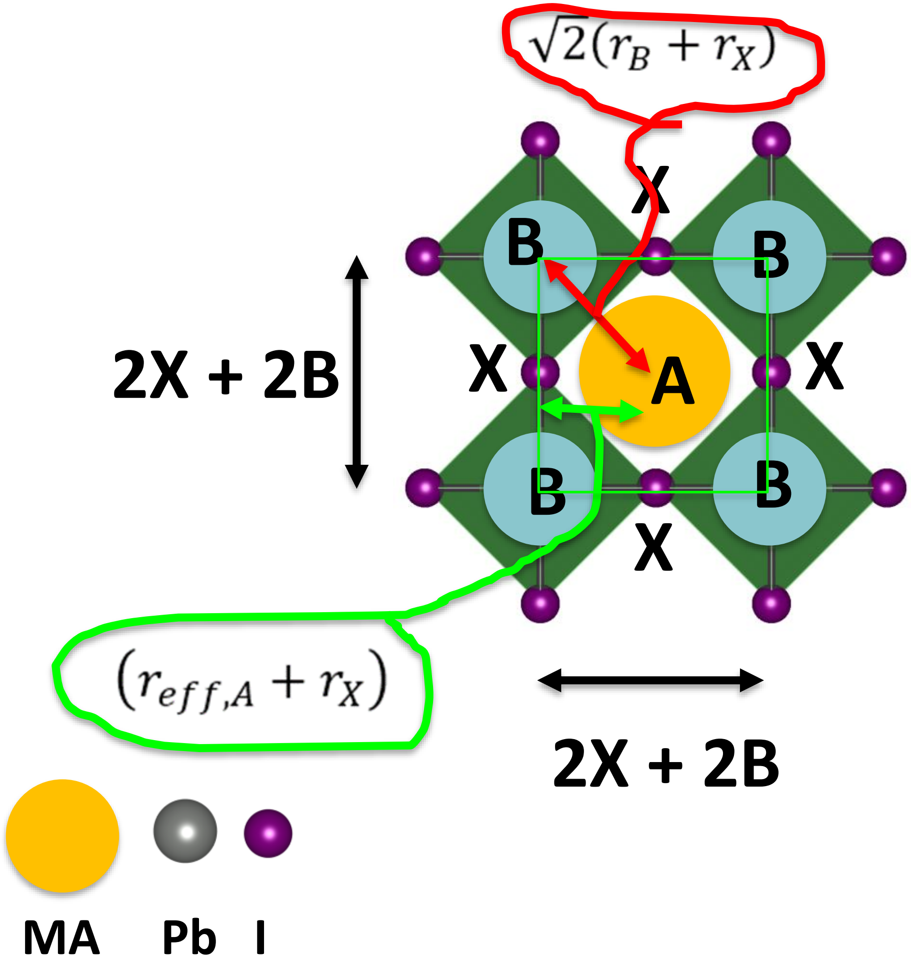


$$d = R_X + R_B$$

$$h = \sqrt{(2_X + 2_B)^2 + (2_X + 2_B)^2)}$$

$$h = \sqrt{2(2_X + 2_B)^2}$$

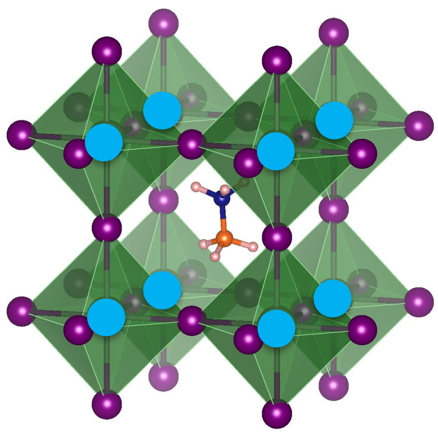
$$h = \sqrt{2}(2_X + 2_B)$$

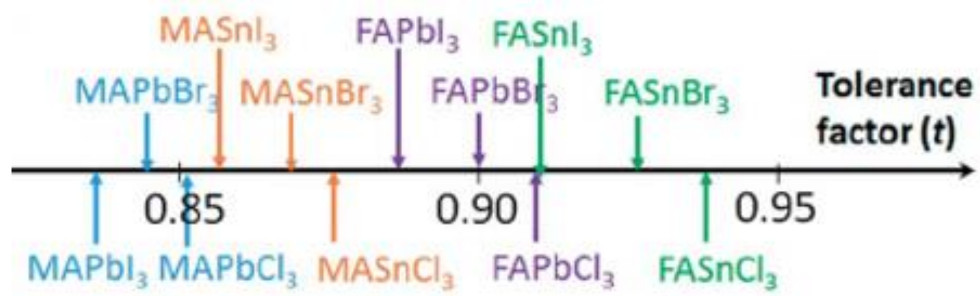
$$\frac{h}{2} = \frac{\sqrt{2}}{2}(2_X + 2_B) = \sqrt{2}(X + B)$$

$$FT = \frac{(r_{eff,A} + r_X)}{\sqrt{2}(r_B + r_X)}$$

- V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente VII-VIII" Skrifter Norske Videnskaps Akademi, Oslo, 1926.

