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Ab-initio investigations on theoretically predicted perovskite and perovskite-like oxynitrides: novel materials for photocatalysis

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[Introduction] Visible light-responsive photo catalysts have recently received wide attention since their high potentiality as water splitters. Among all the suggested materials, metal oxynitrides $MTaO_2N$ (M= Ca, Sr, Ba) in the perovskite polymorph are reported to be extremely performing in H_2 evolution [1]. Noticeable theoretical results predicting the relevant performances of some of these perovskite and perovskite-like oxynitride structures have been already obtained [2], still necessitating of experimental support.

Here, we investigate the structural, electronic, and optical properties of $MgTaO_2N$, a theoretically predicted performing photo catalyst not yet experimentally synthesized. We also investigate those of $CaTaO_2N$ to validate our calculation by comparing the results to the experimentally known properties.

[Experiment] First-principles calculations were performed within the framework of DFT using the VASP, applying PAW potentials. Effects of interelectronic exchange and correlation to the total energies were treated in the GGA-PBE. All results rely on well-converged structures with respect to the energy-cutoff (500 eV) for the pseudo potential and k point sampling. In all the calculations, cell parameters was allowed to fully relax.

Due to the pure theoretical nature of the material, at first we have optimized perovskite structure of $MgTiO_3$ and $CaTiO_3$. We have also optimized the geikielite polymorph of $MgTiO_3$, which is the most stable structure of $MgTiO_3$. Next, we have substituted Ti with Ta and O with N and finally compared the properties of the two so obtained structures of $MgTaO_2N$.

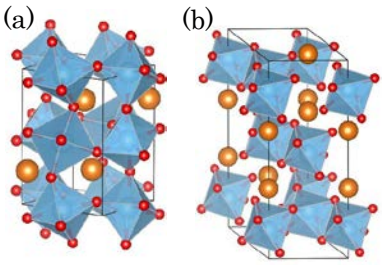

Figure 1 the structures of $MgTiO_3$
(a) Perovskite (b) Geikielite

[Result and Discussion]

I. Favored anion orderings in the perovskite polymorph of $MTaO_2N$ (M = Mg, Ca)

We first investigated the stability of trans-$MTaO_2N$ (Fig.2 (a)) and cis-$MTaO_2N$ (Figure 2). Four spatial configurations of cis-TaO_4N_2 octahedra sharing a common axial N are possible: namely, the “0-deg”, “90-deg”, “180-deg”, and “270-deg” configurations (Fig.2 (b) ~ (e))

Table 1 shows the energy of $MTaO_2N$ in five structural models. The cis-type structures are stable compared to the trans-type ones by at least 0.75 eV / FU in $CaTaO_2N$ and 0.27 eV / FU in $MgTaO_2N$. On the other hand, the energy differences among four configurations of cis-type structures are within 0.01 eV / FU in $CaTaO_2N$ and 0.06 eV / FU in $MgTaO_2N$. From these results, we can guess that there exists varying cis-type structures in the $MTaO_2N$ crystals.

Table 1 The stabilities of perovskite structures [eV / FU]

	trans	cis			
M		0-deg	90-deg	180-deg	270-deg
Ca	-43.88	-44.12	-44.13	-44.12	-44.13
Mg	-42.06	-42.27	-42.33	-42.32	-42.27

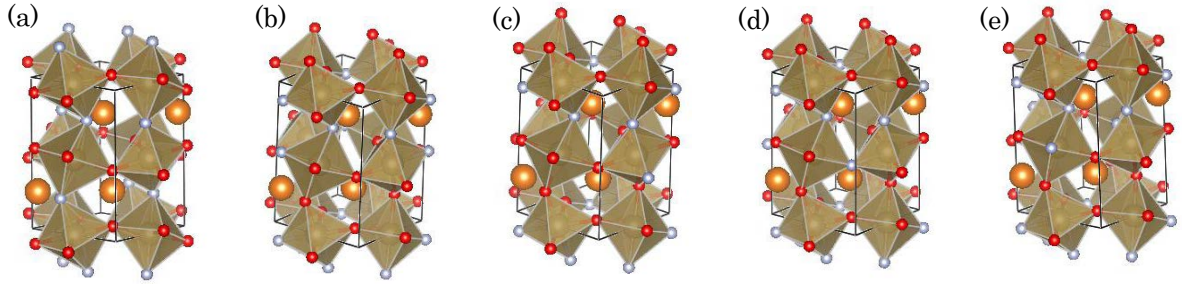

Figure 2 structures of perovskite $MgTaO_2N$. (a) trans (b) "0-deg" (c) "90-deg" (d) "180-deg" (e) "270-deg" [Orange: Mg atoms; red: O; white: N; Ta atoms @ the octahedral center]

II. Favored anion orderings in the geikielite structure of $MgTaO_2N$

Second, we investigated the stability of three spatial configurations of geikielite structures of $MgTaO_2N$, namely "trans", "parallel", and "cis" (Fig.3 (a) ~ (c)). In "trans" structure, there are some N anions which coordinate a Ta ion in trans configuration, while all N anions coordinate in cis configuration in "cis" and "parallel" structures. N anions are put on parallel planes in "parallel", while two N anions line up vertically to the planes in "cis". The most stable one is cis-type consistently with the case of perovskite $MTaO_2N$.

Table 2 The stabilities of geikielite structures [eV / FU]

M	trans	parallel	cis
Mg	-42.53	-42.53	-42.60

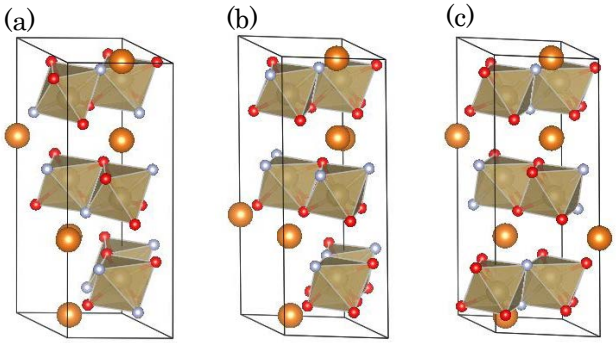

Figure 3 structures of geikielite $MgTaO_2N$ (a) trans (b) parallel (c) cis [same notation as Fig.2]

We will investigate the electronic and optical properties such as band structures using these optimized structures. The results will be shown on the session.

[1] D. Yamasita *et al., Solid State Ionics,* 2004, **172**, 591
[2] I. E. Castelli *et al., Energy and Environmental Science,* 2012, **5**, 5814