Probing the site occupancies of Co-, Ni-, and Mn-substituted biogenic magnetite using XAS and XMCD

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ABSTRACT

Ferrimagnetic nanoparticles have many uses in industry including in magnetic recording media and transformers, however these particles are often expensive to synthesize. In this study, the Fe3+-reducing bacteria Geobacter sulfurreducens and Shewanella oneidensis were used to synthesize spinel ferrite nanoparticles of the general chemical formula $M_xFe_{3-x}O_4$ where $M$ is either Co, Ni, Mn, Zn, or a combination of Mn and Zn. This was done at ambient temperatures through the dissimilatory reduction of Fe3+-oxyhydroxides containing the appropriate substitutional cations. A combination of L-edge and K-edge X-ray absorption spectroscopy (XAS) and L-edge X-ray magnetic circular dichroism (XMCD) was used to determine the site occupancies, valence, and local structure of the Fe and substitutional cations within the spinels. The Ni and Co ferrites produced using each bacterium were very similar and therefore this study concludes that, despite the difference in reduction mechanism of the bacteria used, the end-product is remarkably unaltered. Nickel ferrites contained only Ni2+, with at least 80% in $O_3$ coordination. Cobalt ferrites contained only Co3+ but with a significant proportion (up to 45%) in $T_3$ coordination, showing a slight preference for $T_4$ sites. The Mn-ferrites contained Mn2+ only on the $O_3$ sites but a mixture of Mn2+ and Mn3+ on $T_4$ sites when the amount of Mn exceeded 3% (compared to the amount of Fe) or some Zn was also present. This study successfully produced a range of nanoparticulate ferrites that could be produced industrially using relatively environmentally benign methodologies.

Keywords: Magnetite, Fe3+-reducing bacteria, substituted spinels, Geobacter sulfurreducens, Shewanella oneidensis, nanotechnology

INTRODUCTION

Extracellular nano-sized magnetic particles of magnetite ($Fe_3O_4$) are produced by Geobacter sulfurreducens and Shewanella oneidensis, which are Fe3+-reducing bacteria capable of respiring using amorphous Fe3+ oxides as electron acceptors in anoxic environments (Caccavo et al. 1994). This study demonstrates the capability of these bacteria not only to produce end-member magnetite but also to include the metals ($M$) Co, Ni, Mn, and Zn within the magnetite structure thus forming nanospinel ferrites with the chemical formula $M_xFe_{3-x}O_4$ (Coker et al. 2004). The capability of these bacteria to produce nanomagnets using energy efficient methodologies has yet to be explored by industry even though these particles have electrical, magnetic, and structural properties that differ from coarser-grained materials (Jolivet et al. 2002). Furthermore, although magnetite can be produced from ferrihydrite by the addition of aqueous Fe2+, the particles are tenfold larger than magnetite nanoparticles formed in biotic systems (Hansel et al. 2003). Because ferrite spinels, and especially magnetite-like compounds, are among the most important ferrimagnetic materials for industrial applications, including data storage and as ferrofluids for use in heat transfer, computer systems, or levitation of objects, they have great commercial potential (Jolivet et al. 2002; Safarik and Safarikova 2002). The magnetoresistive properties of spinels also have been of recent interest in the area of spin electronics (Coey et al. 1998) and half-metallic spin injectors (Lu et al. 2004).

The development of technological applications for bio-mineral nanomagnets produced by bacteria has concentrated largely on magnetotactic bacteria, which produce membrane-bound intracellular nano-magnetite crystals. This group of bacteria are of interest because they can produce cubic magnetite particles with very well-constrained particle size and shape (Yeary et al. 2005). The drawback of magnetotactic bacteria is that they are difficult to culture in large quantities and magnetite yields can be relatively low, whereas extracellular manufacture of magnetite can produce large amounts of the bio-mineral. However, the formation of metal-substituted magnetites by bacteria by either intra- or extracellular processes has been little studied with some notable exceptions; the thermophilic extracellular Fe2+-reducer...