2021 Virtual MRS Spring Meeting

Ab Initio Study of Atomic and Electronic Structure of Promising $Ba_4XMn_3O_{12}$ (X = Nb, Ce, Pr) Oxides for Solar Thermochemical Hydrogen Production

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National Renewable Energy Laboratory, Golden, CO 80401

$Ba_4CeMn_3O_{12}$ aka BCM for STCH

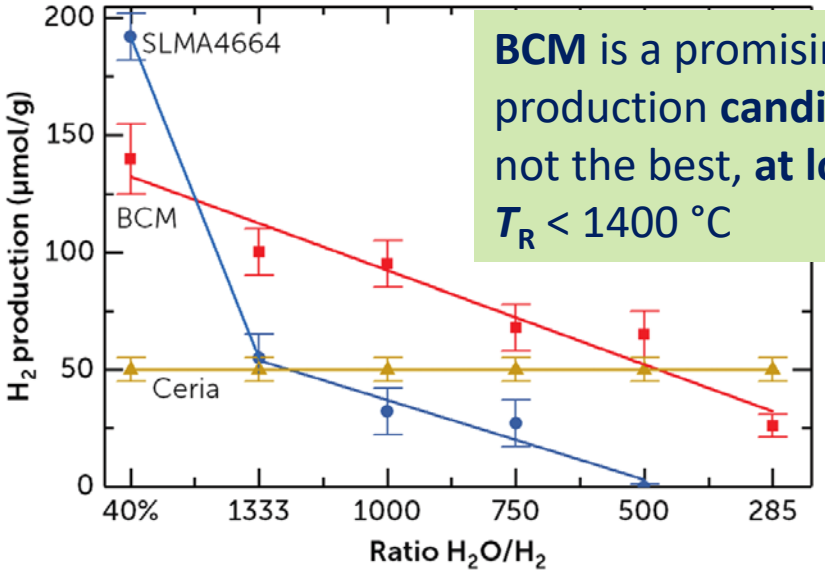
Typical conditions for Solar Thermochemical Hydrogen (STCH)

$$M_xO \rightarrow M_xO_{1-\delta} + \frac{\delta}{2}O_2 \quad \textbf{(reduction)}$$

$T \leq 1400$ °C , $pO_2 \geq 10^{-3}$ atm

$$M_xO_{1-\delta} + \delta H_2O \rightarrow M_xO + \delta H_2 \quad \textbf{(oxidation)}$$

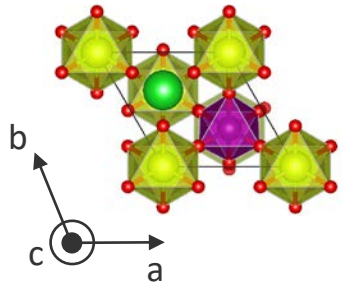
$T \geq 850$ °C , $pH_2O = 1$ atm, $pH_2 \geq 10^{-1}$ atm

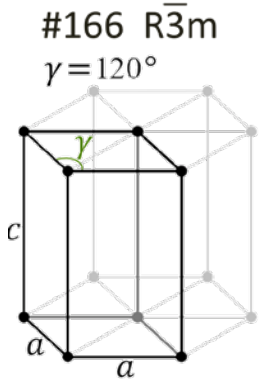


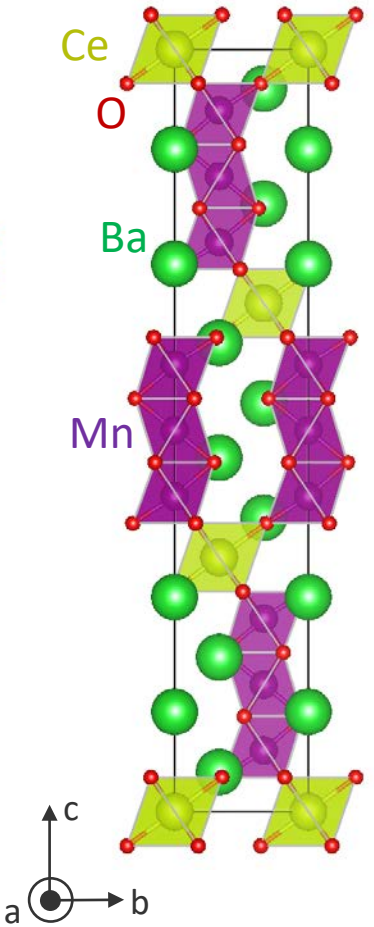
BCM is a promising **H_2** production **candidate[1],** not the best, **at lower T_R** < 1400 °C

12R-$Ba_4CeMn_3O_{12}$ (BCM)

12R BCM perfectly ordered phase[2]







[1]D. R. Barcellos et al., Energy Environ. Sci. 11, 3256 (2018); [2]A. F. Fuentes et al., J. Sol. State Chem. 177, 714 (2004)

$Ba_4CeMn_3O_{12}$ aka BCM and Other Oxides for STCH

Typical conditions for Solar Thermochemical Hydrogen (STCH)

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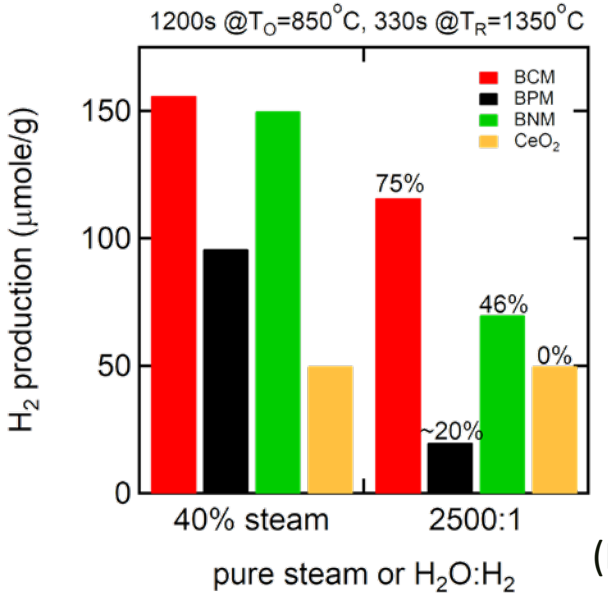
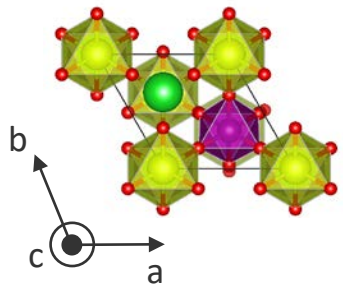


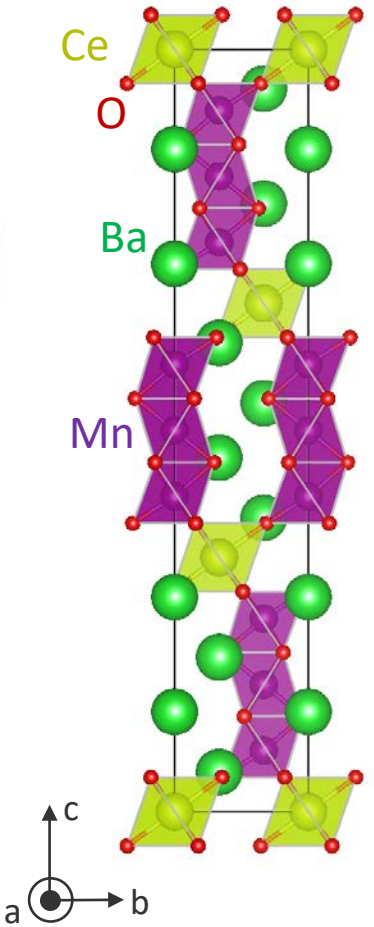
(Figure courtesy A. H. McDaniel)

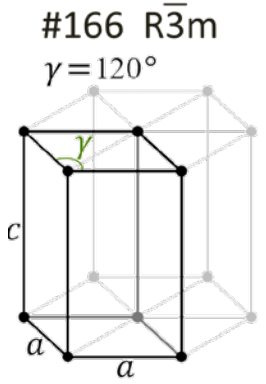
$Ba_4NbMn_3O_{12}$ (BNM) and **$Ba_4PrMn_3O_{12}$ (BPM)** are **structurally identical** compositional variants to **BCM** that also splits H_2O

12R-$Ba_4CeMn_3O_{12}$ (BCM)

12R BCM perfectly ordered phase[2]







