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Mn substitution and distribution in goethite and influences on its photocatalytic properties: A combined study using first-principles calculations and photocatalytic experiments

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Abstract

Goethite and modified goethites have been found as good photocatalysts because their conduction band can mediate electron transfer in various redox processes. Many kinds of metal elements can be incorporated into the structure of goethite to form solid solutions in nature, but their optoelectronic properties have not been well disclosed. Mn-substituted goethite is one of the potential photocatalysts, which can exhibit high-photocatalytic activity in many Earth's surface processes. Based on the first-principles calculation, pairwise interaction energies and static lattice energies of goethite-groutite solid solution were computed, and the most thermodynamically stable configurations of Mn-substituted goethite were determined. The results indicate that Mn^{3+} ion tends to distribute within the cation layer parallel to the (001) plane. Phase relations of goethite-groutite solid solution were derived by subsequent configurational statistics with energies of all 2^{32} configurations of a $2 \times 1 \times 4$ supercell with 32 exchangeable cations. The phase diagram shows that no more than 3 mol% Fe of goethite can be substituted by Mn ions. Therefore, Mn-substituted goethite is thermodynamically metastable or bears groutite-like clusters/lamellae. Furthermore, the effects of Mn substitutions on the band gap were experimentally and theoretically investigated. It is found that a small amount of Mn-substitution can reduce the band gap of goethite significantly, and the decrease ceases when the Mn content is higher than 3–4 mol%. Such a decrease in band gap causes red-shift to the photo response wavelength of goethite and improves the responding capability. This improvement was confirmed in the experiments of photocatalytic degradation of methylene blue (MB). Such kind of photocatalytic reaction probably can happen widely in natural environments. Therefore, the contribution of photocatalysis of natural goethites to geochemical processes on Earth's surface should be considered.

Keywords: Goethite, Mn substitution, solid solution, band gap, photocatalytic property, first-principles calculation