

A DFT STUDY OF THE STRUCTURE AND PROPERTIES OF NITROGEN DOPING SPINEL**MgAl₂O_{3.5}N_{0.5}**

P. K. Leong¹, C. P. Tang¹, S. I. Tam¹ and T. Sekine², ¹State Key Laboratory of Lunar and Planetary Sciences, Macau University of Science and Technology, Macau. E-mail: cptang@must.edu.mo, ²Center for High Pressure Science and Technology Advanced Research (HPSTAR) Shanghai Laboratory of HPSTAR, Shanghai, P.R. China. E-mail: toshimori.sekine@hpstar.ac.cn

Introduction: Since spinel has an important role of planetary composition, doped spinels are also studied for their properties [1-3] (electronic, optical, magnetic, etc.) in astronomical implications. [4] In this work, we report a possible nitrogen-doped oxygen structure of spinel with density functional theory (DFT). The studies of the structural and electronic properties (band structure, density of states and phonon) of the spinel (MgAl₂O₄) and the N doping spinel (MgAl₂O_{3.5}N_{0.5}) compounds are performed using the generalized gradient approximation and the Perdew-Burke-Ernzerh of (GGA/PBE) functional. The density and space group (in brackets) of the two crystal cells are 3.47 g/cm³ (Fd3m) for MgAl₂O₄ and 3.38 g/cm³ (R3m) for MgAl₂O_{3.5}N_{0.5}, respectively. The calculated direct band gaps at the Γ -point are approximately 5.13 eV for MgAl₂O₄ and 4.24 eV for MgAl₂O_{3.5}N_{0.5}. The density of states analysis shows that the tops of the valence bands are constituted ~93% of the p(O) states and ~60% of p(N) + ~32% of p(O) states (for MgAl₂O₄ and MgAl₂O_{3.5}N_{0.5}, respectively). In the phonon analysis, the lowest frequency of MgAl₂O_{3.5}N_{0.5} is redshifted to 36.6 cm⁻¹ (MgAl₂O₄ is 39.8 cm⁻¹) caused by the N-doped. Finally, we calculated the cohesive energy dependence for the pressure of the two spinels. We found that the cohesive energy of MgAl₂O_{3.5}N_{0.5} is lower than MgAl₂O₄ when the pressure is higher than ~115 GPa. It implies that MgAl₂O_{3.5}N_{0.5} is more stability than MgAl₂O₄ at high pressure. Base on these results, we suggest that nitrogen atom would replace the oxygen of spinel in the depths of the earth or other planets.

References: [1] Park M. S. et al. (1999) *Physical Review B* 59:10018–10024. [2] Wang H. et al. (2010) *Journal of Alloys and Compounds* 491:550–559. [3] Kahn M. L. and Zhang Z. J. (2001) *American Institute of Physics* 78:3651–3653. [4] Richter H. et al. (2005) *Mineralogy and Petrology* 85:53–65.