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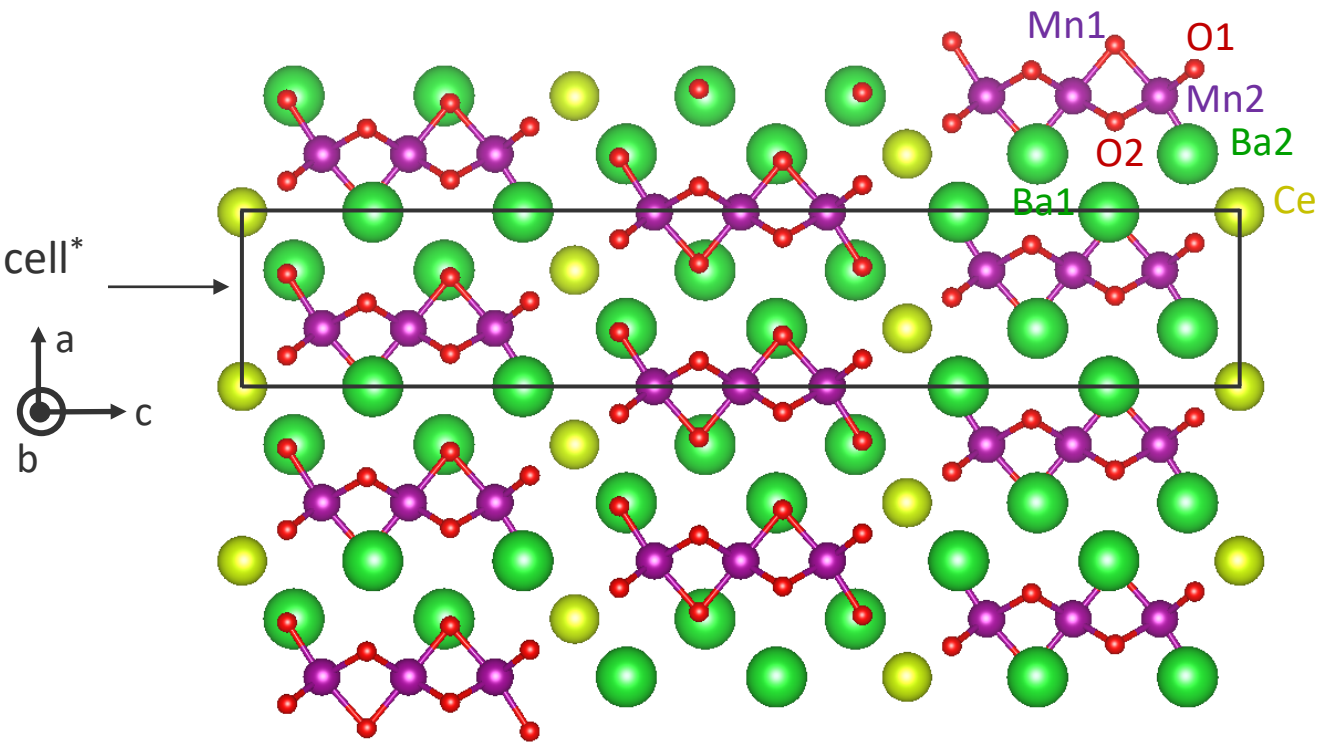
12R-BCM Atomic Structure

12R $Ba_4CeMn_3O_{12}$ (BCM)

CIF (conventional) cell*
(9 Mn-atoms)



12R-BCM consists of two unique Mn, Ba, O sites and single Ce site

Mn^{4+}: $3d^3\ 4s^0$ ← Spin?

Ce^{4+}: $4f^0\ 5d^0\ 6s^0$

Both Mn and Ce are bonded to six neighboring O atoms

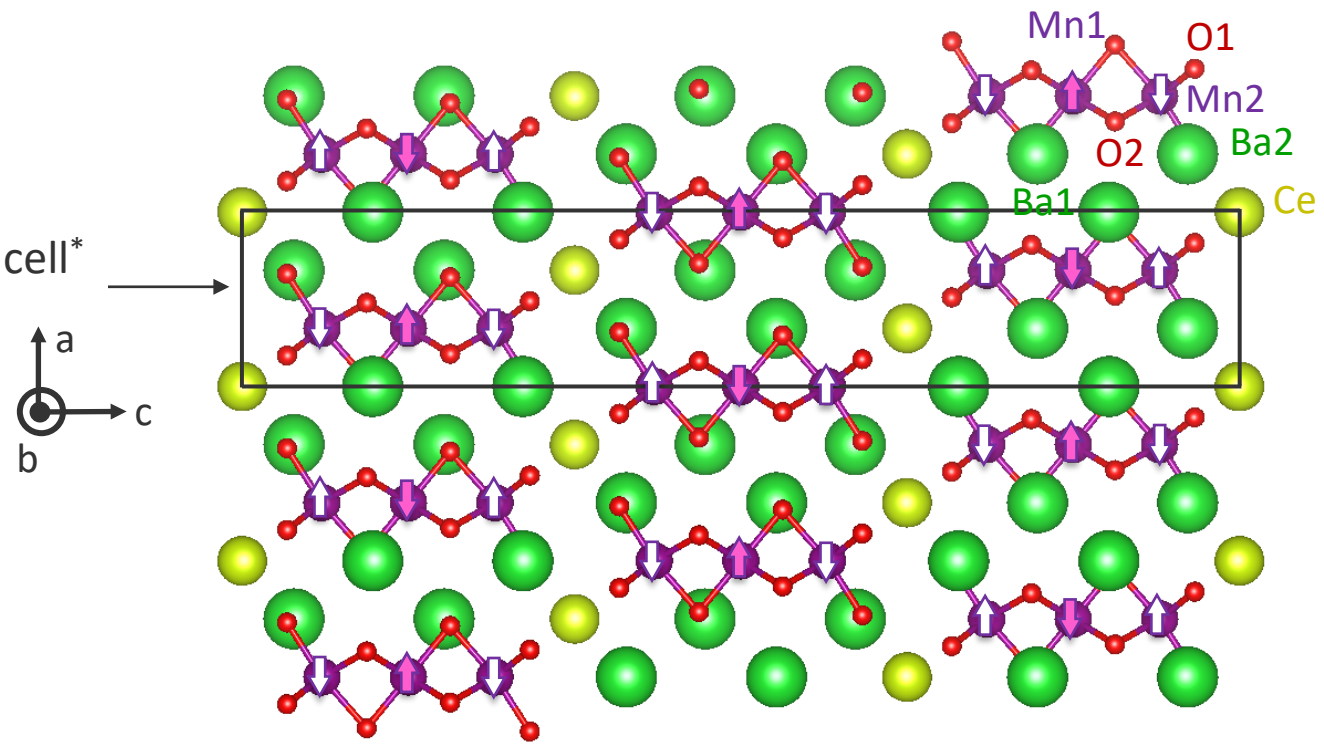
Experimental CIF cell cannot be used for electronic structure calculations as the magnetic structure is not known

*CIF available from ICSD database, A. F. Fuentes et al., J. Sol. State Chem. 177, 714 (2004)

12R-BCM Ground State Magnetic Structure

Anti-ferro magnetic 12R $Ba_4CeMn_3O_{12}$ (BCM)

CIF (conventional) cell*
(9 Mn-atoms)



12R-BCM consists of two unique Mn, Ba, O sites and single Ce site

Mn^{4+}: $3d^3\ 4s^0$ ← Spin!

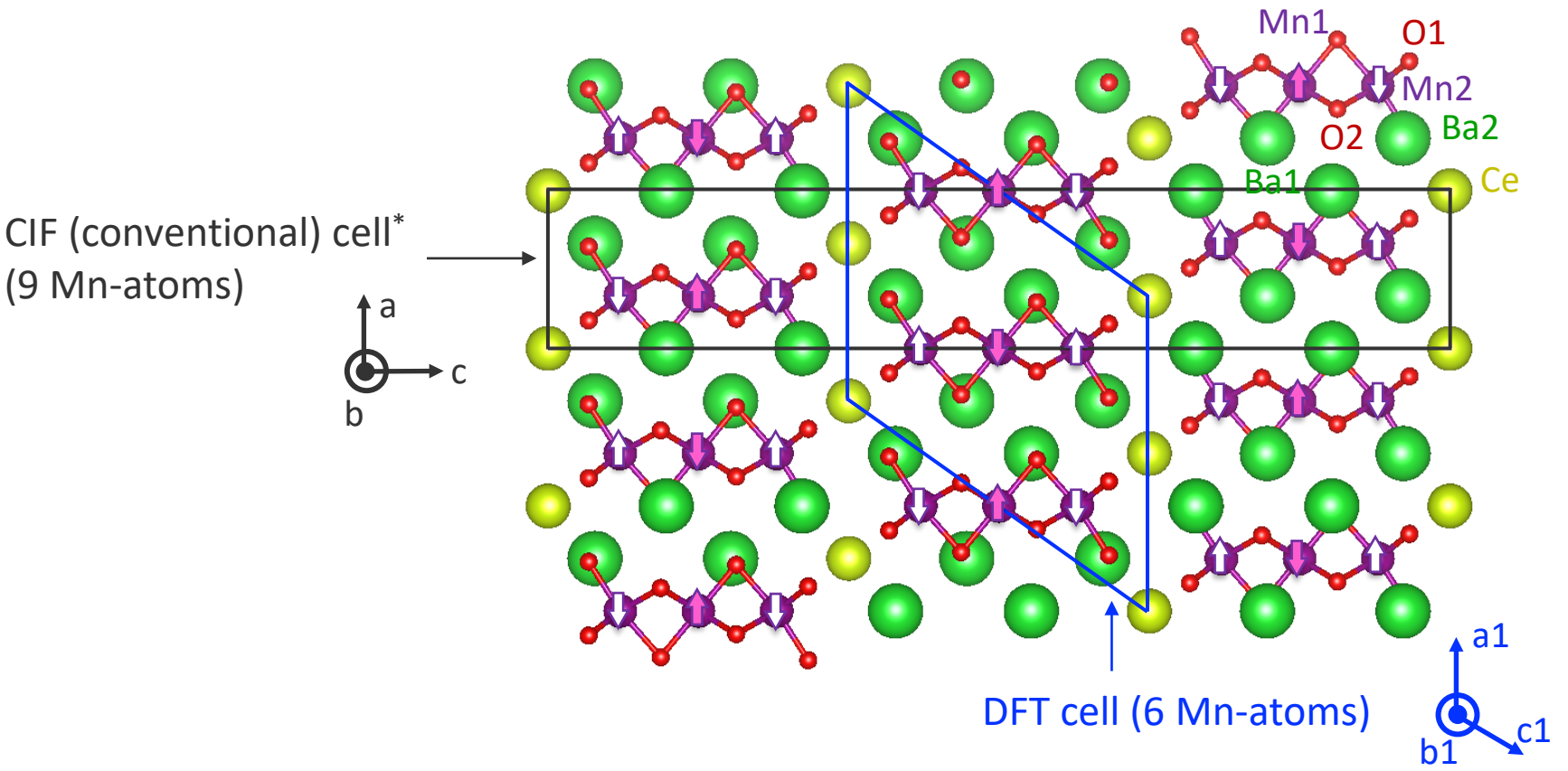
Ce^{4+}: $4f^0\ 5d^0\ 6s^0$

Magnetic configuration (spin arrangement) of Mn^{4+} ions are assigned via Monte-Carlo Sampling

