Temperature dependence of the cation distribution in zinc ferrite (ZnFe$_2$O$_4$) from powder XRD structural refinements.

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Abstract: Zinc ferrite (ZnFe$_2$O$_4$) has the cubic spinel structure with an (approximately) normal cation distribution. It was synthesised by direct reaction of the oxides at 800°C, and also by using a sodium tungstate flux with excess ZnO. Lattice parameters (a$_0$) of samples from both syntheses were measured at room temperature, on samples annealed in air between 500 and 1200°C and then quenched into water; a$_0$ decreases from 8.4419(2) for samples annealed at 500°C, to 8.4400(2) for 950°C, and there is no significant difference between samples from either synthesis method. Annealing at higher temperatures causes no further decrease in a$_0$ in the quenched samples. The change of a$_0$ with time during isothermal annealing at 500°C established that a steady value was reached in about 24 hours.

The cation distributions in quenched samples of the flux-grown material were determined by powder X-ray diffraction, using the Rietveld method of structural refinement. The degree of inversion in ZnFe$_2$O$_4$ increases from 0.02(2) at 500°C to 0.19(2) at 950°C. Samples quenched from higher temperatures show no further increase in x, in agreement with the trend in a$_0$. This is probably due to the rate of re-ordering being too fast to quench above ~950°C.

$^{57}$Fe Mössbauer spectra were collected for a few samples at 80K and 298K. All spectra show only a single doublet with hyperfine parameters characteristic of octahedral Fe$^{3+}$. The tetrahedral Fe$^{3+}$ deduced from the XRD refinements cannot be resolved.

Key-words: spinel, zinc ferrite, cation distribution.

Introduction

The ferrite spinels have the general formula MFe$_3$$^{2+}$O$_4$, where M is a divalent cation. For example, M may be Fe$^{2+}$, as in the mineral magnetite, Fe$_3$O$_4$. Like magnetite, most of the ferrite spinels adopt the inverse cation distribution, in which half the Fe$^{3+}$ cations occupy the tetrahedral sites in the crystal structure, while the M cations mix with the remaining Fe$^{3+}$ on the octahedral sites. This arrangement may be written (Fe$^{3+}$)$_{tet}$[M,Fe$^{3+}$]$_{oct}$O$_4$, although in detail these inverse spinels all show a tendency to disorder further with increasing temperature, tending towards the random cation distribution (maximum configurational entropy), (M$_{1/3}$Fe$_{2/3}$$^{3+}$)$_{tet}$[M$_{2/3}$,Fe$_{1/3}$$^{3+}$]$_{oct}$O$_4$. The actual cation distribution may be described by an inversion parameter, x, defined simply as the fraction of the 3+ cations (e.g. Fe$^{3+}$ in ferrites) in the tetrahedral site: x is 1 for a perfectly inverse spinel, 2/3 for the random arrangement, and would be 0 for a perfectly normal spinel, (M)$_{tet}$[Fe$^{3+}$]$_{oct}$O$_4$.

Ferrite spinels with the largely inverse cation distribution are best known for their magnetic properties. As explained by Néel (1948), their ferrimagnetism (or antiferromagnetism) results from strong, negative superexchange interactions between the cations on the tetrahedrally co-ordi-