

The oxidation state and microstructural environment of transition metals (V, Co and Ni) in magnetite: An XAFS study

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Transition metal-substituted magnetite minerals have attracted increasing attention for their wide application in industry and environmental protection. By altering the valence and distribution of cations in octahedral and tetrahedral sites, isomorphous substitution can tune the physico-chemical properties of magnetite. From previous studies, the distribution and local environment of iron and substituting cations in magnetite structure have been investigated by a number of instrumental techniques, including XRD, TG, XPS, Mössbauer spectroscopy and FTIR, all of which probe the coordination environment of Fe cations, but could not precisely reflect the structural information with respect to the substituting cations.

In this study, the valence and atomic environment of some substituting metals in magnetites ($\text{Fe}_{3-x}\text{M}_x\text{O}_4$, $\text{M} = \text{V}, \text{Co}$ and Ni) were investigated using X-ray absorption fine structure (XAFS) spectroscopy. The results deduced from X-ray absorption near edge structure (XANES) spectroscopy indicated that the valences of V, Co and Ni in $\text{Fe}_{3-x}\text{M}_x\text{O}_4$ were +3, +2 and +2, respectively. Extended X-ray absorption fine structure (EXAFS) spectroscopy suggested that the substituting cations occupied octahedral sites in the magnetite structure. The M-O and M-M/Fe distances were consistent with the $\text{Fe}_{\text{oct}}\text{-O}$ and $\text{Fe}_{\text{oct}}\text{-Fe}$ distances, respectively, in the magnetite (Fe_3O_4) structure. The occupancy of the substituting cations was assessed by crystal-field theory (CFT). The relationship between the chemical environment of substituting cations and their effects on the physico-chemical properties of magnetite including thermal stability, surface properties, and catalytic reactivity, is discussed.