*CIF available from ICSD database, A. F. Fuentes et al., J. Sol. State Chem. 177, 714 (2004)

12R-BCM Atomic and AFM Magnetic Structure

Anti-ferro magnetic 12R $Ba_4CeMn_3O_{12}$ (BCM)



12R-BCM consists of two unique Mn, Ba, O sites and single Ce site

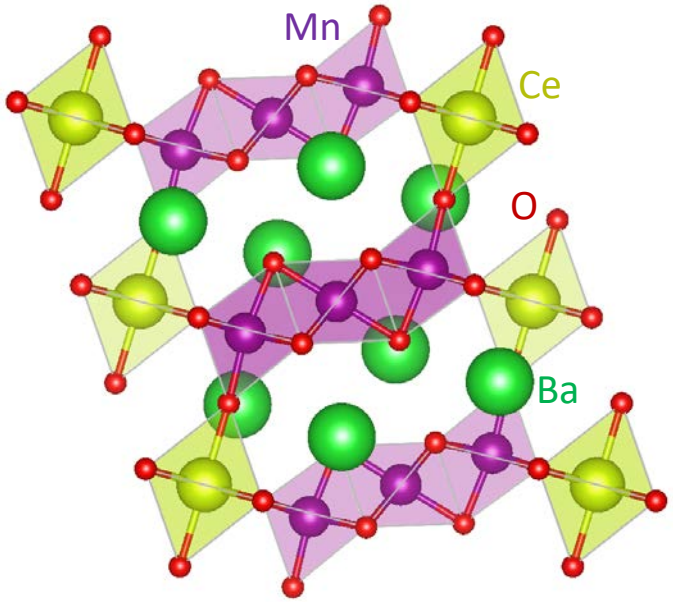
12R-BCM **atomic + magnetic structure** (generated by S. Lany) **available in Data Hub**

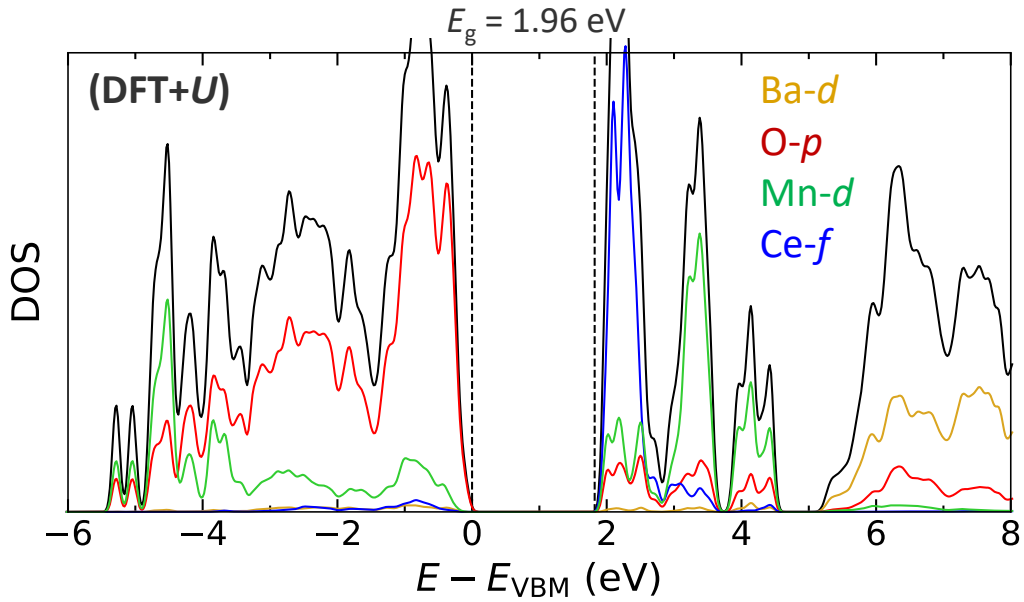
DOI: 10.17025/1532370

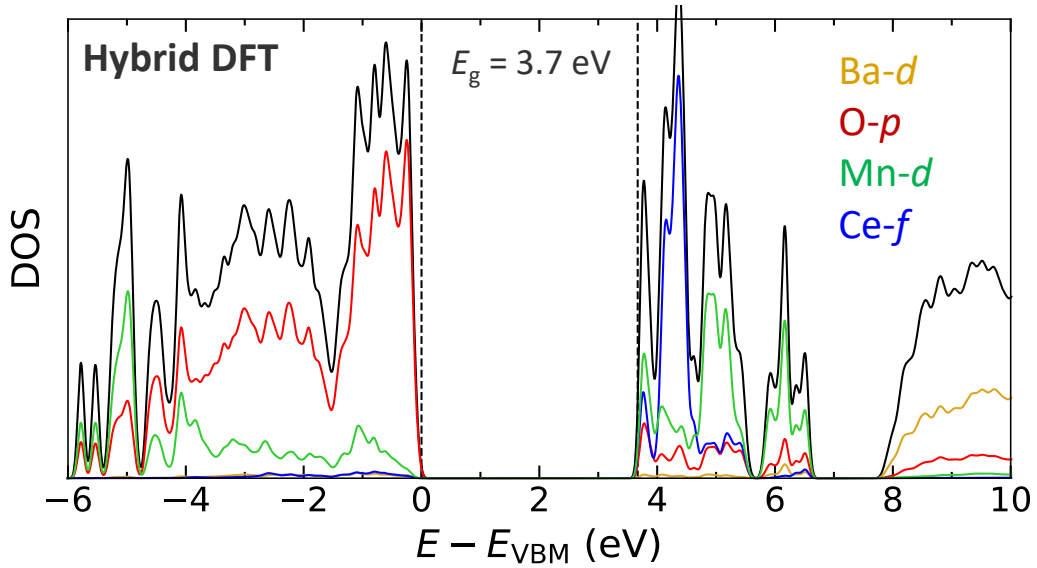
Generated structure can be used for DFT based electronic structure and defect calculations

*CIF available from ICSD database, A. F. Fuentes et al., J. Sol. State Chem. 177, 714 (2004)

Calculated Density of States (DOS) for 12R-BCM

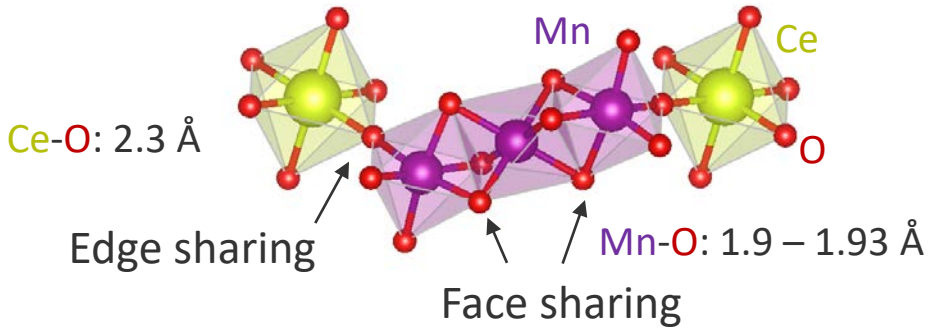






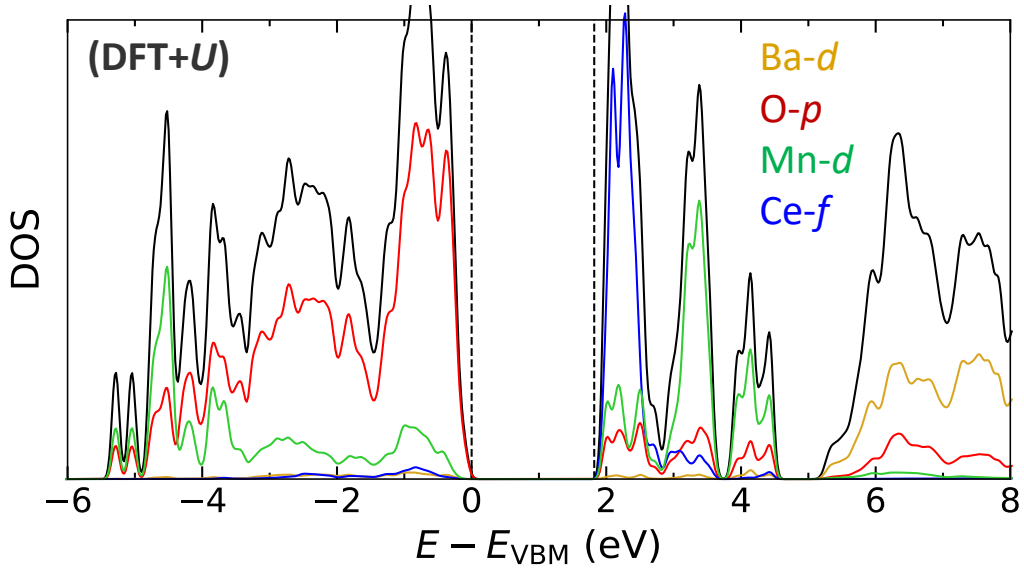
- Near band edges (VBM and CBM) contributions to DOS dominate from **O-*p***, **Mn-*d*** and **Ce-*f***
- **Overall DOS similar across different levels of theory**