$CH_3NH_3PbI_3$





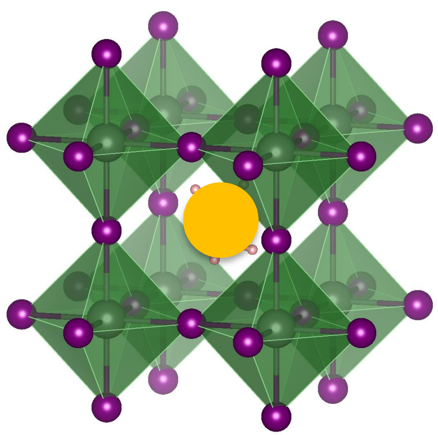
$$FT = \frac{(r_{eff,A} + r_X)}{\sqrt{2}(r_B + r_X)}$$

$$r_{eff,A} = r_{masa} + r_{ion}$$

B = Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ge^{2+}, Sn^{2+}, Eu^{2+}, Tm^{2+}, Yb^{2+}.

- V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente VII-VIII" Skrifter Norske Videnskaps Akademi, Oslo, 1926.

Perovskitas con sustitución del catión orgánico



$CH_3NH_3PbI_3$

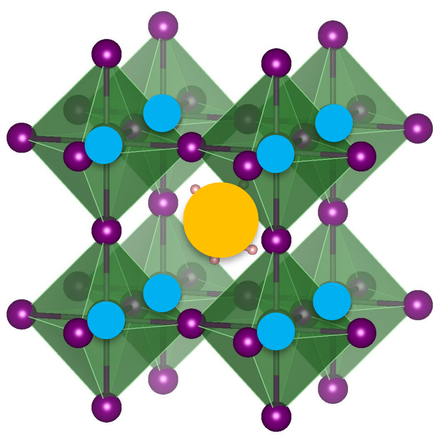
A = $[NH_4]^+$, $[NH_3OH]^+$, $[NH_3NH_2]^+$, $[(CH_2)_3NH_2]^+$, $[CH(NH_2)_2]^+$, $[C_3N_2H_5]^+$, $[(CH_3)_2NH_2]^+$, $[NC_4H_8]^+$, $[(CH_3CH_2)NH_3]^+$, $[(NH_2)_3C]^+$, $[(CH_3)_4N]^+$, $[(HN)(CH_2)_3S]^+$, $[C_7H_7]^+$, Cs^+, MA^+, FA^+, Rb^+, K^+.

$$FT = \frac{(r_{eff,A} + r_X)}{\sqrt{2}(r_B + r_X)}$$

$$r_{eff,A} = r_{masa} + r_{ion}$$

• V. M. Goldschmidt, “Geochemische Verteilungsgesetze der Elemente VII-VIII” Skrifter Norske Videnskaps Akademi, Oslo, 1926.

Perovskitas libres de plomo y estables



$CH_3NH_3PbI_3$

A = $[NH_4]^+$, $[NH_3OH]^+$, $[NH_3NH_2]^+$, $[(CH_2)_3NH_2]^+$, $[CH(NH_2)_2]^+$, $[C_3N_2H_5]^+$, $[(CH_3)_2NH_2]^+$, $[NC_4H_8]^+$, $[(CH_3CH_2)NH_3]^+$, $[(NH_2)_3C]^+$, $[(CH_3)_4N]^+$, $[(HN)(CH_2)_3S]^+$, $[C_7H_7]^+$, Cs^+, MA^+, FA^+, Rb^+, K^+.

B = Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ge^{2+}, Sn^{2+}, Eu^{2+}, Tm^{2+}, Yb^{2+}.

- Masaki Azuma, Shingo Kaimori, Mikio Takano, **Chem. Mater.** 10, 3124, (1998).

