

# Ab initio calculation of photocatalysis - Ionic core potential effect in $\text{CaIn}_2\text{O}_4$ and $\text{SrIn}_2\text{O}_4$ -

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## Introduction

$\text{MIn}_2\text{O}_4$  (M = alkali earth metal) semiconductors show the novel photocatalytic activity under visible light irradiation. It is reported that the activity, K, for Methylene Blue (MB) degradation [1] is increased with decreasing the atomic radius of M,  $K(\text{CaIn}_2\text{O}_4) > K(\text{SrIn}_2\text{O}_4)$ . We investigate the electronic state by using the ab initio calculation and reveal the meaning of the classical atomic radius in the activity.

## Method

Ultrasoft pseudopotential method with gradient correction is implemented for the  $\text{M}_4\text{In}_8\text{O}_{16}$  unit. The structure is optimized within the orthorhombic Pnma symmetry.

## Results

Figures 1 and 2 show the total density of states (DOS) and band structures, respectively. We also show the main contribution of atomic orbital at each band. It is known that band structures are very similar, but the bands of O and In are shifted to the lower energy by permutation from Sr to Ca. It is caused by the fact that the ionic core potential of Ca is deeper than that of Sr.

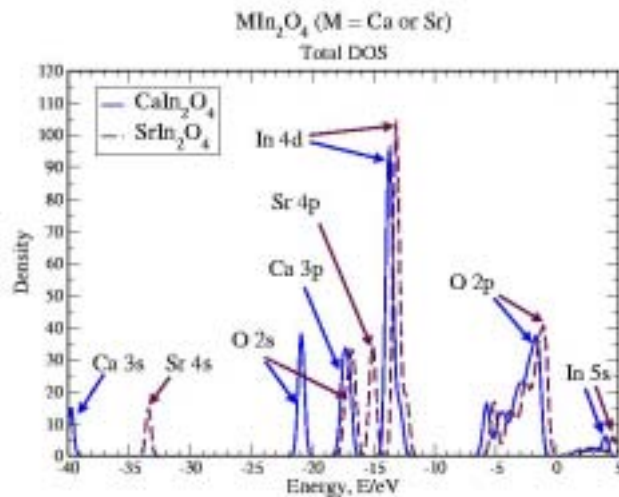


Fig.1 Total density of states for  $\text{CaIn}_2\text{O}_4$  and  $\text{SrIn}_2\text{O}_4$

This effect is more evident at the lower energy bands, because the screening is more imperfect and the shape of the potential has the stronger influence on the lower energy states. In fact, it is

more evident in O 2s than in O 2p. Such a shift is not strongly observed in the conduction band. Then we can imagine that permutation from Sr to Ca shifts top of the valence band to the lower energy state with leaving the bottom of the conduction band and expands the band gap. It means that the activity of oxidation is enhanced by the permutation.

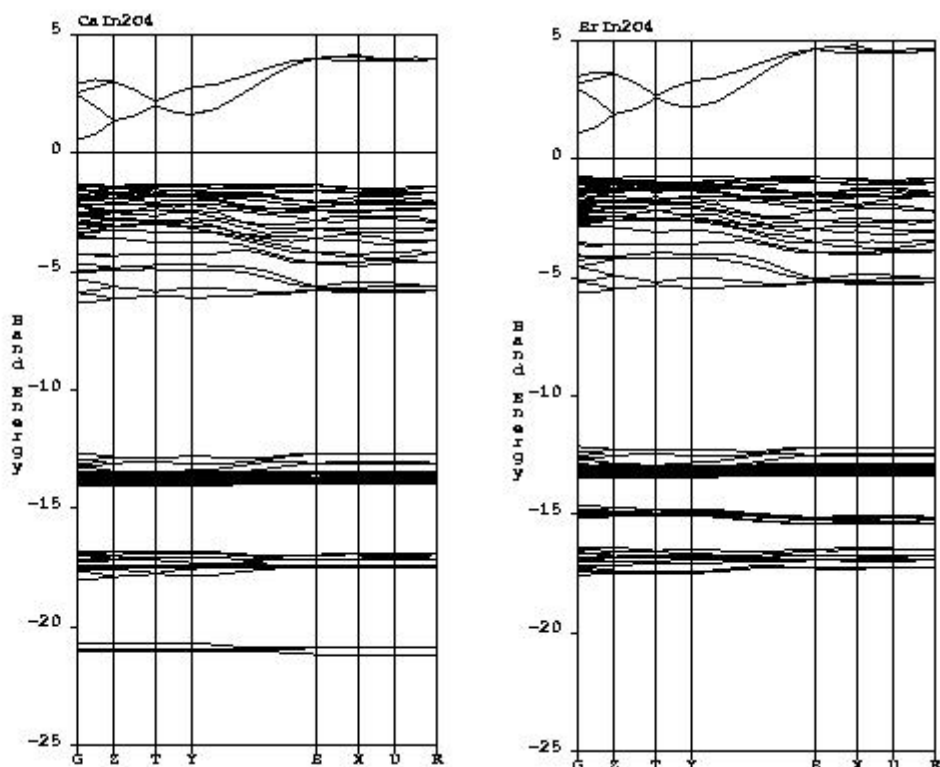


Fig.2 Band structures of  $\text{CaIn}_2\text{O}_4$  (left) and  $\text{SrIn}_2\text{O}_4$  (right)

### Conclusions

$\text{CaIn}_2\text{O}_4$  and  $\text{SrIn}_2\text{O}_4$  have the similar electronic structure but the band gap of  $\text{CaIn}_2\text{O}_4$  becomes larger than that of  $\text{SrIn}_2\text{O}_4$ . It is directly connected to the photocatalytic effect. The difference is attributed to the shape of the ionic core potential. Both compounds have the same number of valence electrons. However Ca with the smaller atomic radius has the sharper and deeper ionic core potential than Sr. As a result, the valence band shifts to the lower energy state, leading to the large band gap. The classical explanation from viewpoint of atomic size is resulting in the argument of the shape of the ionic core potential.

### References

- [1] *J. Tang, Z. Zou, M. Katagiri, T. Kako and J. Ye, Catalysis Today (to be submitted).*