Calculated Density of States (DOS) for 12R-BCM

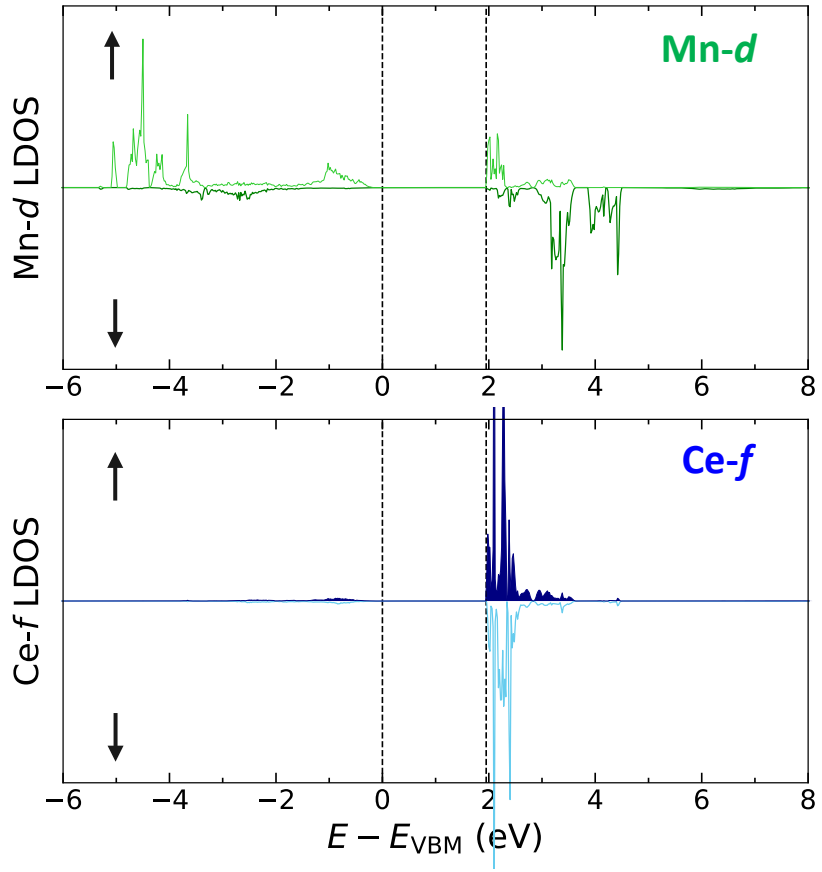


Mn^{4+}: $3d^3\ 4s^0$

Ce^{4+}: $4f^0\ 5d^0\ 6s^0$

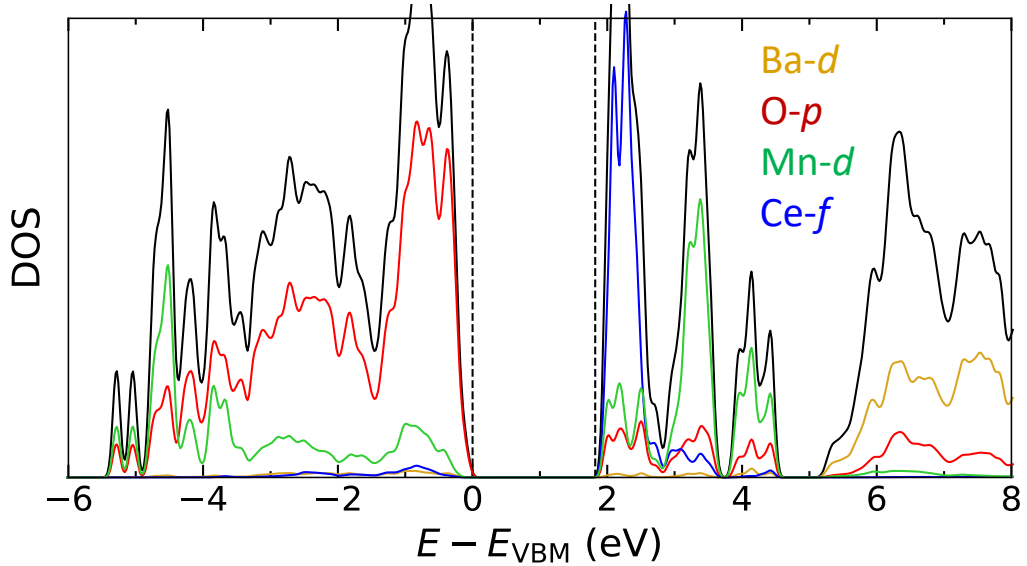


Spin resolved partial DOS



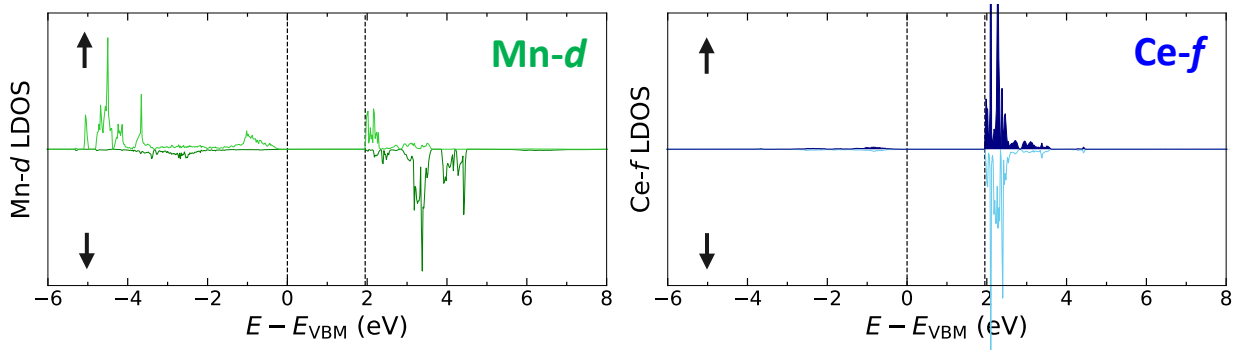
- **Mn and Ce** is **octahedrally bonded** to **O**
- **Strong hybridization** between **Mn-3*d*** and **O-2*p*** creates bonding states (below VBM) and antibonding states (above CBM)
- Empty **Ce-4*f*** states **localized** above CBM

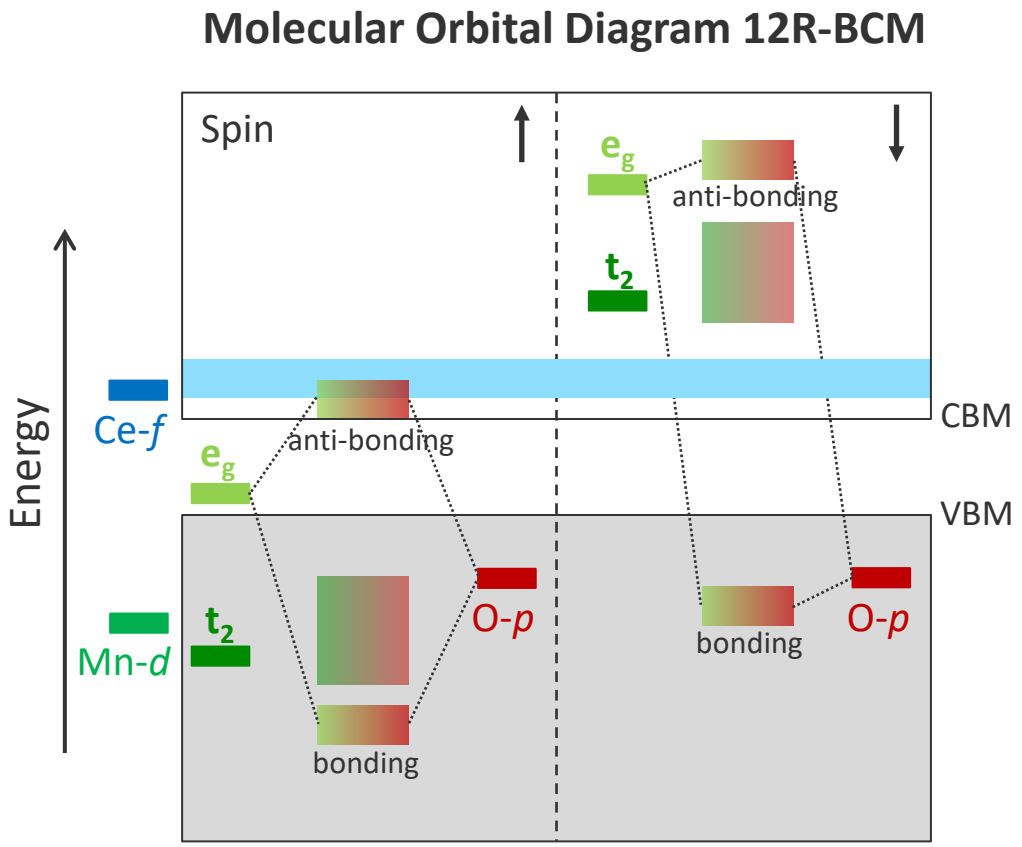
Molecular Orbital Diagram Derived from DOS



