



BAND STRUCTURE PREDICTION FOR PEROVSKITES

Engineering

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ABSTRACT

Conversion of CO₂ can be achieved via photocatalyst and has enormous energy and environmental impact but still remains a big challenge. Perovskites have band edge that are suitable for photocatalytic applications for reduction of CO₂. We present results for Band gap calculation for Perovskite Oxides using different techniques.

KEYWORDS

Perovskite DFT

Introduction

For a considerable amount of time, a lot of attention has been given to the development of photocatalysts to counter the environmental problems. TiO₂ has been able to solve the problem due its favorable properties. The only drawback in using TiO₂ is that its finds applicability only in the UV region.

Thus, there is need to identify photocatalyst that are active even in visible light. Perovskites such as LaCrO₃ have band edge that are suitable for photocatalytic applications but its bandgap is too large. This can be reduced by substituting Fe or Mn in the B site of ABO₃ type perovskite. These B site substitutions can be made in various different ways in order to tune the band gap.

Perovskites are compounds with crystal structure same as CaTiO₃. The general chemical formula for perovskite oxide are ABO₃ where A atoms are larger than B. In an ideal cubic cell, A atom is at the corner of the cube while B sits in the middle with O at face centers. They have varied applications in photovoltaics, lasers, photocatalyst, etc.

Density functional theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. The application of DFT calculations is becoming a standard tool in calculating the properties of materials. One of the problems in DFT is that it underestimates the value of band gap of materials. This can be countered by using certain Hybrid Functionals or approximations in order to get the correct values for band gap.

Density of State describes the number of states per interval of energy at each energy level that are available to be occupied. A high Density of State means that at that energy level, there are many states that are available. Whereas, at points where the density of state is zero, no states can be occupied at that energy level.

Computational Setup

1) Initial Setup

- The Vienna Ab initio Simulation Package (Vasp) was used to perform all the DFT calculations on Perovskite oxide.
- Calculations were performed on the following Perovskite oxides:
 - LaFeO₃
 - LaCrO₃
 - LaMnO₃
 - LaFe_{0.5}Mn_{0.5}O₃
 - LaFe_{0.5}Cr_{0.5}O₃
 - LaMn_{0.5}Cr_{0.5}O₃

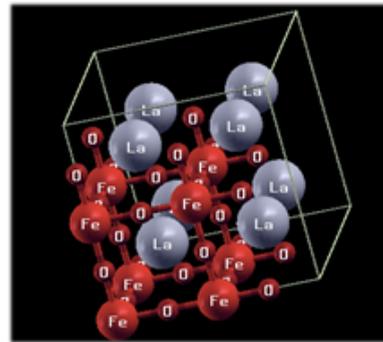
3. All of the Perovskites were assumed to be existing in cubic structure. This was a reasonable assumption as most photocatalytic reaction take place at higher temperature and the most stable structure is thus cubic.

4. For any job submission in VASP, four files are essential:

- INCAR** : This contains the value of all the input variables.
- POSCAR** : This contains the position coordinates of the all the atoms in the periodic unit selected i.e. it contains the lattice

geometry and ionic positions.

- POTCAR** : This contains the pseudo potentials for all the atoms used in the calculations. These files are available at data files to us.
- KPoints** : It contains the K-point coordinates or the mesh size for creating k-points grid.
- The 40 atom repetitive unit used in the calculations in shown below.



40 atom periodic unit

2) Finding the most stable configuration and Lattice Parameter

- For ABO₃ type structures only one configuration exists but when B site consists of 2 elements, 7 different configurations are possible.
- Before proceeding for Band Gap Calculation, the most stable configuration as well as the exact lattice parameter should be known.
- For reasonable accuracy, lattice parameter of all compounds are calculated up to 3 decimal places.
- After the job is complete, the energy can be found either in the **OUTCAR** file or the **OSZICAR** file.
- The most stable structure in case of perovskite can be predicted based on the tolerance factor.

$$t = \frac{r_A - r_O}{\sqrt{2}(r_B + r_O)}$$

- For 0.89 < t < 1, the cubic structure is most stable structure whereas for t < 0.89, orthorhombic is more stable

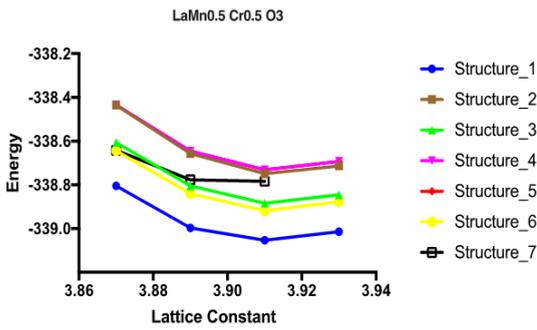
For ABO₃

- Since only one configuration exist, we calculate energies for different lattice parameters.
- The lattice parameter for which a minima is achieved is the exact lattice parameter for the compound. An example of such a plot is shown below.

