Vacancy infilling during the crystallization of Fe-deficient hematite: An in situ synchrotron X-ray diffraction study of non-classical crystal growth

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ABSTRACT

The crystallization of hematite from precursor ferrihydrite was studied using time-resolved, angle-dispersive synchrotron X-ray diffraction in aqueous solutions at pH 10 and 11 and at temperatures ranging from 80 to 170 °C. Rietveld analyses revealed a non-classical crystallization pathway involving vacancy infilling by Fe as defective hematite nanocrystals evolved. At 90 °C and pH 11, incipient hematite particles exhibited an Fe site occupancy as low as 0.68(2), and after 30 min, Fe occupancy plateaued at 0.84(1), achieving a metastable steady state with a composition corresponding to “hydrohematite.” During crystal growth, unit-cell volume increased with an increase in Fe occupancy. The increase in Fe occupancy in hydrohematite was accomplished by deprotonation, resulting in a shortening of the long Fe-O(H) bonds and decreased distortion of the octahedral sites. Once the occupancy stabilized, the unit-cell volume contracted following further nanoparticle growth. Our study documented various synthetic routes to the formation of “hydrohematite” with an Fe vacancy of 10–20 mol% in the final product.

The structure refined for synthetic hydrohematite at 90 °C and pH 11 closely matched that of natural hydrohematite from Salisbury, Connecticut, with a refined Fe occupancy of 0.83(2). Dry heating this natural hydrohematite generated anhydrous, stoichiometric hematite, again by continuous infilling of vacancies. The transformation initiated at 150 °C and was complete at 700 °C, and it was accompanied by the formation of a minor amorphous phase that served as a reservoir for Fe during the inoculation of the defective crystalline phase.

Keywords: Hematite, 2-line ferrihydrite, crystal growth, time-resolved X-ray diffraction, kinetics

INTRODUCTION

Hematite (Hm) occurs as a naturally abundant coating on sediments and soils, often controlling the sorption and redox states of dissolved metals and organic pollutants (Barrón and Torrent 2013; Claudio et al. 2017). Hematite also has been used as a paleoclimate proxy for environments thousands to millions of years in the past, via hematite:goethite ratios (Ji et al. 2004; Hyland et al. 2015) and also as the primary carrier of natural remanent magnetization in red beds, enabling plate tectonic reconstruction (e.g., Walker et al. 1981; Lovlie et al. 1984; Sznajewski et al. 2012). In addition, hematite is an important industrial material that is widely used in pigments, catalysts, batteries, sensors, photoelectrochemical water splitting devices, heavy-metal decontaminants, and many other applications (Paterson 1999; Walter 2006; Lu et al. 2014; McBriarty et al. 2018; Guo et al. 2020).

The presence of vacancies in hematite greatly enhances its efficiency as a photocatalyst (Guo et al. 2020), an adsorbent of radiotoxic elements (Wang et al. 2015; McBriarty et al. 2018), a charge-storage capacitor (Hahn et al. 2011; Lu et al. 2014), and an electrical conductor (Yang et al. 2013). Many studies have focused on the effects of oxygen vacancies and surface iron deficiencies in hematite (Yang et al. 2013; Hu et al. 2016; Kim 2020). In this paper, we explore hematite that exhibits bulk Fe cation deficiencies.

The hematite structure (space group R3c) contains sheets of oxygen anions that are hexagonal closest packed, and Fe fills ⅔ of the octahedral sites (Blake et al. 1966). The substitution of 3H3+ ↔ 1Fe3+ yields the following general formula for hydrohematite: Fe2-x3+x(OH)O3-x (Fig. 1). Wolska and Schwertmann (1989) designated the term “hydrohematite” for the compositional range 0.5 ≥ x > 0, and “protohematite” for 1 ≥ x > 0.5. “Protohematite” with Fe vacancies up to 10 mol% has been observed as an intermediate during the heating of goethite (Gualtieri and Venturelli 1999; Burgina et al. 2000). In their study of the transformation of akageneite to hematite, however, Peterson et al. (2015, 2016) reported transient hematite-like precursors with Fe vacancy concentrations greatly exceeding 10 mol%. Despite the importance of hematite for commercial, technological, and paleoenvironmental applications, little is known about its tolerance for Fe deficiencies and the range of Fe occupations in natural and synthetic hematite minerals.

Figure 1 represents the Fe stoichiometries along a join con-