Mn^{4+}: $3d^3\ 4s^0$

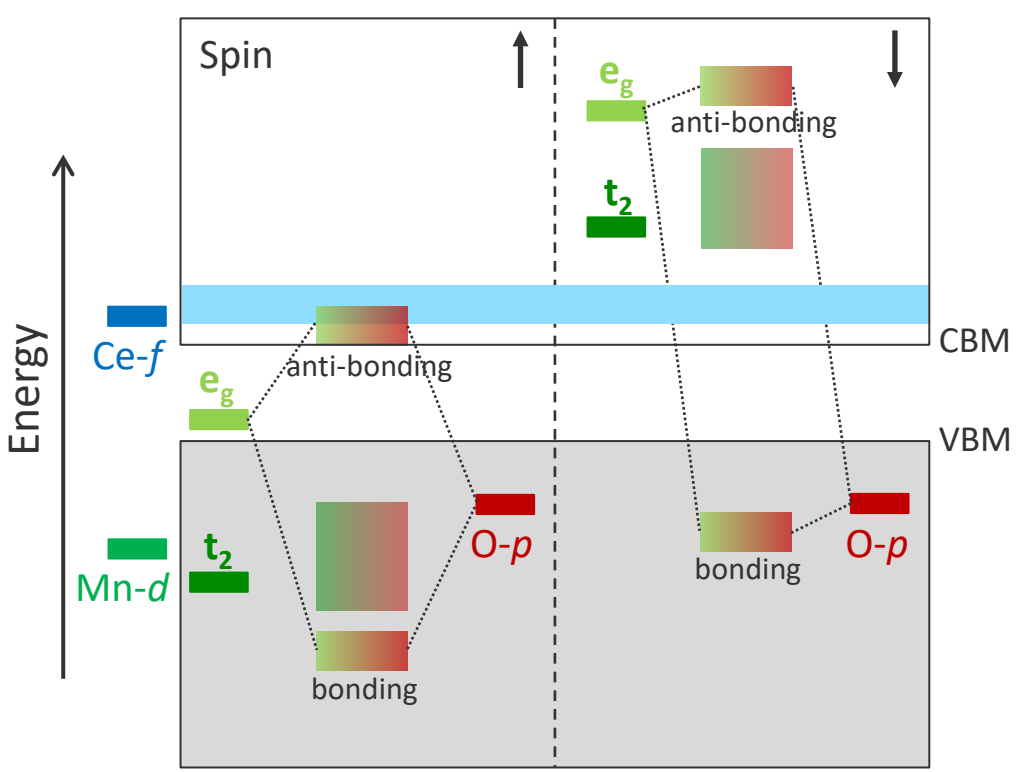
Ce^{4+}: $4f^0\ 5d^0\ 6s^0$

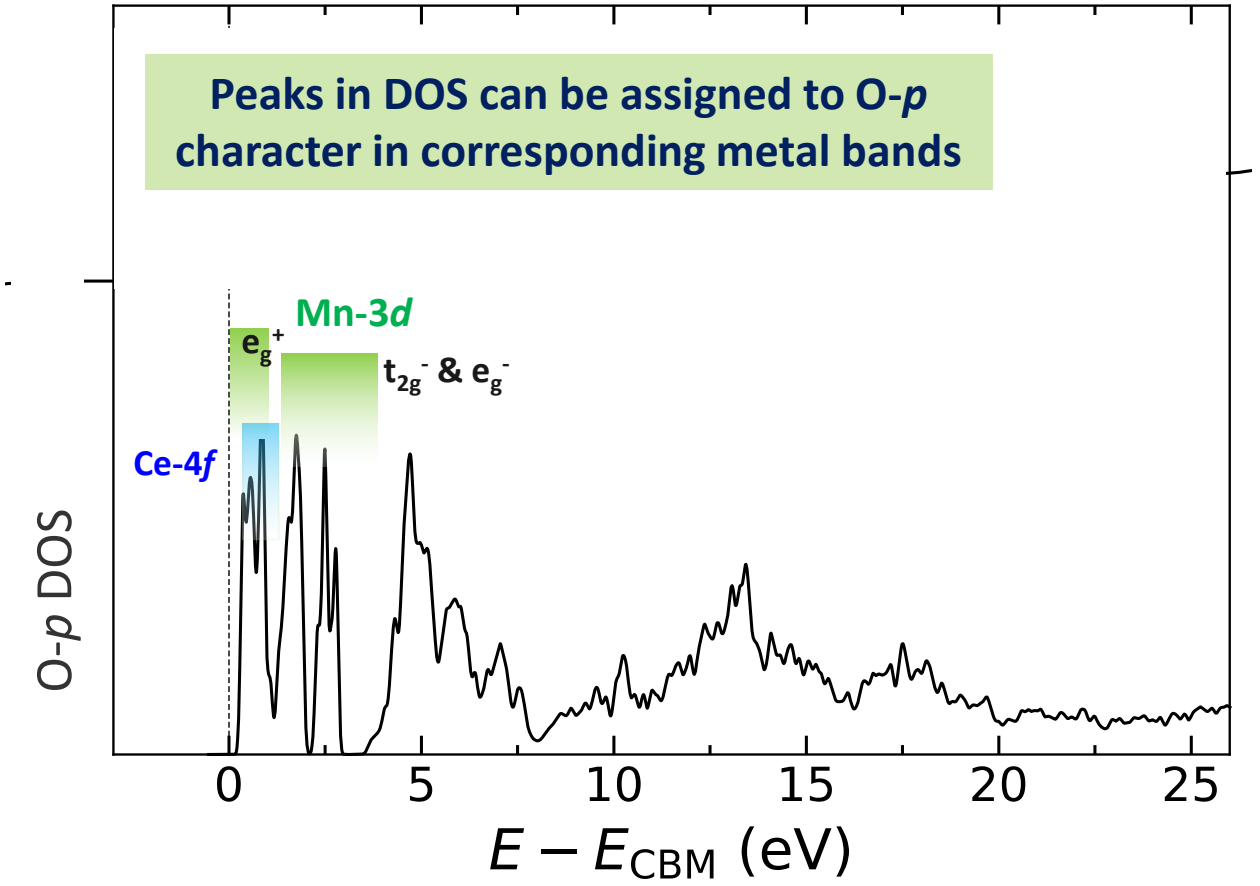




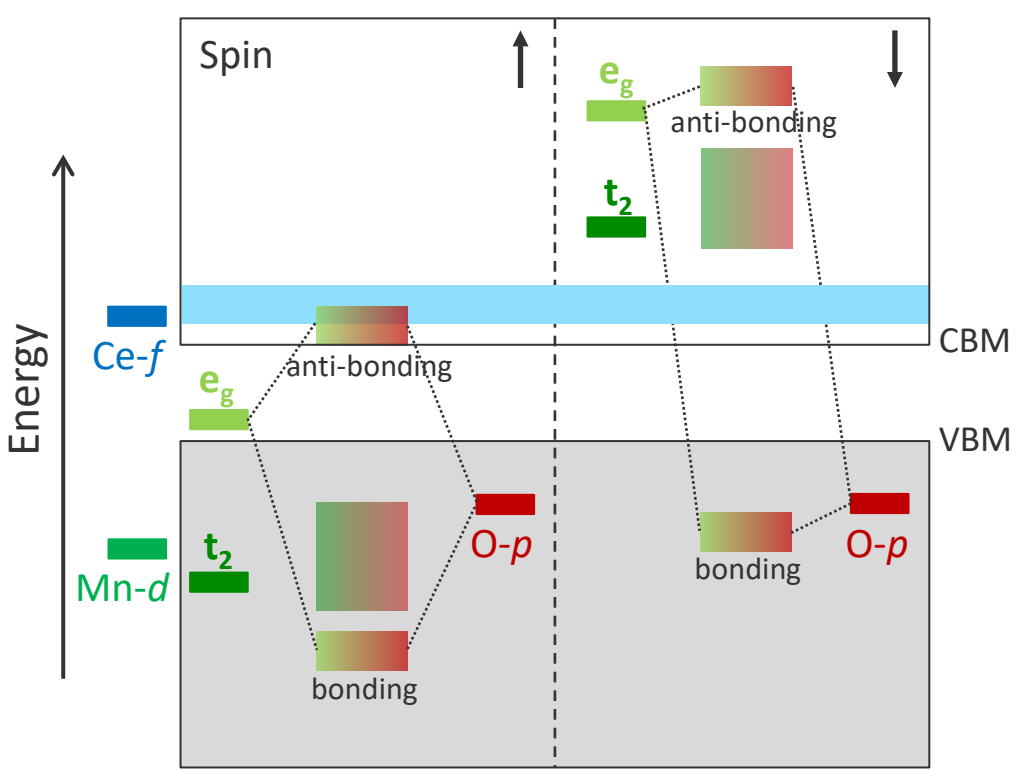
- Crystal field **splitting of Mn-3*d*** into t_{2g} & e_g orbitals
- Empty **Ce-4*f*** states **localized** above CBM
- **Strong hybridization** between **Mn-3*d*** and **O-2*p*** creates bonding states (below VBM) and antibonding states (above CBM)

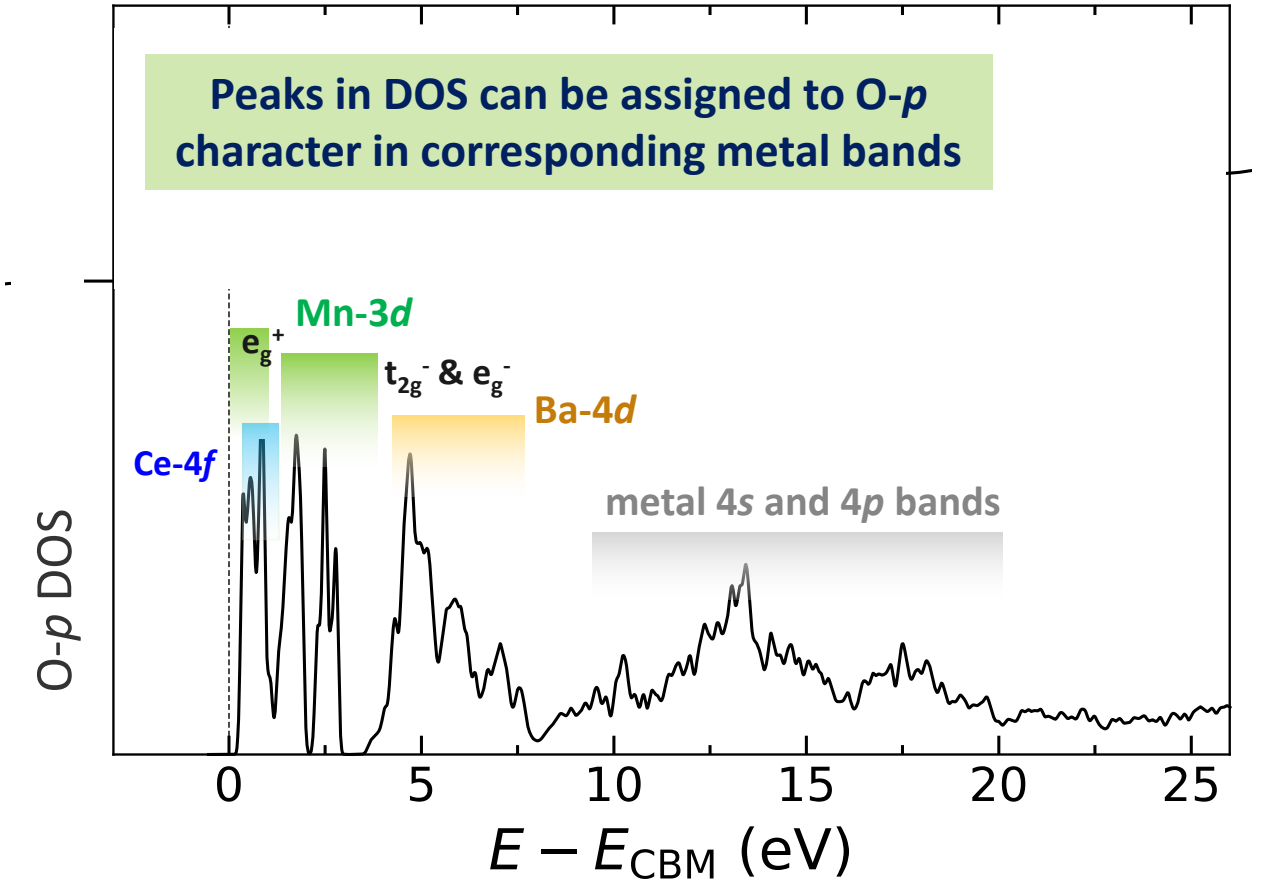
12R-BCM: Metal Bands Contribution to O-*p* DOS





