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Magnetic response of microbially synthesized transition metal- and lanthanide-substituted nano-sized magnetites

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Abstract

The magnetic susceptibility (κ_{RT}) and saturation magnetization (M_{S}) of microbially synthesized magnetites were systematically examined. Transition metal (Cr, Mn, Co, Ni and Zn)- and lanthanide (Nd, Gd, Tb, Ho and Er)-substituted magnetites were microbially synthesized by the incubation of transition metal (TM)- and lanthanide (L)-mixed magnetite precursors with either thermophilic (TOR-39) or psychrotolerant (PV-4) metal-reducing bacteria (MRB). Zinc incorporated congruently into both the precursor and substituted magnetite, while Ni and Er predominantly did not. Microbially synthesized Mn- and Zn-substituted magnetites had higher κ_{RT} than pure biomagnetite depending on bacterial species and they exhibited a maximum κ_{RT} at 0.2 cationic mole fraction (CMF). Other TMs' substitution linearly decreased the κ_{RT} with increasing substitution amount. Based on the M_{S} values of TM- and L-substituted magnetite at 0.1 and 0.02 CMF, respectively, Zn (90.7 emu/g for TOR-39 and 93.2 emu/g for PV-4)- and Mn (88.3 emu/g by PV-4)-substituted magnetite exhibited higher M_{S} than standard chemical magnetite (84.7 emu/g) or pure biomagnetite without metal substitution (76.6 emu/g for TOR-39 and 80.3 emu/g for PV-4). Lanthanides tended to decrease M_{S}, with Gd- and Ho-substituted magnetites having the highest magnetization. The higher magnetization of microbially synthesized TM-substituted magnetites by the psychrotroph, PV-4 may be explained by the magnetite formation taking place at low temperatures slowing mechanics, which may alter the magnetic properties compared to the thermophile, through suppression of the random distribution of substituted cations.

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Keywords: Microbial synthesis; Magnetite; Transition metal; Lanthanide; Magnetism

1. Introduction

Magnetic colloids have been used commercially in numerous devices such as rotating shaft seals, exclusion seals, loudspeakers, dampers and inclinometers [1] and magnetic fluids [2,3]. The production of iron oxides (e.g. magnetite or maghemite) has been accomplished by synthesis and sizing methods such as chemical co-precipitation [4,5], grinding [6], mechanochemical methods with room temperature milling [7], hydrothermal methods [8], solid state reaction [9] and microbial synthesis using metal-reducing bacteria (MRB, e.g. *Thermoanaerobacter ethanolicus*) [10,11].

Although chemical synthesis from solution offers some advantages: mild conditions, control of the particle size and composition and modification of the surface facilitating stable dispersions in various liquid or solid media, it is

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necessary to operate at 50–100 °C with the TM^{2+}/Fe^{3+} ratio (transition metal, TM) larger than 0.3 to obtain only ferrite rather than a poorly crystallized TM-ferrihydrite or a mixture with $TM(OH)_2$ [4]. Wet grinding does not have the speed of production found in the chemical precipitation methods.

However, microbial synthesis of magnetites does not need high-temperature, high-pressure, high-energy consumption or solutions used in chemical and mechanical synthesis [6,9]. MRB have shown their ability to produce magnetites even in low temperatures around 4 °C (*Shewanella* species like PV-1 and W3-6-1) [11] and they incorporate high amounts of substituting metals using a precursor method that could be toxic to the bacteria if the metal ions were added in salt form [12]. Importantly, preliminary experiments demonstrated that microbial production of extracellular magnetite by *T. ethanolicus* (TOR-39) is easily scalable from milligram to greater than kilogram quantities.

There has been intensive research to enhance magnetization of magnetite using dopants like TMs [13,14] and organic acids or to solve environmental problems like applying Fe(III)-reducing bacteria to Zn immobilization [15]. Rare earth elements were also substituted into magnetite structures to modify magnetic and electric properties leading to decreased Curie temperatures [16,17].

