A DFT STUDY OF THE STRUCTURE AND PROPERTIES OF NITROGEN DOPING SPINEL
MgAl₂O₃.₅N₀.₅

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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 (MgAl₂O₄) and the N doping spinel (MgAl₂O₃.₅N₀.₅) 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 MgAl₂O₃.₅N₀.₅, respectively. The calculated direct band gaps at the Γ-point are approximately 5.13 eV for MgAl₂O₄ and 4.24 eV for MgAl₂O₃.₅N₀.₅. 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 MgAl₂O₃.₅N₀.₅, respectively). In the phonon analysis, the lowest frequency of MgAl₂O₃.₅N₀.₅ 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 MgAl₂O₃.₅N₀.₅ is lower than MgAl₂O₄ when the pressure is higher than ~115 GPa. It implies that MgAl₂O₃.₅N₀.₅ 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.