12R-BCM: Metal Bands Contribution to O-*p* DOS

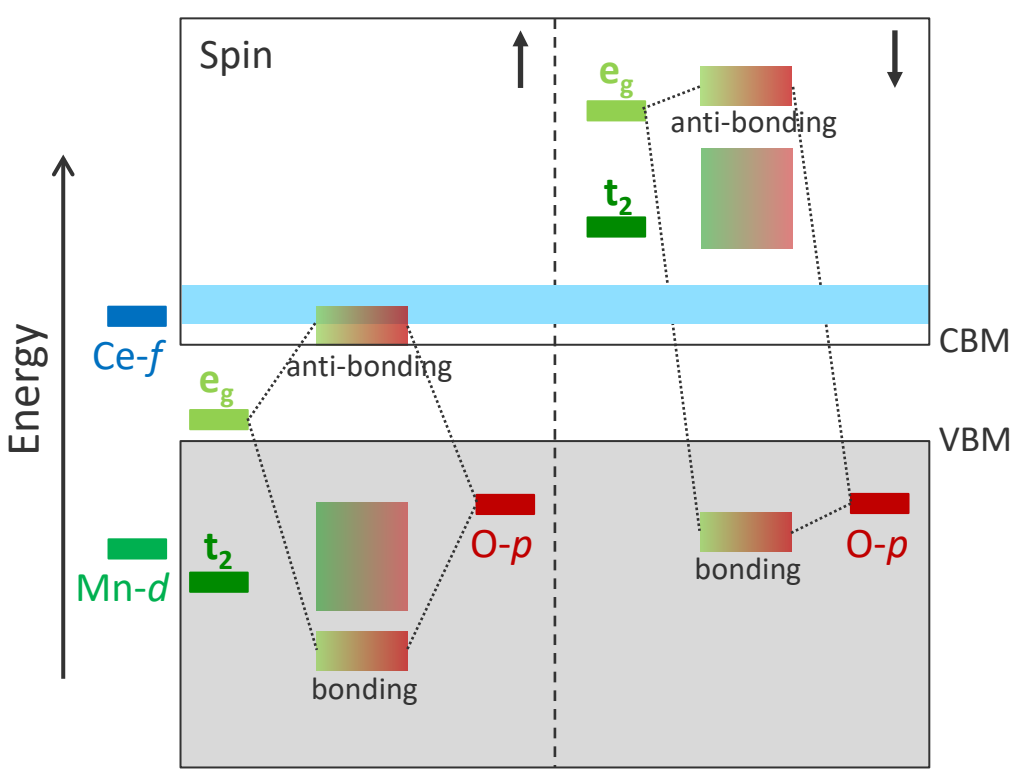


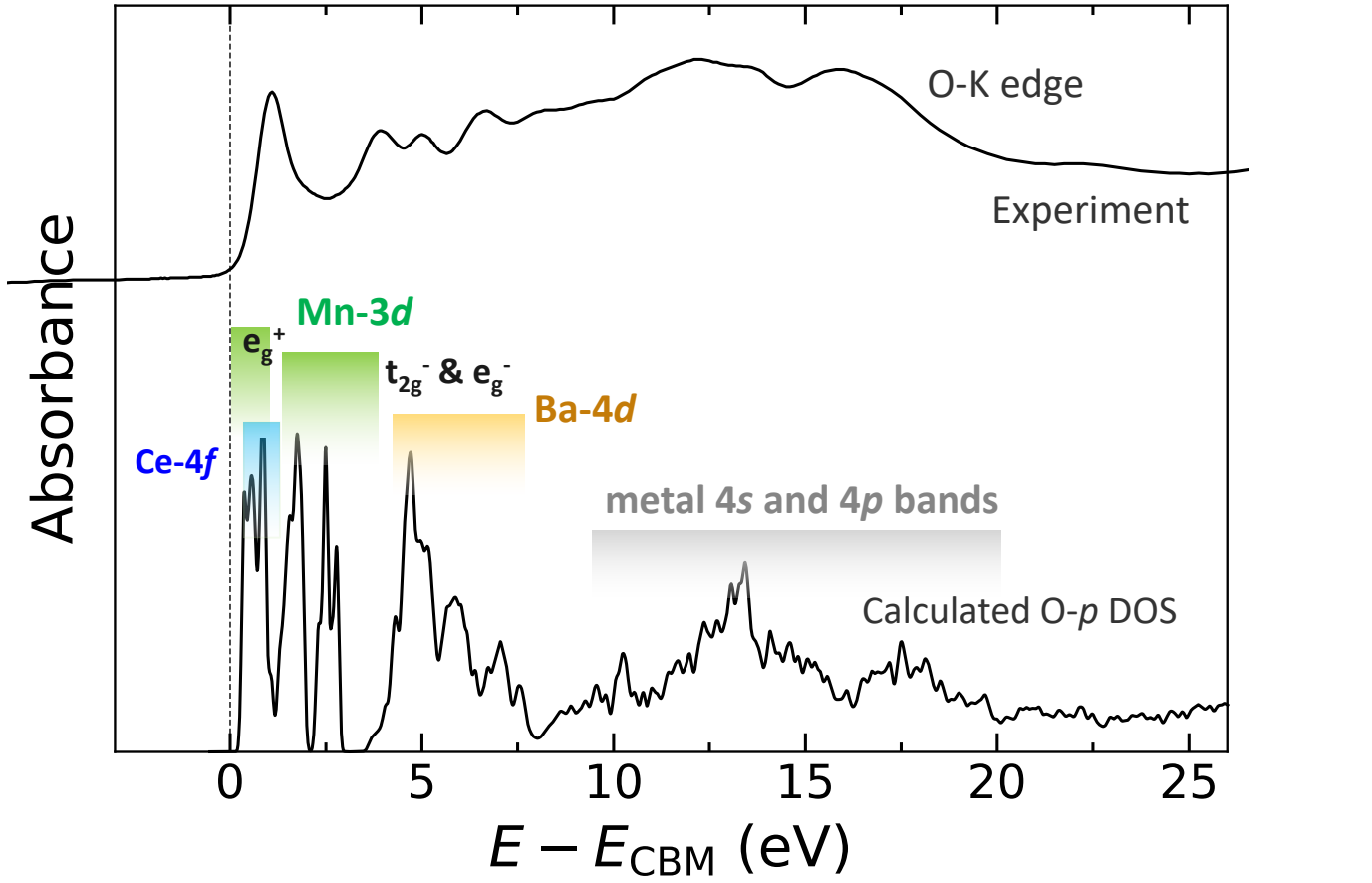


Comparing Measured XAS O-K edge with O-*p* DOS Calculations

Relevance? Can be compared with experiments oxygen 1s X-ray absorption spectrum

(Experimental data courtesy S. Shulda at NREL)

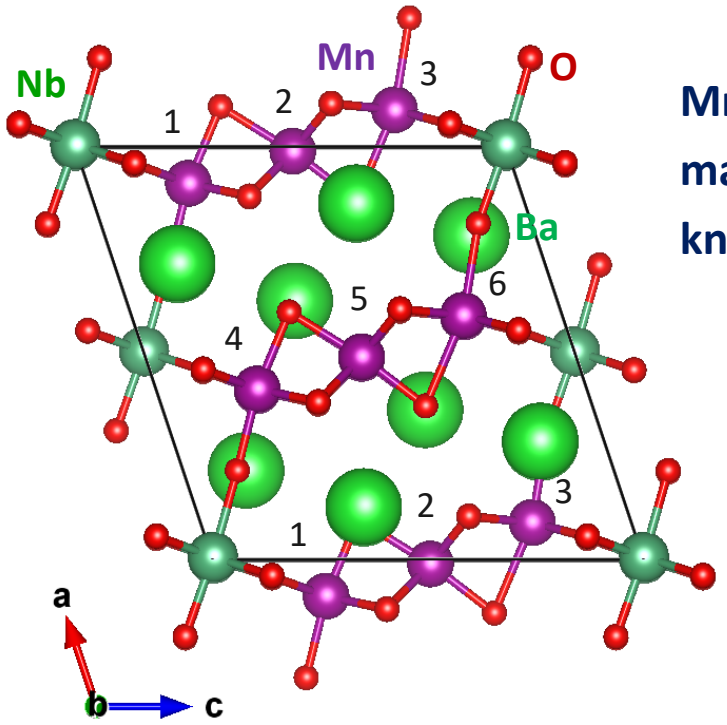




DOS and molecular orbital picture can help develop qualitative understanding of EELS and XAS spectrums