Considerable work has been reported on biomineralization using MRB [10,11,18–20], yet only recently has the magnetization of microbially synthesized magnetites been characterized [3,21] and few comparisons are available for microbially synthesized TM- or lanthanide (L)-substituted magnetites. The objective of this study was to compare the magnetic response of various microbially synthesized TM- or L-substituted magnetites ($TM,L_yFe_{3-y}O_4$) transformed from TM- or L-mixed amorphous Fe(III) oxyhydroxide precursors (β-$(TM,L)_xFe_{1-x}OOH$, akaganeite) using thermophilic (TOR-39) and psychrotolerant (PV-4) MRB.

2. Materials and methods

2.1. Preparation of precursors and incubation conditions

Diverse TM- and L-mixed-Fe(III) oxyhydroxides as magnetite precursors were prepared and aged as mixed precursor solutions at least 1 month prior to experimentation [12]. Mixed-TM precursors were initially produced in a series of $x = 0.01$–0.3 (where x was cation mole fraction, CMF, in $TM_xFe_{1-x}OOH$) and mixed-L precursors ranged from 0.01 to 0.02. Microbially synthesized TM- or L-substituted magnetites that were preliminarily screened by color change of the precursors from brown to black and by attraction to a hand-held magnet [12,22] were further characterized for our magnetization study.

The culture medium had the same basal composition as described previously [10] supplemented with Oak Ridge National Laboratory (ORNL) trace minerals and ORNL vitamin solutions [23]. No reducing agents were added to the medium. The thermophilic Fe(III)-reducing bacteria, *T. ethanolicus* (TOR-39) [24] and psychrotolerant bacteria, *Shewanella* sp. strain PV-4 [25] were used. The incubation was initiated with 40 mM of TM- or L-mixed precursor, 2% inoculum of mid-log growth bacteria, 10 mM of glucose and 15 mM of 3-(*N*-morpholino)propanesulfonic acid (MOPS) buffer (titrated to pH 7.8 with NaOH) at 65 °C for 30 days for TOR-39. Batches of PV-4 were inoculated with 40 mM of TM- or L-mixed precursor, 2% inoculum of mid-log growth bacteria, 10 mM of lactate and incubated at room temperature for 75 days. Each control received unsubstituted akaganeite for comparison.

2.2. Mineralogical, chemical and magnetic analyses

To obtain TM- or L-substituted magnetites without unreacted precursor, centrifuged precipitates were treated with ammonium oxalate solution [26]. Samples were then washed and collected by freeze drying.

Microbially synthesized nano-sized magnetite was mixed with methanol and the slurry was applied to a silica zero-background plate for X-ray diffraction analysis. The phase identification of the microbially synthesized magnetites was determined using an X-ray diffractometer (XRD, PAD V, Scintag Inc., Sunnyvale, CA) equipped with CuKα radiation at 45 kV/40 mA with a scan rate of $2^\circ\ 2\theta\,\mathrm{min}^{-1}$ between 10° and 70° 2θ and JADE software package (Materials Data Inc., MDI).

A scanning electron microscope (SEM, XL30-FEG, Phillips) with energy dispersive X-ray analysis (EDX) was used for the analysis of morphology, mineralogy and chemistry of the synthesized mineral phases by MRB. Basic properties of final medium solution such as pH, Eh and acid (0.5N HCl)-extractable ferrous ion and TM or L concentration were obtained by the same procedures as described previously [12] after the termination of incubation.

A magnetic susceptibility (κ_{RT}) meter (SM-30, Terraplus, Inc., CO), with a measuring field of the order of 10^{-6} SI was used for screening the samples at the room temperature. Five readings for each mounting were taken for each sample. The saturation magnetization (M_S) was measured using a superconducting quantum interference device (SQUID, MPMS-7, Quantum Design Inc., San Diego, CA) based magnetometer. Measurements were performed at 5 K and 0–60 kOe range. Magnetite powders from 10 to 20 mg were loaded (forming a hemispherical mass) into a plastic capsule and held tightly in place with cotton packing during analysis.

3. Results and discussion

3.1. Synthesis of TM- and L-substituted magnetites

Previously, microbially synthesized magnetites from 0.4 CMF of Zn-magnetite precursor ($Zn_{0.4}Fe_{0.6}OOH$) and higher did not pass the preliminary test [12]. A visual color test was utilized because it was observed that the brown