First-principle study of the structural and electronic properties of N-doped $MgAl_2O_4$ spinel

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On basis of the first principle calculation, we report a possible nitrogen doped structure of $MgAl_2O_4$ spinel. The structural and electronic properties (include the band structure, density of states and phonon) of spinel ($MgAl_2O_4$) and N-doped spinel ($MgAl_2O_{3.5}N_{0.5}$) compounds are performed using density functional theory (DFT). The density and space group of 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 about 5.13 eV for $MgAl_2O_4$ and 4.24 eV for $MgAl_2O_{3.5}N_{0.5}$, respectively. The projected density of states (PDOS) shows that the tops of the valence bands are built up from ~93% of *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} ($MgAl_2O_4$ is 39.8 cm^{-1}) caused by the N-doped. We also calculate their cohesive energy in the pressure range of 0-150 GPa. We found that the cohesive energy of $MgAl_2O_{3.5}N_{0.5}$ is lower than $MgAl_2O_4$ at the pressure higher than ~115 GPa, it implies that $MgAl_2O_{3.5}N_{0.5}$ is more stable than $MgAl_2O_4$ at high pressure. Finally, we suggest that nitrogen atom would replace the oxygen of spinel in the depths of the earth. The results imply the deep mantle may storage a considerable amount of nitrogen.

Keywords: First principle calculation, Density functional theory, Spinel