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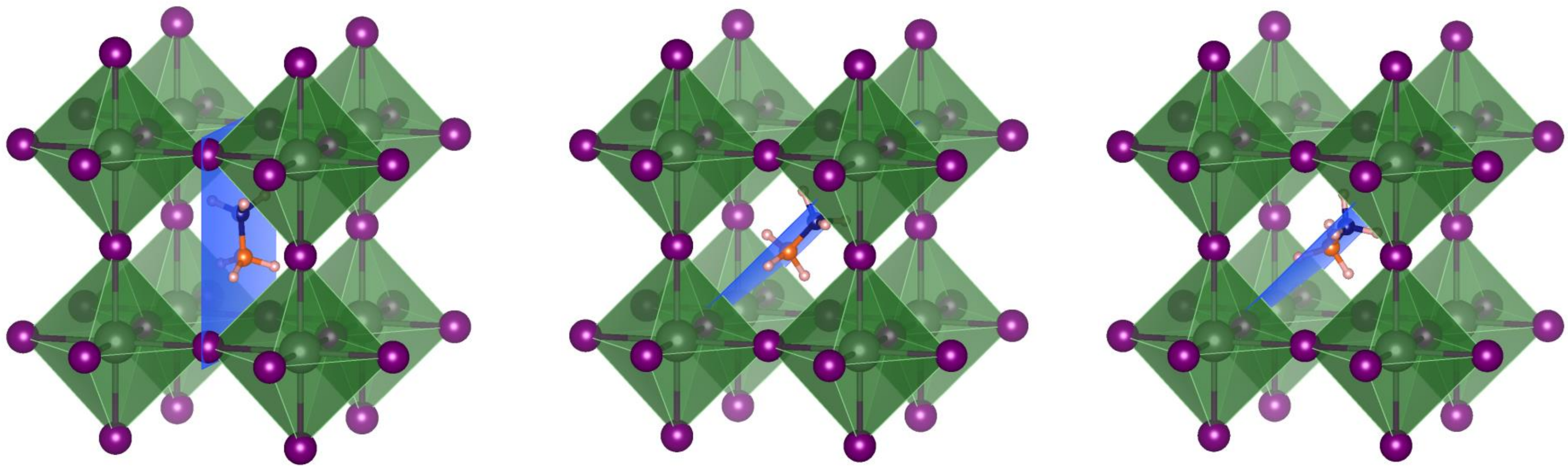
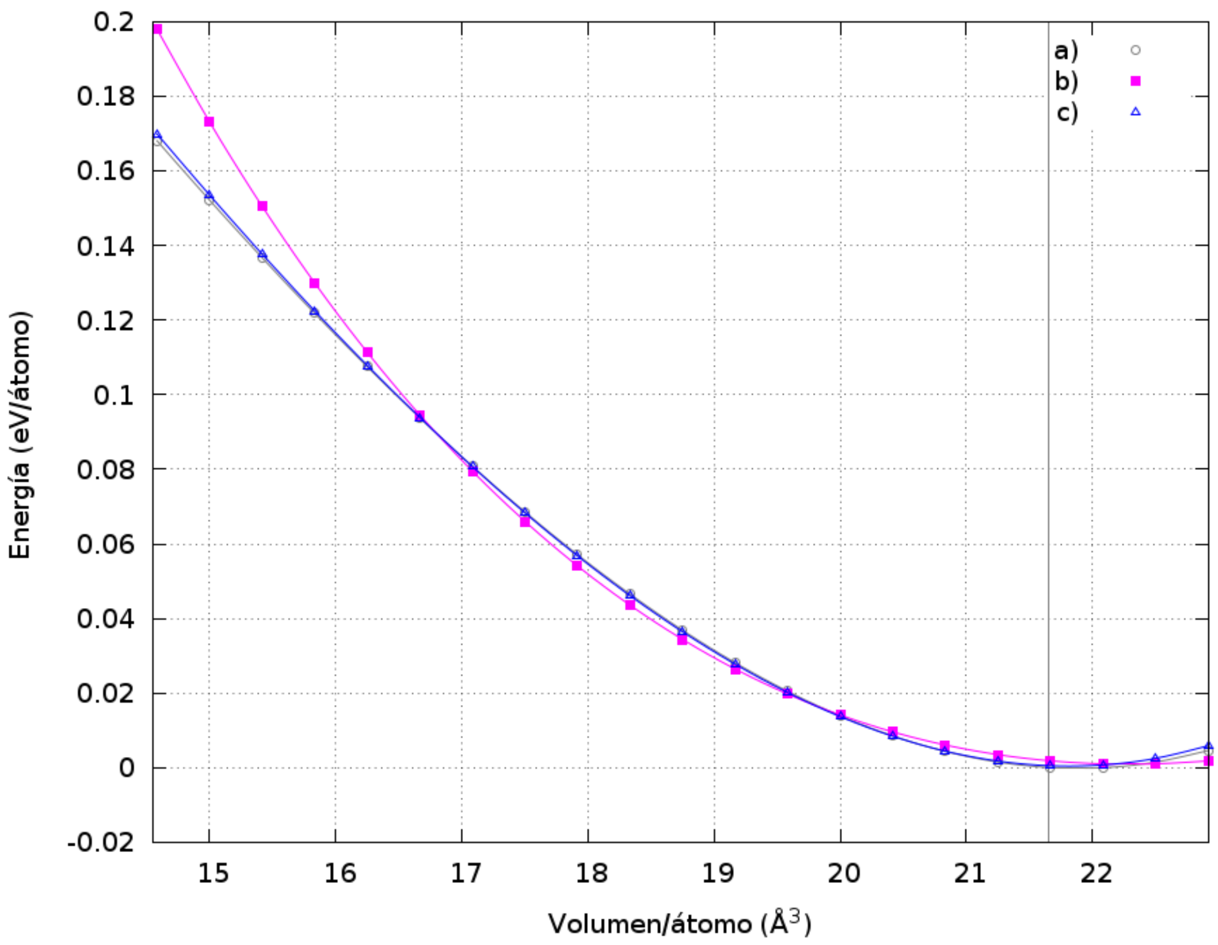
Resultados



