A DFT STUDY OF THE STRUCTURE AND PROPERTIES OF NITROGEN DOPING SPINEL $MgAl_2O_{3.5}N_{0.5}$

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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 ($MgAl_2O_4$) and the N doping spinel ($MgAl_2O_{3.5}N_{0.5}$) 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/cm^3 (Fd3m) for $MgAl_2O_4$ and 3.38 g/cm^3 (R3m) for $MgAl_2O_{3.5}N_{0.5}$, respectively. The calculated direct band gaps at the Γ-point are approximately 5.13 eV for $MgAl_2O_4$ and 4.24 eV for $MgAl_2O_{3.5}N_{0.5}$. 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 $MgAl_2O_4$ and $MgAl_2O_{3.5}N_{0.5}$, respectively). In the phonon analysis, the lowest frequency of $MgAl_2O_{3.5}N_{0.5}$ 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 $MgAl_2O_{3.5}N_{0.5}$ is lower than $MgAl_2O_4$ when the pressure is higher than ~115 GPa. It implies that $MgAl_2O_{3.5}N_{0.5}$ is more stability than $MgAl_2O_4$ 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.