UNIVERSIDAD COMPLUTENSE MADRID

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FIRST PRINCIPLES STUDY ON THE FEATURES OF $Ca_xSr_{2-x}Ta_2O_7$ AS PHOTOCATALYTIC MATERIALS

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INTRODUCTION

PHOTOCATALYSTS

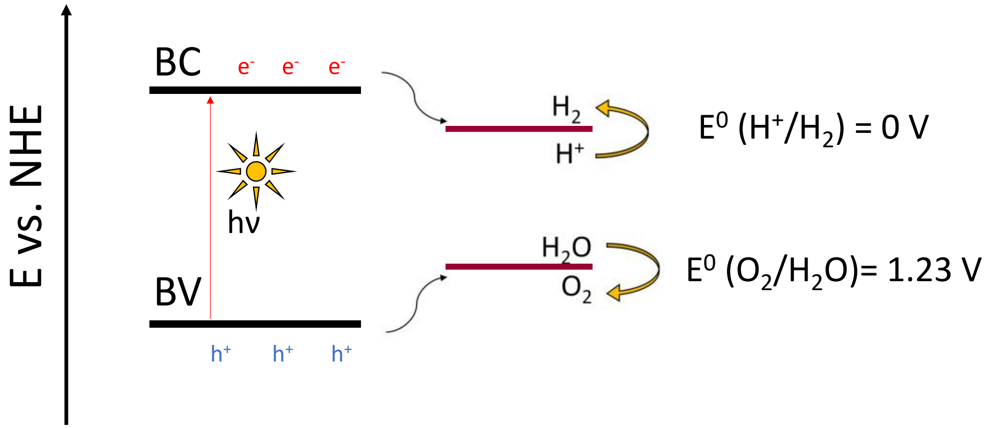
Basic requirements for photocatalyst with application in water splitting

Hydrogen production through water splitting using sunlight might be vital for green hydrogen generation

Photocatalysts are semiconductors materials that are able to absorb **sunlight**, leading to the **promotion of electrons** from the valence band to the conduction band

Sunlight is composed by 7.2% UV + 45.6% IR + **47.2% visible**

For **H_2** production through **water splitting**, **bands positions** are key



band gap should be between 1.23 eV and 3.0 eV

CB minimum should be **above** the H_2O/H_2 reduction potential (0.0 eV)

VB maximum should be **below** the O_2/H_2O oxidation potential

Among other photocatalysts, $Sr_2Ta_2O_7$ shows some exciting features, but its large band gap (4.6 eV) restricts the absorption to the UV region

PHOTOCATALYSTS

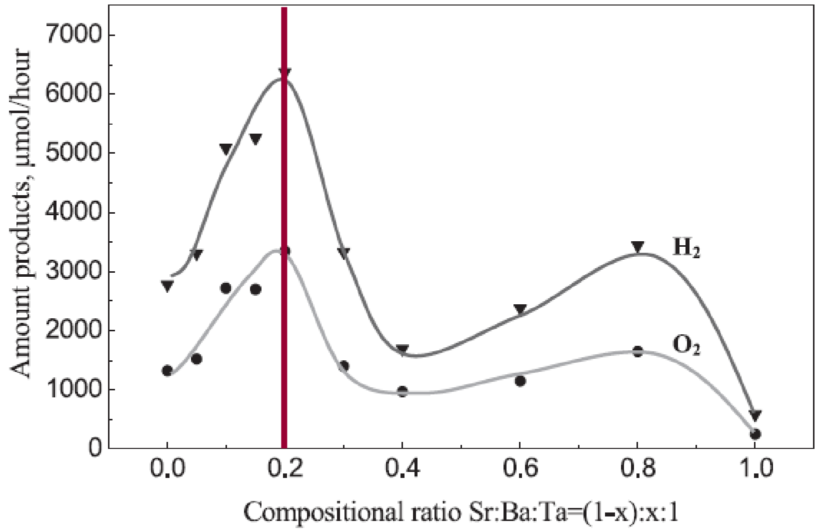
Characteristics that make $Sr_2Ta_2O_7$ an appealing compound for photocatalysis

$Sr_2Ta_2O_7$ shows a **large CB** position relative to H_2O/H_2 reduction potential

Kim et al.[1] have demonstrated that the **partial substitution** of Sr with Ba in the $Sr_{2-x}Ba_xTa_2O_7$ ($0 < x < 0.4$) family can lead to upgrading in photocatalytic activity.