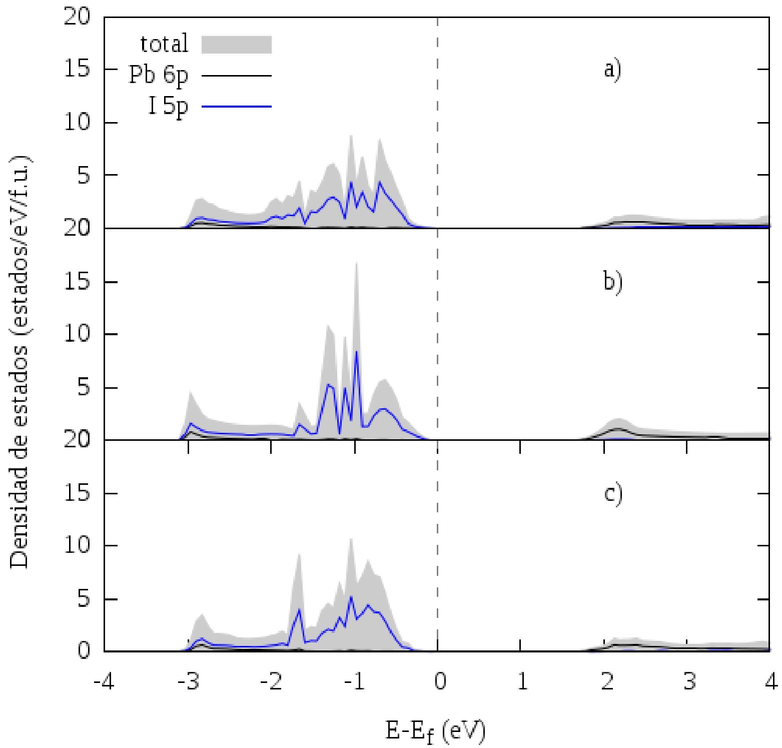
Posición	Vo ($Å^3$/átomo)	E(eV/átomo)	Bo(GPa)
1	262.60	0.00	30.04
2	267.45	0.01	16.31
3	261.78	0.07	30.14

Resultados

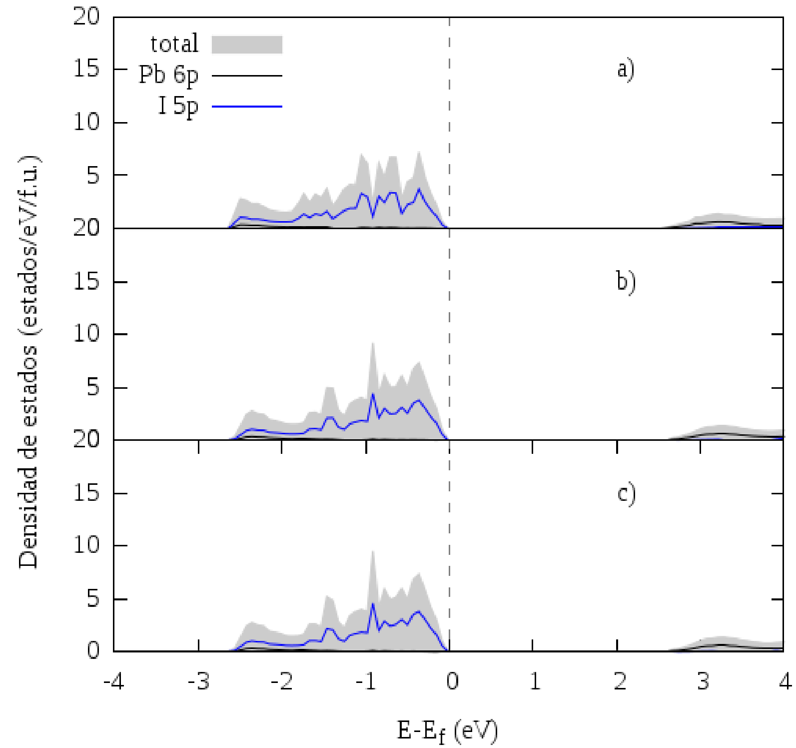


0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
Energía (eV/átomo)
15
16
17
18
19
20
21
22
Volumen/átomo (Å3)
a)
b)
c)