For AB¹_{0.5}B²_{0.5}O₃

- Since different configurations exist, the most stable configuration is to be found out first before finding the exact lattice parameter.
- The first step is to calculate energy for all the configurations and then proceed forward with the most stable one and calculate lattice

parameter up to 3rd decimal. A graph obtained in such a case is as follows:



3) Testing Different Methods For Band Gap Calculation

1. The following methods were tested for Band gap calculation for perovskites:

- i. DFT
- ii. DFT+U
- iii. GW Approximation
- iv. DFT+HF methods : HSE06 and PBE0

2. Jobs were tested for LaFeO3 using all the above schemes using procedures as illustrated in the VASP manual.

3. The following were the observations for each method:

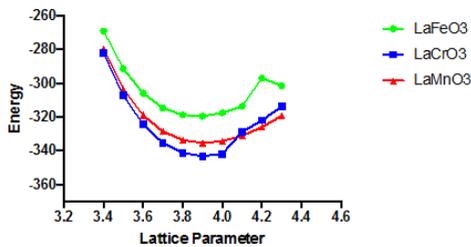
- i. DFT: Underestimates the Band gap to a large extent. Hence not favourable.
- ii. DFT + U : Uncertainty exists on the value of U to be used. However, job processing is fast and reliable.
- iii. DFT + HF methods: Over estimates Band Gap and takes a lot of computational time and memory.
- iv. GW Approximation: Accurate but takes a lot of computational time and memory.

4) Performing Density of State (DOS) Calculation using DFT + U method (preferred method)

- 1. U correction are only applied to Cr, Fe and Mn.
- 2. The correct U values of these elements were obtained from literature.
- 3. Density of state analysis is done for values of U=0,3,4,5 for the compounds in order to find the band gap.

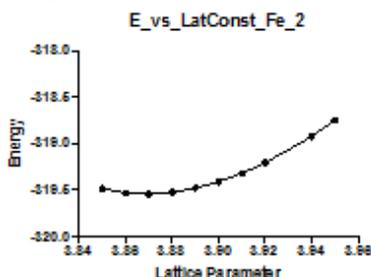
Results

1) Lattice Parameter for LaFeO₃, LaCrO₃, LaMnO₃



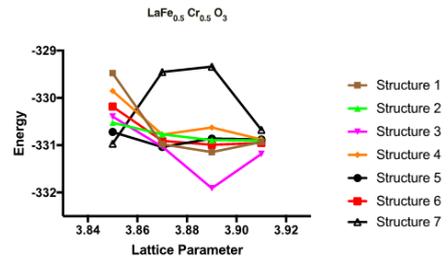
The graph of Energy Vs Lattice Parameter for the 3 compounds

Another run is performed to find the lattice constant with greater accuracy. The graphs for those are as shown below:

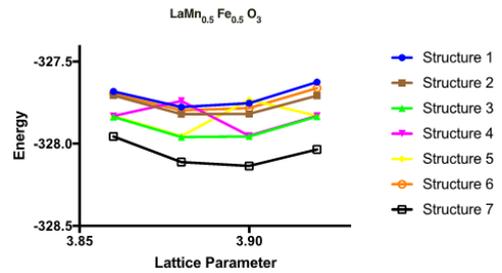


2) Lattice Parameter for LaMn_{0.5}Fe_{0.5}O₃, LaMn_{0.5}Cr_{0.5}O₃, La Cr 0.5 Fe0.5O3

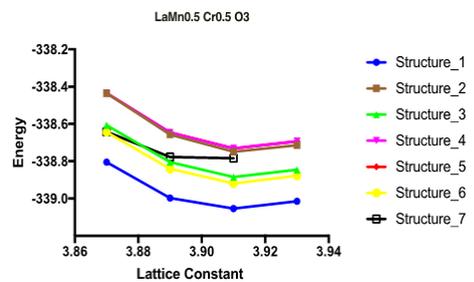
1. The most stable configuration for these compounds can be found from the graphs shown below.