The photocatalytic activity in solid solution $Sr_{2-x}Ba_xTa_2O_7$ is **maximum** when $x = 0.4$.

Figure from [1]



Would partial substitution of Sr with **Ca** have the same effect?

This work focuses on the **computational study** through **DFT** calculations of the structural and electronic changes that the substitution of Sr with Ca can provoke in the $Sr_{2-x}Ca_xTa_2O_7$ family

1. Resources Processing 2009, 56, 138-144

METHODOLOGY

DFT

INPUT

Crystallographic models

DFT

OUTPUT

Crystal and electronic structures

$$\hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{ext} + \boxed{\hat{V}_{xc}}$$

In this work, SCAN meta-GGA XC-functional is used to study a photocatalysts' family

Calculations have been performed using VASP (Vienna ab-initio simulation package)

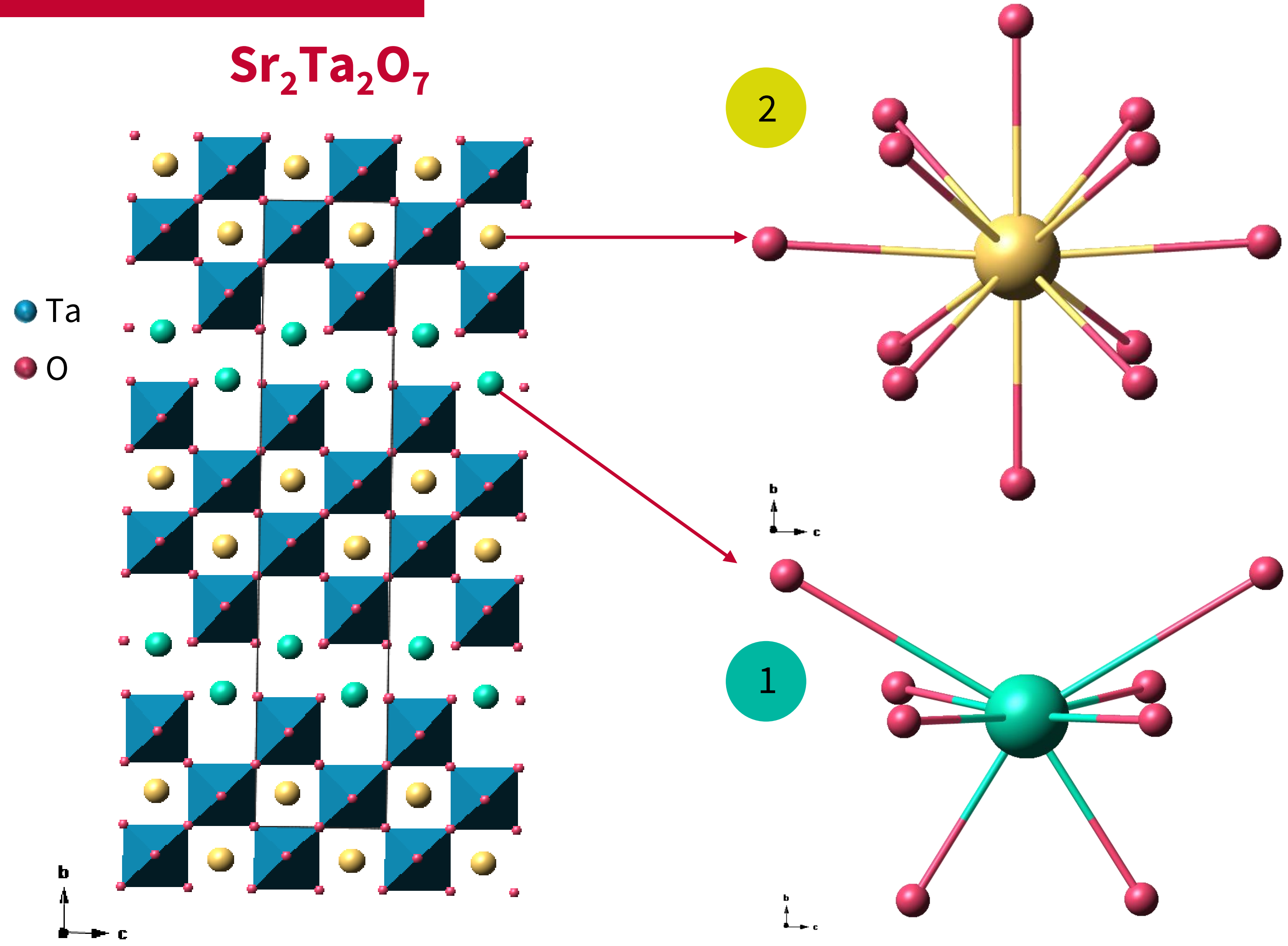
Interaction of core electrons with nuclei was described through the PAW (Projector Augmented Wave method)