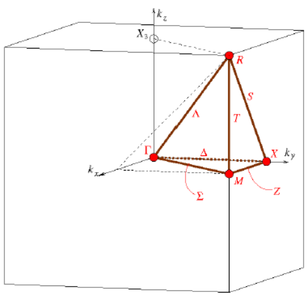
PBE

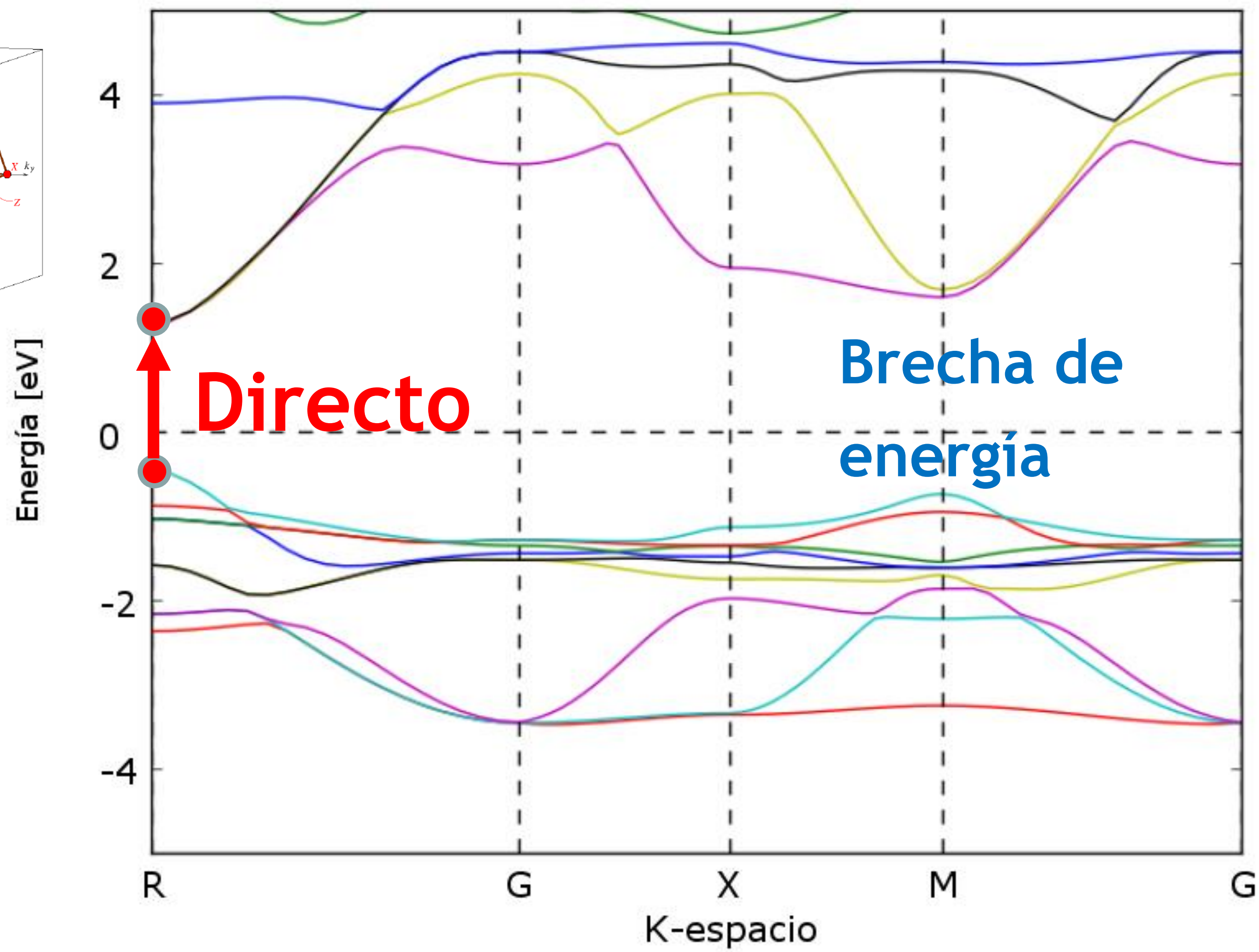

total
Pb 6p
I 5p
a)
b)
c)
Densidad de estados (estados/eV/f.u.)
E-E$_f$ (eV)
20
15
10
5
0
-4
-3
-2
-1
0
1
2
3
4

PBE + U (5eV)

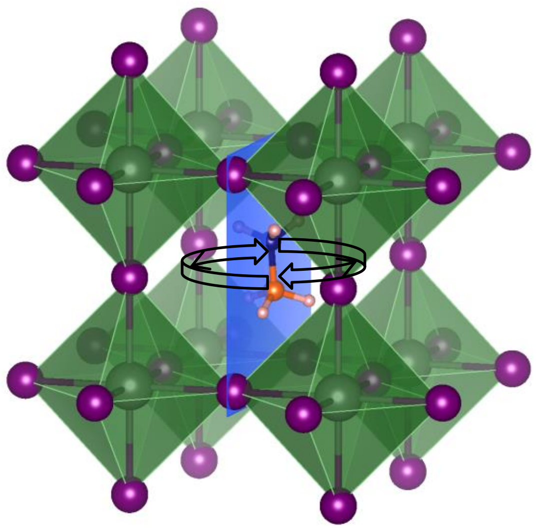

total
Pb 6p
I 5p
a)
b)
c)
Densidad de estados (estados/eV/f.u.)
E-E$_f$ (eV)
20
15
10
5
0
-4
-3
-2
-1
0
1
2
3
4