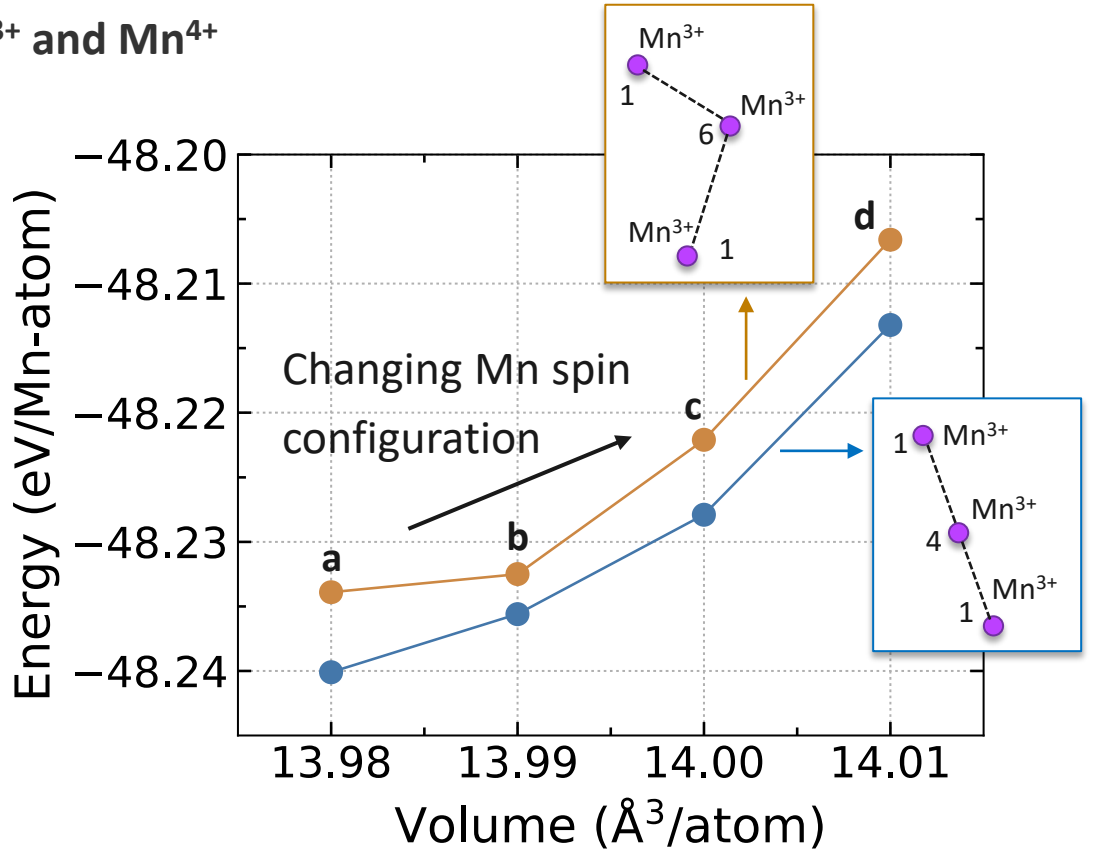
12R-BNM: Charge and Magnetic Structure

12R $Ba_4NbMn_3O_{12}$ (BNM): Nb stable as Nb^{5+} and Mn as both Mn^{3+} and Mn^{4+}



Mn^{3+},Mn^{4+} arrangement and magnetic configuration is not known*

Mn1 site (2 and 5),
Mn2 site (1, 3, 4 and 6)



Using DFT explored 120 configurations; differ in Mn charge (Mn^{4+} , Mn^{3+}) and spin configurations (AFM,FM)

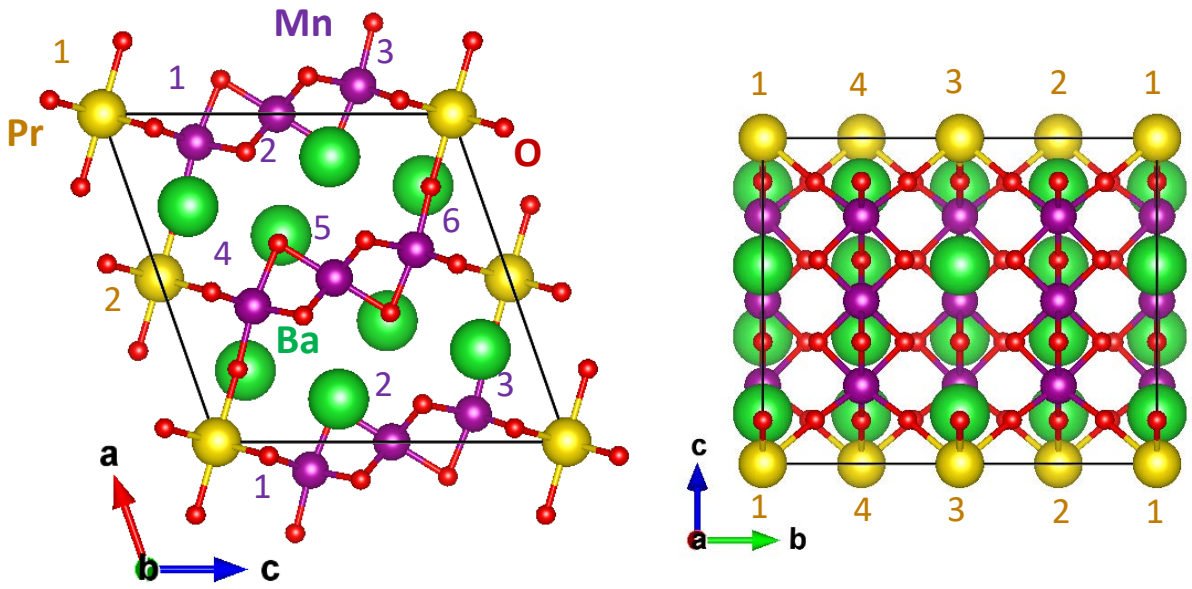
Structure will be made available on datahub

Type	#	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6
Anti-ferromagnetic	a	↓	↑	↓	↑	↓	↑
Ferri-magnetic	b	↓	↑	↓	↓	↑	↓
Anti-ferromagnetic	c	↑	↑	↓	↓	↓	↑
Anti-ferromagnetic	d	↑	↑	↑	↓	↓	↓

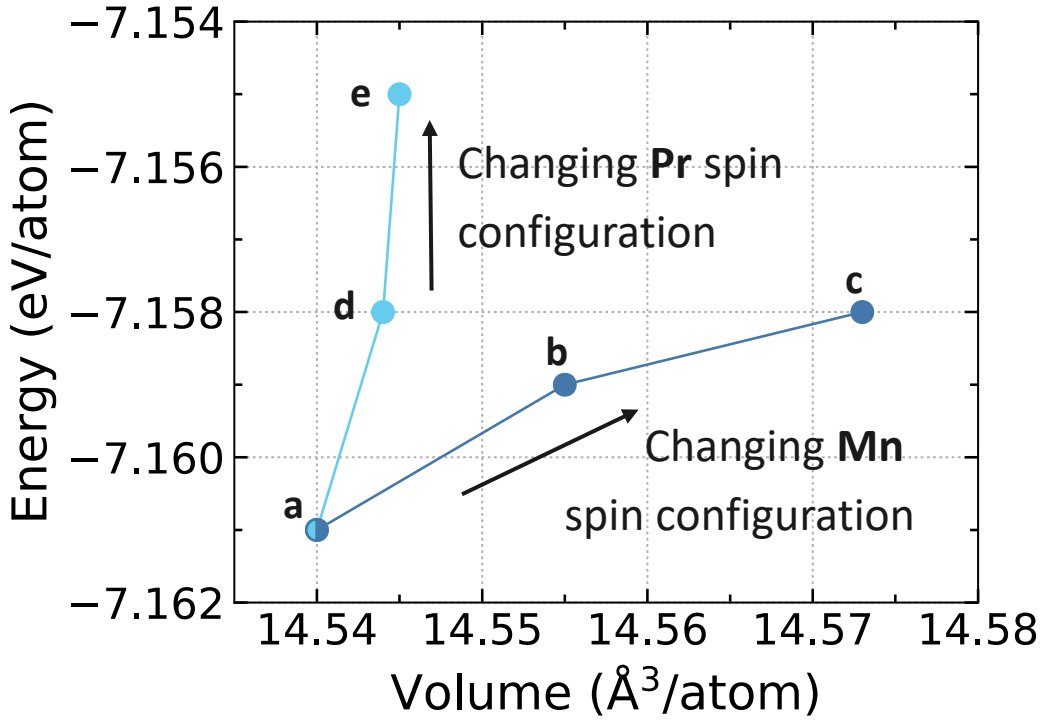
*Nguyen et al. Mater. Res. Express 6 056108 (2019)

12R-BPM Magnetic Structure

12R $Ba_4PrMn_3O_{12}$ (BPM): Pr^{4+} ($4f^1$) and Mn^{4+} ($3d^3$)



Energy sensitivity on the spin configuration



Pr and Mn magnetic configurations search performed on 40 and 80 atom supercells

Structure will be made available on datahub

A. F. Fuentes et al., J. Sol. State Chem. 177, 714 (2004)

Type	#	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Pr1	Pr2	Pr3	Pr4
Antiferromagnetic	a	↓	↑	↓	↑	↓	↑	↑	↓	↑	↓
Antiferromagnetic	b	↑	↑	↓	↓	↓	↑	↑	↓	↑	↓
Antiferromagnetic	c	↑	↑	↑	↓	↓	↓	↑	↓	↑	↓
Ferrimagnetic	d	↓	↑	↓	↑	↓	↑	↑	↑	↓	↑
Ferrimagnetic	e	↓	↑	↓	↑	↓	↑	↑	↓	↑	↑