Energy cut-off was set at 600 eV

K-point meses were 6 x 2 x 6 in all calculations (Monkhorts-Pack scheme)

CRYSTAL STRUCTURE

$Sr_2Ta_2O_7$



$Sr_{2-x}Ca_xTa_2O_7$

Ca substitution is studied using **two** different models

Model 1

Substitution of Sr(1) with Ca

$CaSrTa_2O_7$(2)

Model 2

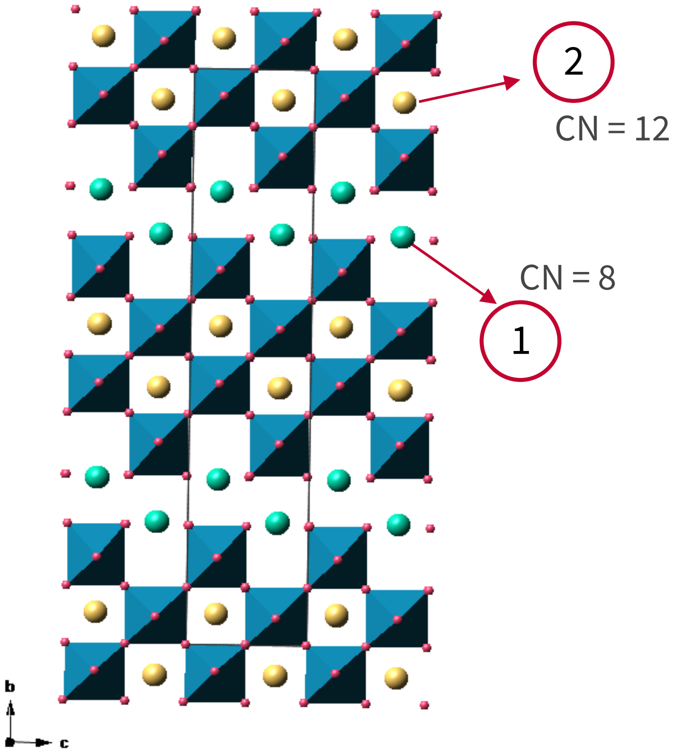
Substitution of Sr(2) with Ca

$CaSrTa_2O_7$(2)

RESULTS

CRYSTAL STRUCTURE

- SCAN functional correctly reproduces distances and lattice parameters of $Sr_2Ta_2O_7$
- $CaSrTa_2O_7$ models preserves the initial structure of the parent $Sr_2Ta_2O_7$ (SG C_{mcm})



Lattice parameters (Å)					
	$Sr_2Ta_2O_7$			$CaSrTa_2O_7$(1)	$CaSrTa_2O_7$ (2)
	experimental	**calculated**	**% error**	**calculated**	**calculated**
a	3.9376	3.9537	0.4	3.9084	3.9273
b	27.1986	27.1894	0.03	27.0999	27.0855
c	5.6927	5.6951	0.04	5.6119	5.6646
Volume ($Å^3$)	609.50	612.22	0.4	594.40	602.56