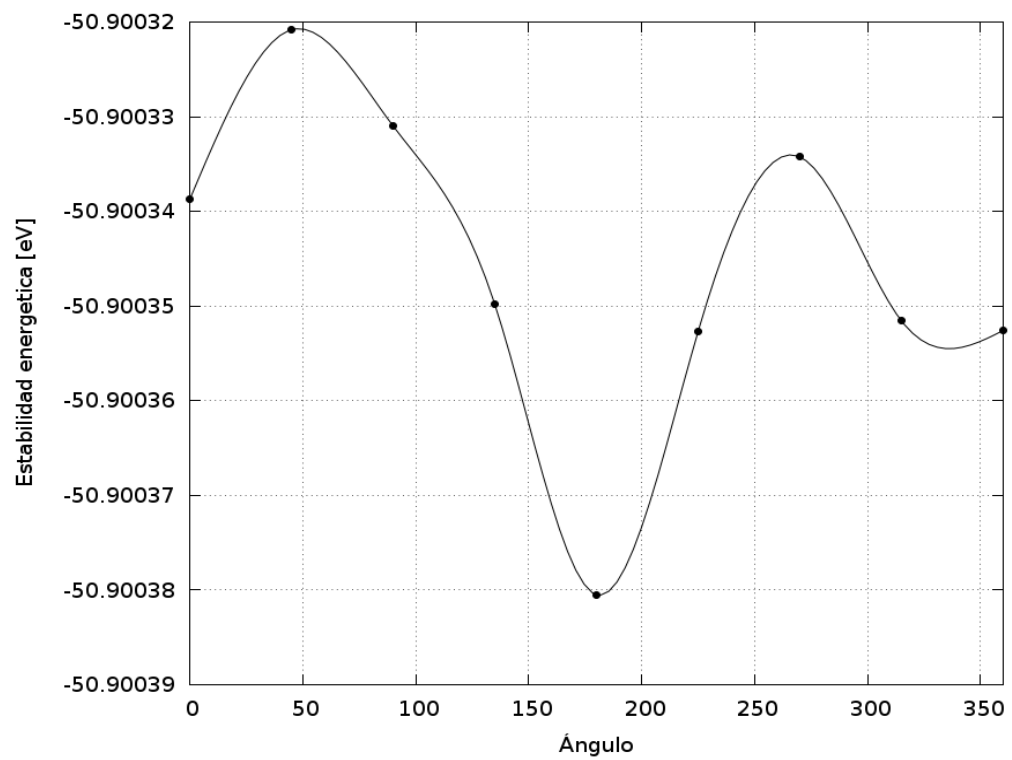
Resultados





Resultados




-50.90032
-50.90033
-50.90034
-50.90035
-50.90036
-50.90037
-50.90038
-50.90039
Estabilidad energetica [eV]
0
50
100
150
200
250
300
350
Ángulo

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Fases en función de la temperatura (T)

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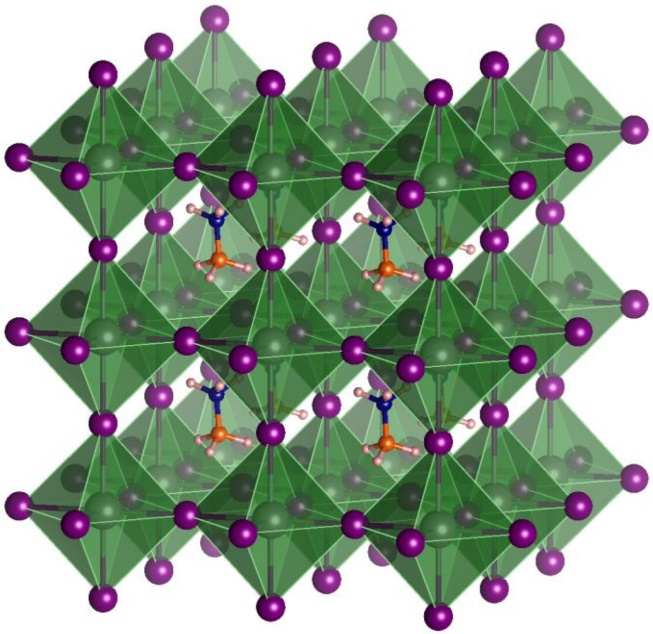
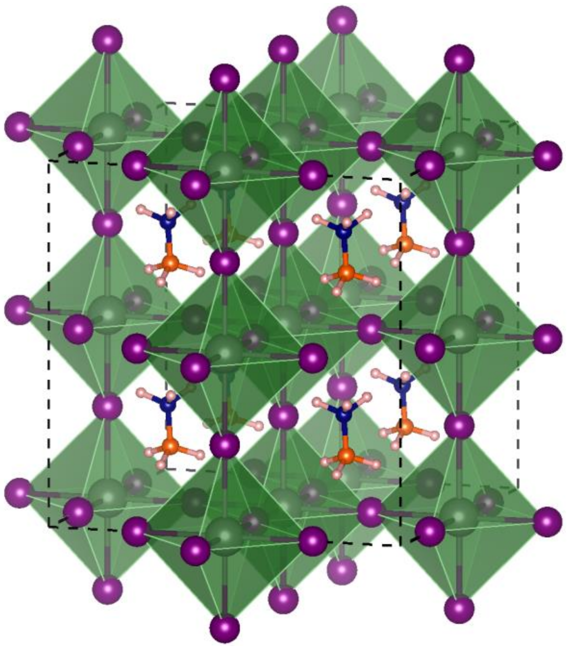
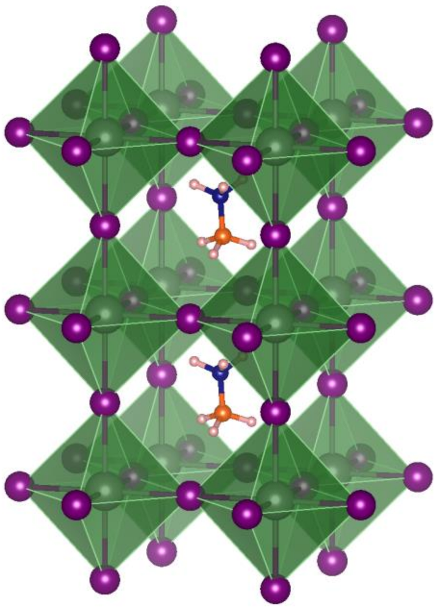


