Cation distribution in synthetic zinc ferrite \((\text{Zn}_{0.97}\text{Fe}_{2.02}\text{O}_4)\) from in situ high-temperature neutron powder diffraction

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ABSTRACT

Neutron powder diffraction experiments at high temperature (300–1600 K) were performed at BENSsc (Berlin, D), on synthetic \(\text{Zn}_{0.96}\text{Fe}_{2.02}\text{O}_4\), to investigate the cation partitioning of Zn and Fe over the tetrahedral and octahedral sites as a function of \(T\). The data analysis combined Rietveld structure refinements with minimization techniques. The thermodynamic behavior of the thermally activated order-disorder transformation occurring in Zn-ferrite was interpreted by the O’Neill-Navrotsky model \((\alpha = 49.3 \pm 0.4 \text{ and } \beta = –31.6 \pm 2.0 \text{ kJ/mol})\) and by the equilibrium Landau theory. We obtain \(\Delta F = 2.813 \pm 0.002/\text{K}, T_c = 1022 \pm 37 \text{ K}\) using a “pure” Landau approach, and \(h = –1.164 \pm 0.002 \text{ kJ/mol}, c = 9.868 \pm 0.06 \text{ kJ/mol}, T_e = –742 \pm 10 \text{ K}\), if the configurational contribution to entropy is explicitly accounted. The results are in agreement with the earlier powder XRD work of O’Neill (1992) on quenched specimens, but extend the temperature over which measurements were obtained to 1600 K.

INTRODUCTION

Ferrite spinels (space group \(Fd\overline{3}m\)) have the general chemical composition \(\text{AFe}_2\text{O}_4\), where \(\text{A}\) is a divalent cation. Their unit cell contains 32 O atoms in cubic closest-packing, eight tetrahedral (T) and 16 octahedral (M) sites, hosting Fe and A cations. In the ideal “normal” structure the A-cations enter fourfold coordination, whereas iron occupies the M-sites; in the “inverse” structure, common in ferrites, all of the A values move to the octahedral sites, and are replaced in the fourfold-coordination positions by half the Fe atoms. Intermediate configurations often occur, and are described by the inversion parameter \(x\) (see O’Neill and Navrotsky 1983) which accounts for the amount of Fe on the tetrahedral sites. Ferrites have been studied mostly for their magnetic properties, which depend on the distribution of iron over the two sublattices corresponding to the T- and M-sites.

Zinc ferrite (franklinite) was inferred to have a normal cation distribution regardless of the temperature of preparation or of equilibration, according to Mössbauer spectroscopy [see Marshall and Dollase (1984), and references therein]. Such a notion, however, was at variance with elementary crystal-chemical considerations, and motivated a study by O’Neill (1992), which demonstrated that order-disorder reactions occur in this compound as well. O’Neill (1992) performed his investigations on quenched specimens. Now, taking into account that: (1) no in-situ high-temperature investigation on Zn ferrite is available in literature, (2) the results of O’Neill (1992) rely upon quenched samples and do not provide information above 1200 K, we carried out a suite of in-situ high-temperature neutron powder diffraction experiments, on a synthetic sample, to investigate the order-disorder (OD)-reactions occurring in Zn ferrite. Given that zinc and iron have remarkable neutron scattering length contrast \(b_{\text{Zn}} = 0.568 \text{ vs. } b_{\text{Fe}} = 0.954 \times 10^{-12} \text{ cm}\), against \(Z_{\text{Zn}} = 30 \text{ vs. } Z_{\text{Fe}} = 26\); neutron scattering lengths values from General Structure Analysis System (GSAS) (Larson and Von Dreese 1987; Lovesey 1984), neutron diffraction is an appropriate technique to obtain the Zn and Fe distribution, which was determined, in this work, by combining Rietveld structure refinements with minimization techniques.

EXPERIMENTAL METHODS

Sample

The sample used was synthesised by solid state reaction of oxides, heating for 48 hours at 1400 K a stoichiometric mixture of analytical purity \(\text{ZnO}\) and \(\text{Fe}_2\text{O}_3\) reagent grades, compressed into a 10 g pellet to favor their reaction. The temperature was then decreased at \(\approx 15 \text{ K/h}\), down to 800 K, maintained for 24 hours, and finally brought to room temperature at the same rate; the process took about one week. The crystallinity of the sample was checked by X-ray powder diffraction by means of a Bragg-Brentano PHILIPS X’PERT diffractometer, using NBS-silicon as an internal standard. The cell parameter \([a = 8.4418(5) \text{ Å}]\) determined by full profile fitting method is in agreement with values from the literature for synthetic Zn ferrite (Waerenborgh et al. 1994; O’Neill 1992).

We measured \(^{57}\text{Fe}\) Mössbauer spectra at room temperature using a conventional constant acceleration spectrometer (rhodium matrix \(^{57}\text{Co}\) source with nominal strength 50 nCi) to investigate the oxidation state of iron. Approximately 20 mg of finely ground material was suspended in vaseline, placed in