CRYSTAL STRUCTURE

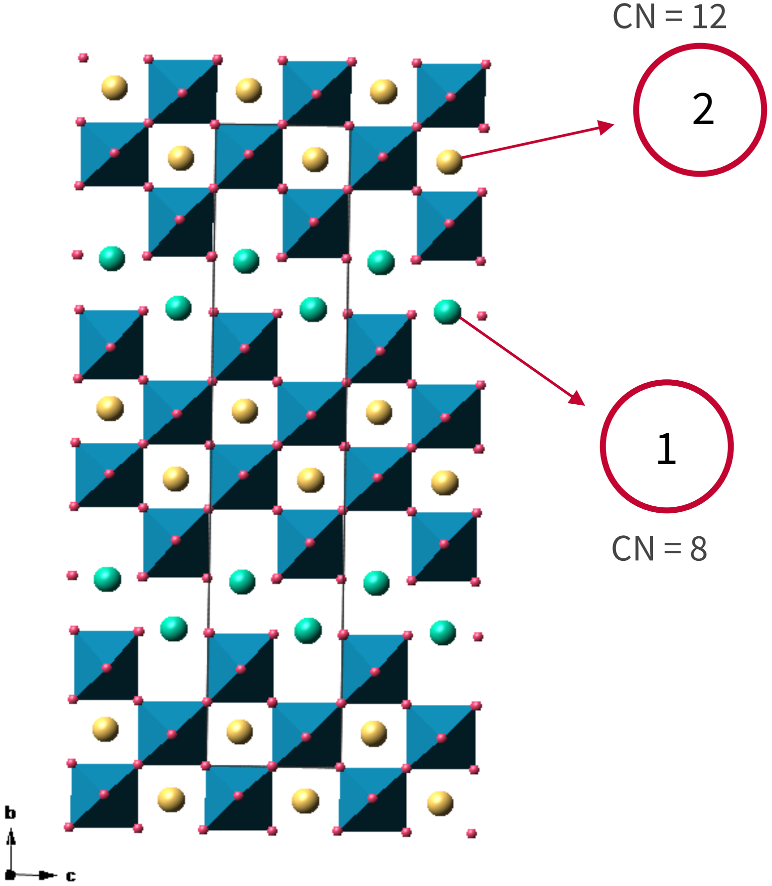
$Sr_{2-x}Ca_xTa_2O_7$

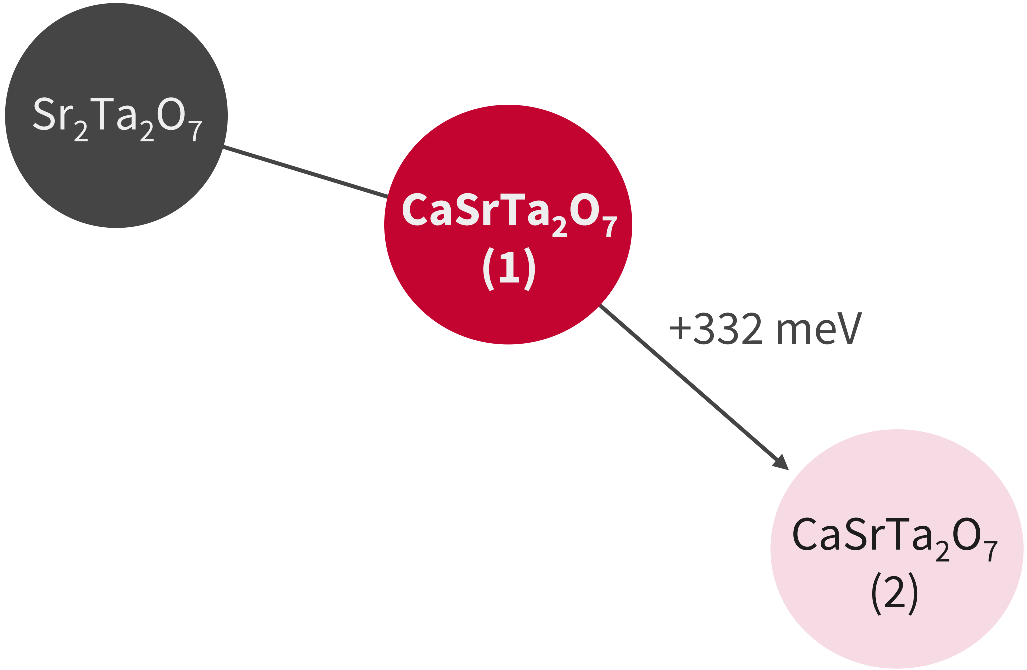
Model 1

Substitution of Sr(1) with Ca

Model 2

Substitution of Sr(2) with Ca





$Sr_2Ta_2O_7$

$CaSrTa_2O_7$ (1)