cúbica



tetragonal



ortorrómbica

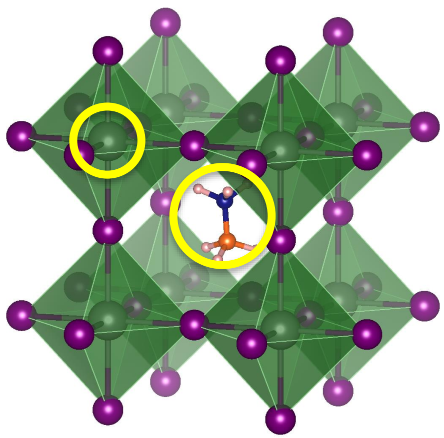
Factores de estabilidad Perovskitas


```
for i=1:a
  for j=1:b
    for k=1:x
        N = N + 1;
        %Perovskite's name
        Perovskite{N,1}= strcat(A{i,1},B{j,1},X{k,1});

        %Tolerance factor Goldsmicht: column 2
        Perovskite{N,2}=(A{i,2}+X{k,2})/(sqrt(2)*(B{j,2}+X{k,2}));

        %Perovskite that observe 0.8<TF<1.0
        if ( Perovskite{N,2} > minVal_G ) && ( Perovskite{N,2} < maxVal_G )
          fit_G=fit_G+1;
          Perovskite_G{fit_G,1}= Perovskite{N,1};
          Perovskite_G{fit_G,2}= Perovskite{N,2};
        end

        %Perovskite that observe 0:414<RB/RX<0.732
        Ratio_BX = B{j,2}/X{k,2};
        if ( Ratio_BX > 0.414 ) && ( Ratio_BX < 0.732 )
          fit_Ratio_BX=fit_Ratio_BX + 1;
          Perovskite_Ratio{fit_Ratio_BX,1}= Perovskite{N,1};
          Perovskite_Ratio{fit_Ratio_BX,2}= Ratio_BX;
        end

        if (Perovskite{N,2} > 0.77) && (Perovskite{N,2} < 1.0)
          Ratio_AX = A{i,2}/X{k,2};
          if ( Ratio_BX > 1.203*Ratio_AX - 0.488 )
             fit_Ratio_AX=fit_Ratio_AX + 1;
             Perovskite_Ratio_AX{fit_Ratio_AX,1} = Perovskite{N,1};
             Perovskite_Ratio_AX{fit_Ratio_AX,2} = 'True';

          end
        end
```

