

## DFT study of water adsorption on (001) $\text{Mn}_3\text{O}_4$ surface

Paulo R. G. Gonçalves Jr, E. C. Santos, H. A. de Abreu, H. A. Duarte

*GPQIT, Departamento de Química – ICEX, UFMG, 31.270-901, Belo Horizonte - MG*

**Abstract:** Hausmannite ( $\text{Mn}_3\text{O}_4$ ) is a material with normal spinel structure that presents the formula  $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4$  where tetrahedral sites are occupied by the  $\text{Mn}^{2+}$  and the octahedral sites by  $\text{Mn}^{3+}$  cations. This oxide has tetragonal arrangement with space group  $I41/amd$ . In recent years, this material has attracted interest for applications in water treatment[1, 2]. The  $\text{Mn}_3\text{O}_4$  show polar surfaces, formally characterized by an unbalanced electrostatic potential, which gives rise to a dipole moment perpendicular to the surface. However, Kresse and co-workers [3] have shown that this formal instability is an artificial consequence of the simplified ionic model and can be removed by mechanisms involving changes near of the surface such as charge redistribution, reconstruction, and interactions with neighboring atoms. It has been reported that the cleavage of hausmannite[4, 5] leads indistinctly to the oriented plane (001). Nevertheless, a study of the formation of thin films of  $\text{Mn}_3\text{O}_4$  oriented in other crystallographic directions, such as the  $\text{SrTiO}_3$  substrate oriented surface (110) has also been reported[6]. In this sense, based on the optimized bulk structure, we tested several hausmannite slab models (figure 1) to compare the cleavage energies of different planes, and we investigated the adsorption of water molecules on the most stable surface calculated.

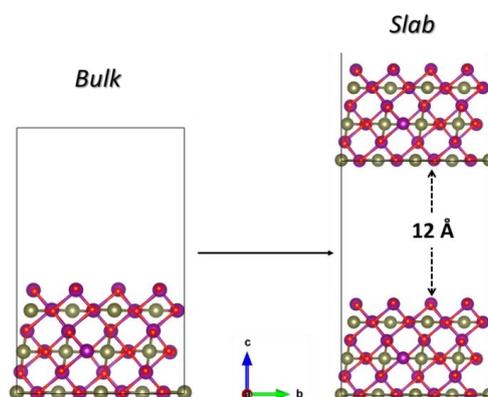


Figure 1. Slab models from the  $\text{Mn}_3\text{O}_4$  bulk.  $\text{Mn}^{2+}$  (green),  $\text{Mn}^{3+}$  (purple) and Oxygen (red).

The calculation of  $\text{Mn}_3\text{O}_4$  surfaces were investigated using DFT/planewaves and GGA/PBE functional as implemented in Quantum-ESPRESSO package. It was used a cutoff energy of 40 Ry,  $3 \times 3 \times 1$   $k$ -point mesh sampling based on the Monkhorst-Pack scheme,  $2 \times 2 \times 1$  supercell and  $12 \text{ \AA}$  vacuum layer were chosen for the slab calculation. After optimization of the surfaces, the values of surface and cleavage energies are presented in table 1.



# XIX SBOQT

Simpósio Brasileiro de Química Teórica 2017

12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Table 1. Cleavage and surface energies, surface area and coordination number of the different  $Mn_3O_4$  plane models.

Surfaces	$E_{cleavage}$ ( $J.m^{-2}$ )	$E_{surface}$ ( $J.m^{-2}$ )	Coordination number	
			$Mn_{tetrahedral}^{2+}$	$Mn_{octahedral}^{3+}$
<i>Bulk</i>	-	-	4	6
(001)	2.33	1.40	2	5
(100) = (010)	5.07	1.93	3	3
(101) = (011)	3.38	1.96	4	3, 4
(110)	6.49	1.85	1, 3	3
(111)	3.54	1.68	4	4, 5
(112)	3.14	1.78	4	4

According to our calculations, the surface (001) is the most favorable to cleave in comparison to the other simulated planes, being therefore the most stable surface of  $Mn_3O_4$ . This cleavage exposes the  $Mn^{+2}$ ,  $Mn^{+3}$  and  $O^{-2}$  ions asymmetrically. Based on this estimate, we studied the adsorption of water molecules on the surfaces (001), which presented 3 types: molecular, hydrogen bond interaction, and dissociative. The results indicated that water adsorption occurs dissociatively, with adsorption energy of about  $-28 \text{ kcal mol}^{-1}$ .

**Keywords:**  $Mn_3O_4$ , surfaces, DFT, planewaves, adsorption.

**Support:** This work has been supported by IFMA, FAPEMA, FAPEMIG and INCT-ACQUA.

**References:**

- [1] G.C. Silva, V.S.T. Ciminelli, A.M. Ferreira, N.C. Pissolati, P.R.P. Paiva and J.L. López, *Materials Research Bulletin*, 49 (2014) 544.
- [2] K. Babaeiveli, A.P. Khodadoust and D. Bogdan, *Journal of Environmental Science and Health, Part A*, 49 (2014) 1462.
- [3] G. Kresse, O. Dulub and U. Diebold, *Physical Review B*, 68 (2003) 245409.
- [4] V. Bayer, R. Podloucky, C. Franchini, F. Allegretti, B. Xu, G. Parteder, M.G. Ramsey, S. Surnev and F.P. Netzer, *Physical Review B*, 76 (2007) 165428.
- [5] W.Y. Li and Q.L. Chen, *Advanced Materials Research* 2012.
- [6] O.Y. Gorbenko, I.E. Graboy, V.A. Amelichev, A.A. Bosak, A.R. Kaul, B. Güttler, V.L. Svetchnikov and H.W. Zandbergen, *Solid State Communications*, 124 (2002) 15.