+332 meV

$CaSrTa_2O_7$ (2)

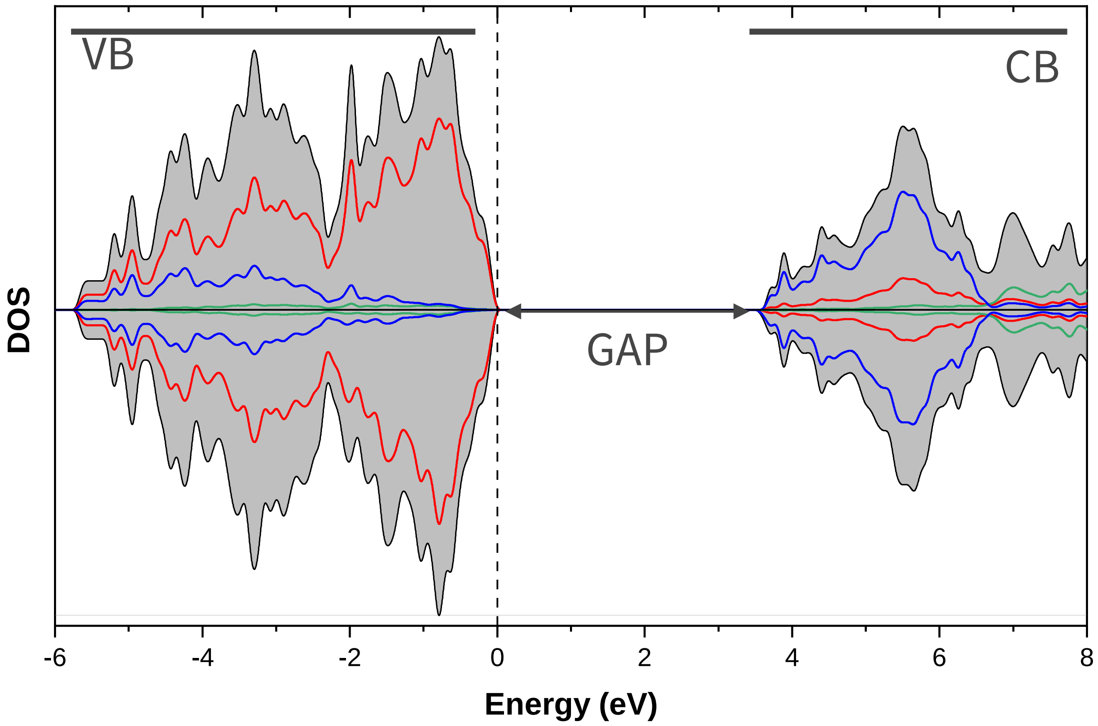
Ca^{2+}
r = 1.12 Å for CN = 8
r = 1.34 Å for CN = 12