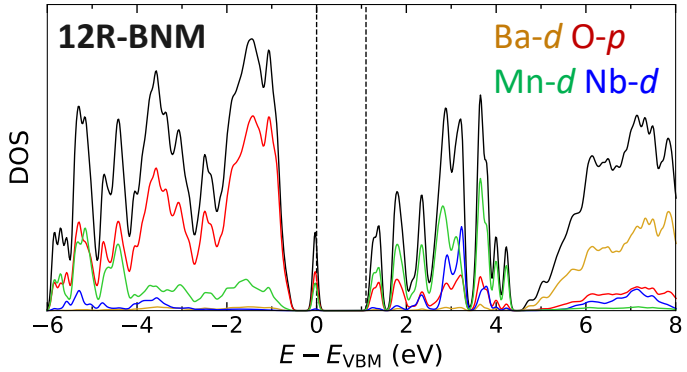
Calculated (DFT+*U*) density of states (DOS) and the molecular orbital diagram for 12R-BNM and 12R-BPM

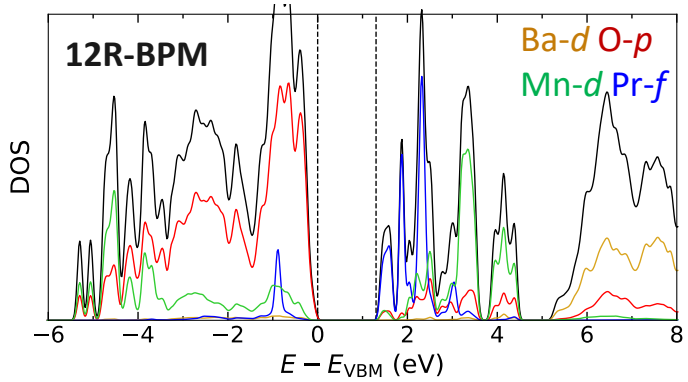
12R-BNM (O-*p* DOS)

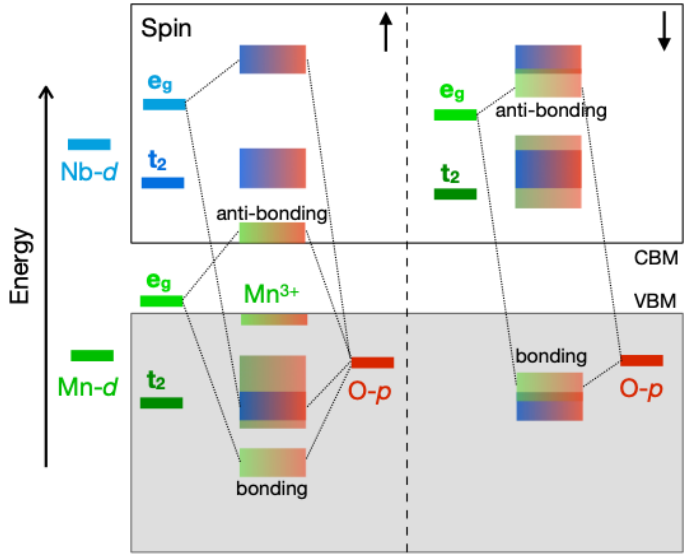
- <1 eV from CBM, O-*p* and Mn-3*d* (e_g^+) hybridized bands dominate
- >1 eV from CBM, O-*p* character in Mn-3*d* and Nb-4*d* bands

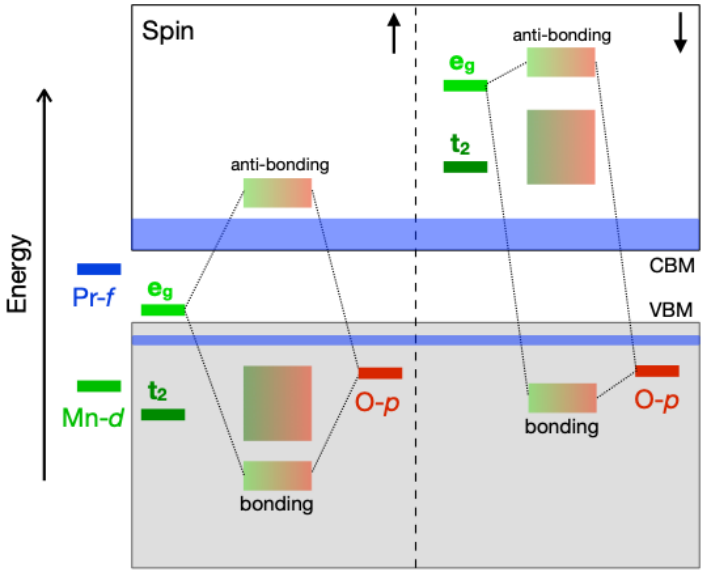
12R-BPM (O-*p* DOS)

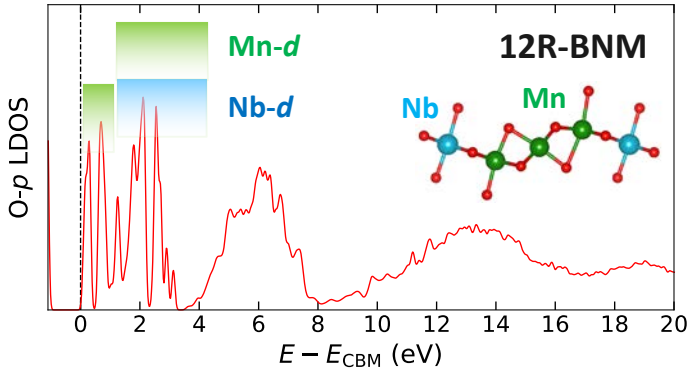
- < 1 eV from CBM, O-*p* and Pr-4*f* hybridized bands dominates
- > 1eV from CBM, hybridization of O-*p* with Mn-3*d* bands

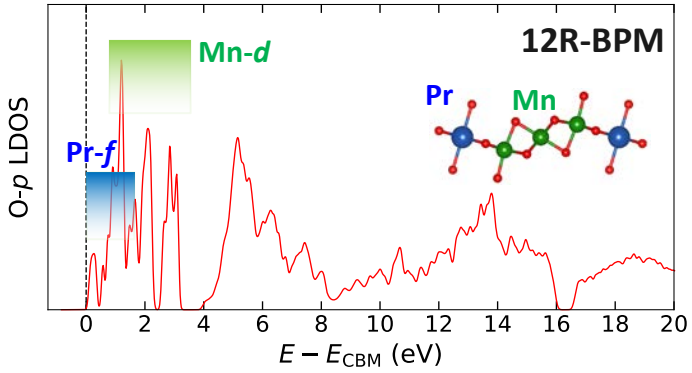








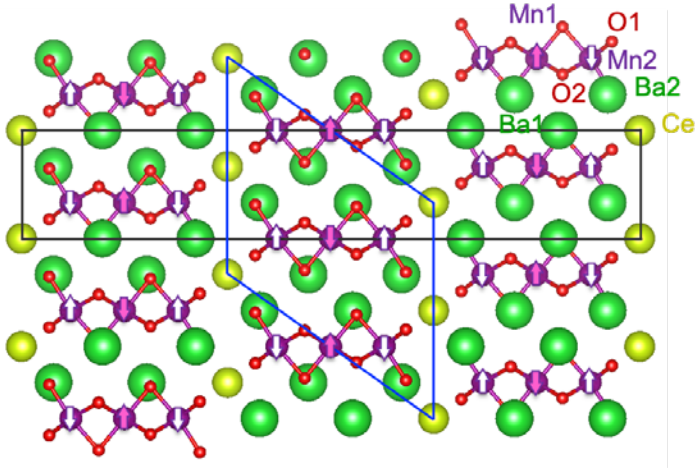


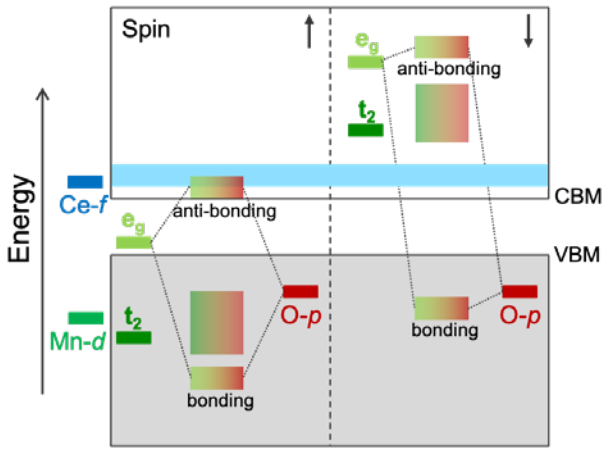


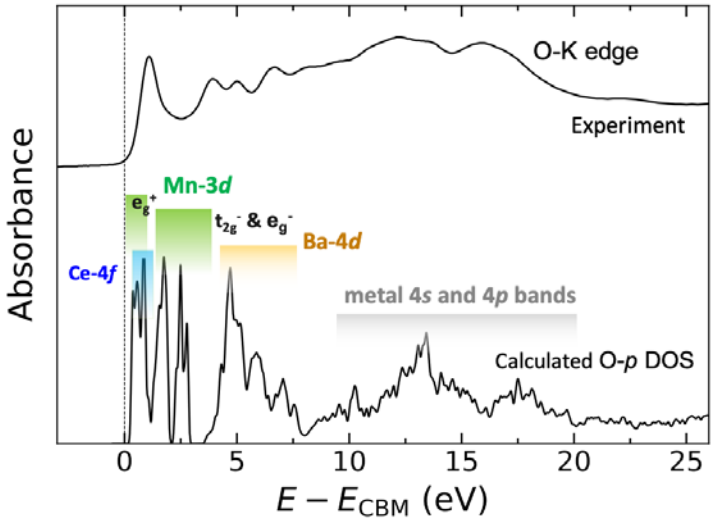
Ab Initio Study of Structure of Complex Oxides for STCH

- **Theory helps characterize the magnetic structure of complex oxides**
- **These structures to be used to predict defect energies and thermodynamics under STCH conditions**
- **DOS and molecular orbital picture can help provide qualitative understanding of experimental x-ray absorption spectrum**

12R $Ba_4CeMn_3O_{12}$ (BCM)







HydroGEN Advanced Water Splitting Materials

U.S. DEPARTMENT OF ENERGY

Questions and feedback: anuj.goyal@nrel.gov

Thank you!

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