Most Stable Configuration – Configuration-3



Most stable Configuration- Configuration 7



Most stable configuration – Configuration 1

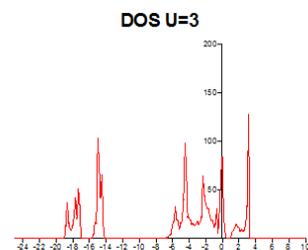
2. Further runs are performed to find the accurate lattice parameter for each.

Here is the table summarizing all the lattice constants for the compounds

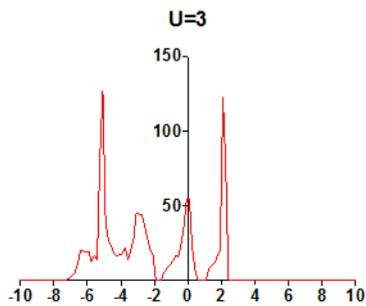
	Calculated Lattice Parameter(in Å)	Experimental Lattice Parameter(in Å)	Error	Tolerance
LaFeO ₃	3.868	3.92	1.32%	0.883
LaCrO ₃	3.903	3.894	0.66%	0.897
LaMnO ₃	3.909	3.89	0.48%	0.912
LaMn _{0.5} Fe _{0.5} O ₃	3.894	3.923	0.74%	0.897
LaMn _{0.5} Cr _{0.5} O ₃	3.911	3.893	0.46%	0.905
LaFe _{0.5} Cr _{0.5} O ₃	3.889	3.911	0.56%	0.912

3) DFT+U analysis of LaFeO₃, LaMnO₃

For LaFeO₃



For U=3, Band gap = 0.5 eV

For LaMnO_3 ,For $U=3$, Band gap = 0.4954 eV

Conclusion

1. Lattice Parameter

- 1) The lattice parameters have been compared with experimental values.
- 2) It can be observed that the compounds having lesser tolerance have a greater error.
- 3) This is because in compounds having $t < 0.89$, the orthorhombic structure is most stable. Since all structures have been considered cubic, the trend in percentage error is justifiable.

2. Different Methods for Band Gap Calculation

- 1) DFT - It underestimates the value of Band Gap. Almost all compounds show band gap as zero using simple DFT.
- 2) DFT + U - The value of U is uncertain in this case. However, accurate value of U can be found in literature. The run time for the jobs is reasonable.
- 3) Hybrid Functionals (HSE06 and PBE0) - It overestimates the value of Band gap. The run time for jobs is quite large and the memory required is also large.
- 4) GW approximation - It is the most accurate method available, however the run time as well as the memory requirement is very high.
- 5) Considering the above mentioned points, DFT + U method was chosen to be the most favorable method and subsequent calculations were based on this method only.

3. DFT + U analysis

- 1) LaFeO_3 - The value of U for LaFeO_3 in literature is mentioned to be 5.3 eV. The value for $U=5$ is 1.66 eV which is in reasonable agreement with values reported which are about 2 eV.
- 2) LaMnO_3 - The value of U for LaMnO_3 in literature is mentioned as 3.9 eV. The value of 0.8325 eV is in agreement with values from literature.
- 3) LaCrO_3 - The value of U for LaMnO_3 in literature is mentioned as 3.7 eV. However, unexpected results were obtained using DFT + U analysis.

$\text{LaMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ - Exact Band gap for this compound could not be found from literature, however trends were analysed by changing the U values of Mn and Fe. An interesting result obtained was that: Band gap was constant for U correction in Mn from (1 to 2) and (3 to 4). However, no specific reason could be identified for the same and further analysis was required

References

- 1) An Investigation on the Band Gap and Band Edge of Semi-Conducting Lanthanum Transition Metal Perovskites for Photocatalytic Applications- Divya Suresh
- 2) Electronic structure of A-type antiferromagnetic LaMnO_3 by GW approximation - Y. Nohara¹, A. Yamasaki², S. Kobayashi³, and T. Fujiwara
- 3) The electronic and thermodynamic properties of Ca doped LaFeO_3 - a first principles study using density functional theory - Davis George Daniel
- 4) Vasp Manual - <http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html>
- 5) Vasp Examples - http://cms.mpi.univie.ac.at/wiki/index.php/VASP_example_calculations
- 6) Density functional theory - A Practical Introduction: David S. Sholl, Janice A. Steckel
- 7) Materials Project - materialsproject.org