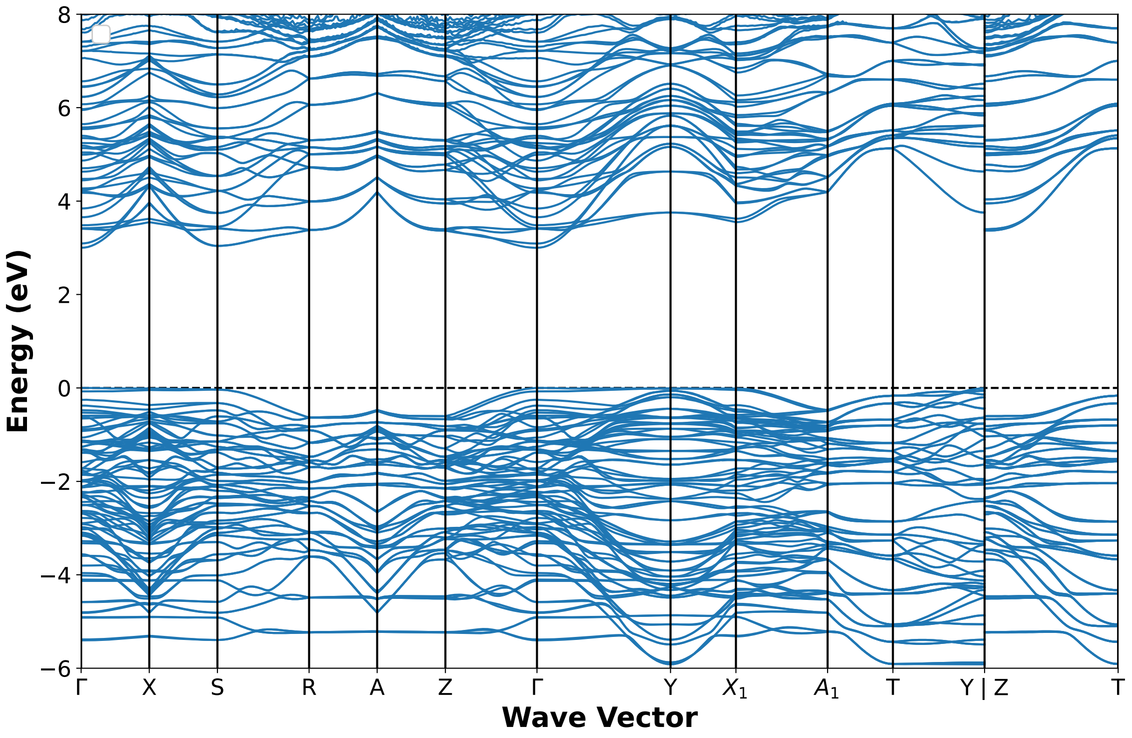
Sr^{2+}
r = 1.26 Å for CN = 8
r = 1.44 Å for CN = 12

- **Model 1** has lower energy when compared to Model 2 → A more stable structure forms if the larger Sr^{2+} cation occupies the position inside perovskite blocks, i.e. position 2.