Factores de estabilidad Perovskitas

'RbGeI3'	[0.9195]	[7.0453]	[9.7235]	[7.2497]	[11.8509]	[13.5585]	[8.2474]
'RbSnCl3'	[0.8730]	[6.6175]	[8.9509]	[6.4337]	[10.6904]	[10.3958]	[6.8580]
'RbSnBr3'	[0.8645]	[6.8693]	[9.3425]	[6.9115]	[11.2988]	[11.7217]	[7.5564]
'RbSnI3'	[0.8526]	[7.2723]	[9.9691]	[7.6759]	[12.2722]	[13.8430]	[8.6738]
'RbEuCl3'	[0.7776]	[6.9531]	[9.3140]	[7.0637]	[11.3133]	[10.8164]	[7.4883]
'RbEuBr3'	[0.7743]	[7.2049]	[9.7056]	[7.5415]	[11.9217]	[12.1423]	[8.1867]
'RbEuI3'	[0.7697]	[7.6079]	[10.3323]	[8.3059]	[12.8951]	[14.2636]	[9.3042]
'RbTmCl3'	[0.8515]	[6.6866]	[9.0256]	[6.5634]	[10.8186]	[10.4824]	[6.9878]
'RbTmBr3'	[0.8443]	[6.9384]	[9.4173]	[7.0412]	[11.4270]	[11.8083]	[7.6862]
'RbTmI3'	[0.8341]	[7.3414]	[10.0439]	[7.8056]	[12.4005]	[13.9296]	[8.8036]
'RbYbCl3'	[0.8545]	[6.6767]	[9.0149]	[6.5449]	[10.8003]	[10.4700]	[6.9692]
'RbYbBr3'	[0.8471]	[6.9286]	[9.4066]	[7.0226]	[11.4087]	[11.7959]	[7.6676]
'RbYbI3'	[0.8367]	[7.3315]	[10.0332]	[7.7870]	[12.3821]	[13.9173]	[8.7851]
'KPbCl3'	[0.7825]	[6.7786]	[9.0959]	[6.8537]	[11.0187]	[10.5992]	[7.2446]
'KPbBr3'	[0.7789]	[7.0305]	[9.4875]	[7.3314]	[11.6271]	[11.9251]	[7.9430]
'KPbI3'	[0.7739]	[7.4334]	[10.1142]	[8.0958]	[12.6006]	[14.0464]	[9.0604]
'KBeCl3'	[1.1287]	[5.8706]	[8.1133]	[5.1489]	[9.3333]	[9.4612]	[5.5389]
'KBeBr3'	[1.1003]	[6.1224]	[8.5050]	[5.6267]	[9.9417]	[10.7870]	[6.2373]
'KBeI3'	[1.0621]	[6.5254]	[9.1316]	[6.3911]	[10.9151]	[12.9084]	[7.3548]
'KMgCl3'	[0.9279]	[6.3147]	[8.5939]	[5.9828]	[10.1577]	[10.0178]	[6.3732]
'KMgBr3'	[0.9155]	[6.5666]	[8.9856]	[6.4605]	[10.7661]	[11.3437]	[7.0716]
'KMgI3'	[0.8984]	[6.9695]	[9.6122]	[7.2249]	[11.7395]	[13.4651]	[8.1891]
'KCaCl3'	[0.8012]	[6.7095]	[9.0211]	[6.7240]	[10.8905]	[10.5126]	[7.1148]
'KCaBr3'	[0.7966]	[6.9614]	[9.4128]	[7.2017]	[11.4989]	[11.8385]	[7.8132]
'KCaI3'	[0.7902]	[7.3643]	[10.0394]	[7.9661]	[12.4723]	[13.9599]	[8.9307]
'KSrCl3'	[0.7647]	[6.8477]	[9.1707]	[6.9834]	[11.1470]	[10.6858]	[7.3744]
'KSrBr3'	[0.7620]	[7.0995]	[9.5623]	[7.4612]	[11.7554]	[12.0117]	[8.0728]
'KSrI3'	[0.7582]	[7.5025]	[10.1889]	[8.2256]	[12.7288]	[14.1330]	[9.1902]
'KBaCl3'	[0.7268]	[7.0056]	[9.3415]	[7.2799]	[11.4401]	[10.8837]	[7.6710]
'KBaBr3'	[0.7259]	[7.2575]	[9.7332]	[7.7576]	[12.0485]	[12.2096]	[8.3694]
'KBaI3'	[0.7247]	[7.6604]	[10.3598]	[8.5220]	[13.0219]	[14.3310]	[9.4869]
'KMnCl3'	[0.8892]	[6.4233]	[8.7114]	[6.1866]	[10.3592]	[10.1539]	[6.5772]
'KMnBr3'	[0.8794]	[6.6751]	[9.1031]	[6.6644]	[10.9676]	[11.4798]	[7.2756]
'KMnI3'	[0.8658]	[7.0781]	[9.7297]	[7.4288]	[11.9411]	[13.6011]	[8.3930]
'KFeCl3'	[0.9064]	[6.3739]	[8.6580]	[6.0940]	[10.2676]	[10.0921]	[6.4845]
'KFeBr3'	[0.8955]	[6.6258]	[9.0497]	[6.5717]	[10.8760]	[11.4179]	[7.1829]
'KFeI3'	[0.8803]	[7.0288]	[9.6763]	[7.3361]	[11.8495]	[13.5393]	[8.3003]
'KCoCl3'	[0.9188]	[6.3394]	[8.6206]	[6.0291]	[10.2035]	[10.0488]	[6.4196]
'KCoBr3'	[0.9071]	[6.5912]	[9.0123]	[6.5069]	[10.8119]	[11.3746]	[7.1180]

Conclusiones



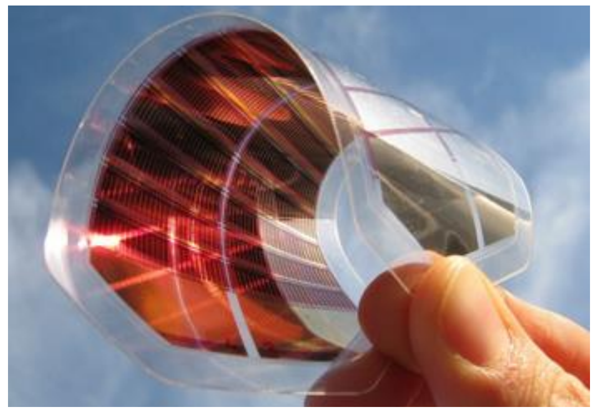
- **Comprender las propiedades de la perovskita tipo ABX_3**
- **Metodología que evite toxicidad y mejore la estabilidad**
- **Metodología para la estabilidad en condiciones de humedad**
- **Generar modelos análogos de celda fotovoltaica de perovskita libre de plomo y estable**

Azcapotzalco

Agradezco su atención

Laboratorio de Física Atómica
Molecular y Aplicada

CONGRESO NACIONAL DE CIENCIA
E INGENIERÍA EN MATERIALES



Doctorado en Ciencias
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VASP
Vienna Ab-initio Simulation Package

CRYSTAL
a computational tool for solid state chemistry and physics

UAMI
LABORATORIO DE SUPERCOMPUTO
Y VISUALIZACION EN PARALELO

Abacus
CINVESTAV

Modulo de bulk

$$B_0 = -V\left(\frac{\partial P}{\partial V}\right)_T \qquad B_0(V) = V\left(\frac{\partial^2 E}{\partial V^2}\right)_{T,S}$$

Ec. Birch-Murnaghan

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_0^{'} + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2 \left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\}$$

Ec. Vinet

$$E(V) = E_0 + \frac{2V_0B_0}{\left(B_0^{'} - 1\right)^2}\left\{2 - \left[5 + 3\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\left(B_0^{'} - 1\right) - 3B_0^{'}\right] \times \exp\left[-\frac{3}{2}\left(B_0^{'} - 1\right)\left[\left(\frac{V}{V_0}\right)^{\frac{1}{3}} - 1\right]\right]\right\}$$