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

XIN LIU1,2, HUAN LIU1,2, MEIRONG ZONG3, MENG CHEN3, HONGPING HE3,4, RUCHENG WANG1, and XIANCAI LU1,2,5,*

1State Key Lab for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, 210023, Nanjing, China
2Frontiers Science Center for Critical Earth Material Cycling, Nanjing University, 210023, Nanjing, China
3CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Institutions of Earth Science, Chinese Academy of Sciences (CAS), 510640, Guangzhou, China
4University of Chinese Academy of Sciences, 100049, Beijing, China.
5Key Laboratory of Surficial Geochemistry, Ministry of Education, School of Earth Sciences and Engineering, Nanjing University, 210023, Nanjing, China

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 Mn3+ 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 232 configurations of a 2 × 1 × 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 photoresponse 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

INTRODUCTION

Goethite is one of the most important and common minerals among natural iron oxides and is usually applied to adsorb various toxic anions or heavy metals in environments (Granados-Correa et al. 2011; Mamindy-Pajany et al. 2011; Rahimi et al. 2015). Goethite and modified goethites are good photocatalysts because of their nontoxic nature and natural abundance and have been widely investigated to develop the performance for photocatalytic decomposition of both natural molecules like nucleic acid, aldehydes (Kakuta et al. 2014; Murakami et al. 2011; Shkrob et al. 2011) and artificial organic pollutants such as dyes, aniline, plastic, and so on (Du et al. 2008; Liu et al. 2010, 2011; Zhou et al. 2010). The band gap of pure goethite is 1.6–2.5 eV [wavelength (nm) = 1240/band gap (eV)] due to the particle size (Sherman 2005; Zhang et al. 2011), so it is a visible-light-responsive photocatalyst but does not cover the whole visible spectrum. Many studies revealed that doped goethite shows higher photocatalytic ability than pristine one (Liu et al. 2010, 2011).

Natural goethite can incorporate many di-, tri-, and tetravalent cations (e.g., Mn3+, Ni2+, Al3+, Co2+, Cr3+, Pb2+, etc.) on the Fe sites, and the incorporated ions can modify many properties of goethite such as thermodynamic stability, photocatalytic activity, and adsorption characteristics (Alvarez et al. 2007, 2008, 2015; Carvalho-E-Silva et al. 2003; Kaur et al. 2009; Kusuyama et al. 2002; Liu et al. 2018). Among all the impurity elements, Mn3+ is the most similar cation to Fe3+ because they have the same valence and similar cation radii (≈0.645 Å) (Shannon 1976). Thus, Mn can be readily incorporated into the goethite structure to form goethite-groutite solid solutions, where the Mn-Fe substitution can be up to 15 mol% (Cornell and Giovanoli 1987; Gasser et al. 1999; Scheinost et al. 2001).