ELECTRONIC STRUCTURE

$Sr_2Ta_2O_7$

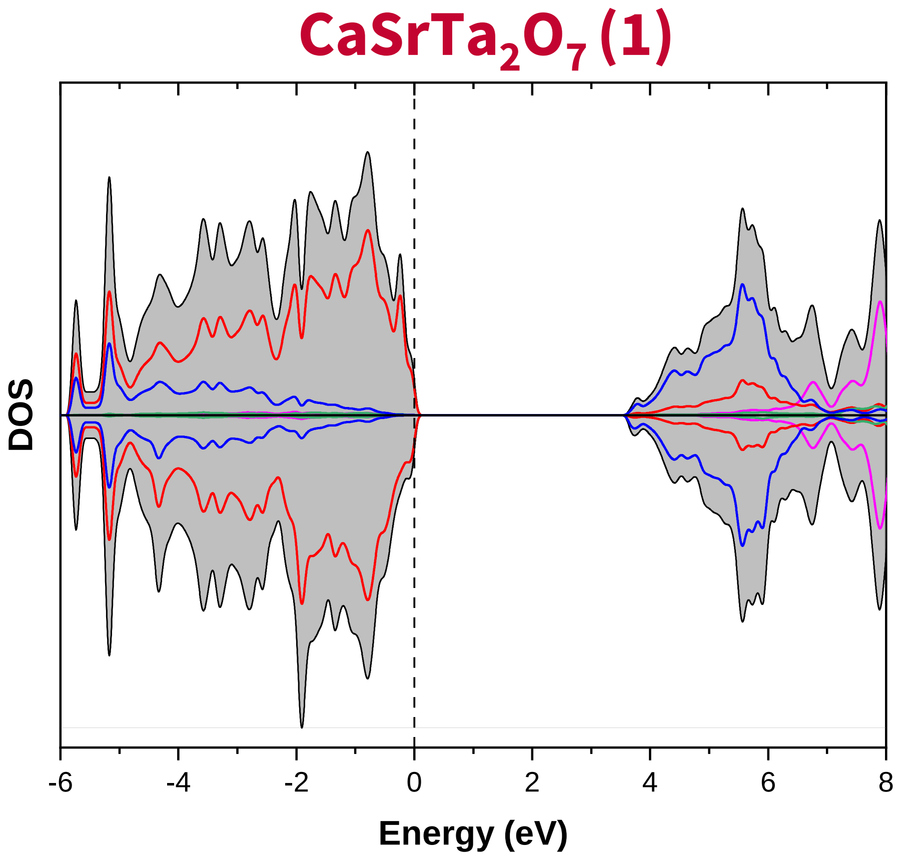


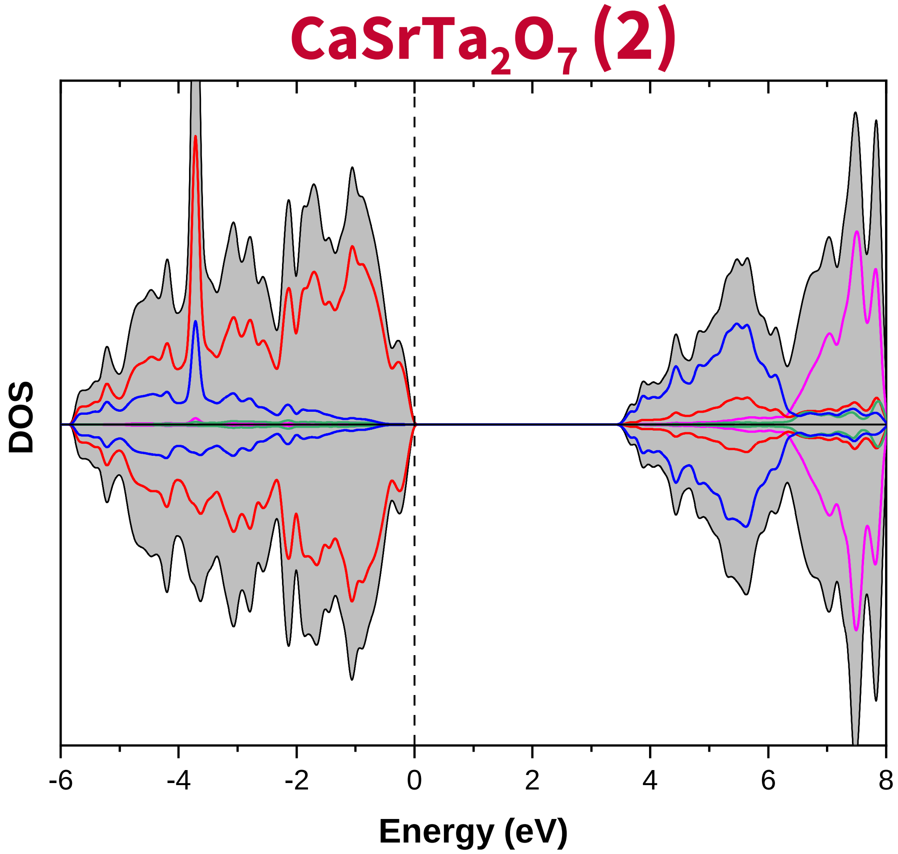


- Calculated band gap of 3.65 eV
- VB formed mainly by 2*p* O states while 5*d* Ta forms CB
- Hybridization exists in both bands

- Direct band gap

ELECTRONIC STRUCTURE





- Band gap of 3.55 eV

- Band gap of 3.50 eV

- VB and CB have esseantially the same features as in Sr$_2$Ta$_2$O$_7$

Substitution of Sr with Ca does not lead to a significative change in band gap

CONCLUSIONS

CONCLUSIONS

Computational investigations at the level of Density Functional Theory (DFT) permit predicting some basic and critical features in view of the photocatalytic activity of materials

- The x = 1 phases of $Sr_{2-x}Ca_xTa_2O_7$ family preserve the perovskite-related structure of $Sr_2Ta_2O_7$ parent compound
- Band-gap narrowing of 0.10-0.15 eV with partial substitution of Sr by Ca
- Absorption of sunlight is still limited to the UV region
- Work is in progress to investigate other substitutions