American Mineralogist, Volume 93, pages 1119–1132, 2008

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 Fe^{3+}-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 Fe^{3+}-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 Ni^{2+}, with at least 80% in O_h coordination. Cobalt ferrites contained only Co^{2+} but with a significant proportion (up to 45%) in T_d coordination, showing a slight preference for T_d sites. The Mn-ferrites contained Mn^{2+} only on the O_h sites but a mixture of Mn^{2+} and Mn^{3+} on T_d 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, Fe^{3+}-reducing bacteria, substituted spinels, *Geobacter sulfurreducens*, *Shewanella oneidensis*, nanotechnology