

Structural Characterization of Divalent Magnesium-Doped α -Fe₂O₃

Frank J. Berry,* Alberto Bohorquez,*¹ Colin Greaves,[†] Julia McManus,* Elaine A. Moore,* and Michael Mortimer*

*Department of Chemistry, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom; and [†]School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

Received February 25, 1998; in revised form May 22, 1998; accepted May 27, 1998

The defect structure of divalent magnesium-doped α -Fe₂O₃ has been examined by Rietveld structure refinement of the X-ray powder diffraction data. The results show that the Mg²⁺ ions occupy the vacant interstitial octahedral sites as well as substituting on the two adjacent octahedral Fe³⁺ sites in the corundum-related α -Fe₂O₃ structure. The structure therefore involves a linear cluster of three Mg²⁺ ions replacing two Fe³⁺ ions. Interatomic potential calculations indicate that this is the most energetically favorable defect cluster for the system. © 1998

Academic Press

INTRODUCTION

The influence of dopant cations on the electrical, magnetic, and other physical properties of α -Fe₂O₃ has been an area of interest for some time. We have recently shown (1) that, and in contrast to previous expectations, the tetravalent cations tin and titanium adopt two distinct sites when doped into α -Fe₂O₃; in addition to partially substituting at the octahedral Fe³⁺ sites they also occupy the interstitial octahedral sites, which are vacant in the α -Fe₂O₃ structure. The structure represented microstructural regions of the rutile structure within a matrix of α -Fe₂O₃. We report here on an investigation by X-ray powder diffraction, with Rietveld structure refinement, of the structure of divalent magnesium-doped α -Fe₂O₃. The defect structure is further investigated by using interatomic potential calculations.

EXPERIMENTAL

The compound of nominal composition α -Fe_{1.8}Mg_{0.2}O₃ was prepared by precipitating aqueous mixtures of iron(III) chloride hexahydrate and magnesium(II) nitrate hexahydrate with aqueous ammonia and hydrothermally processing the precipitates in a Teflon-lined autoclave at 200°C and

15 atm pressure for 3 h. The product was removed by filtration and washed with 95% ethanol until no chloride ions were detected by silver nitrate solution. The product was allowed to dry in air.

X-ray powder diffraction (XRD) data were recorded with a Siemens D5000 diffractometer in reflection mode using CuK α radiation. The program FULLPROF (2) was used for Rietveld refinement and simulation of patterns for specific structural models.

Interatomic potential calculations were performed using a pair potential shell model on a DEC alpha 600 workstation using the program GULP (3). The interatomic potentials for Fe³⁺, Mg²⁺, and O²⁻ were taken from a recently reported compilation (4).

RESULTS AND DISCUSSION

Structural Characterization

The XRD profile indicated the Mg²⁺-doped material to be single phase and isostructural with α -Fe₂O₃. Various structural models were examined using Rietveld refinement methods, and the most satisfactory involved a combination of both interstitial and substitutional Mg²⁺ ions in octahedral coordination. The α -Fe₂O₃ structure comprises an ordered distribution of Fe³⁺ ions in 2/3 of the octahedral interstices formed by a hexagonally close-packed arrangement of O²⁻ ions. The resulting structure contains chains of face-sharing octahedra running along [001], with the Fe³⁺ ions pairing up as shown in Fig. 1a. In a previous study (1), we showed that the incorporation of M⁴⁺ cations (M⁴⁺ = Sn⁴⁺, Ti⁴⁺) into α -Fe₂O₃ involves the partial occupation of the interstitial octahedral sites, but to avoid the highly repulsive electrostatic interactions between M⁴⁺ and Fe³⁺ ions in linked face-sharing octahedra, the octahedral sites on both sides of the MO₆ units are vacant. In fact, it was proposed that linear clusters of three M⁴⁺ ions replace four Fe³⁺ ions to achieve charge balance while avoiding all face-sharing of MO₆ octahedra. The incorporation of divalent Mg²⁺ ions into α -Fe₂O₃ is expected to be less

¹Permanent address: Departamento de Física, Universidad del Valle, AA25360, Cali, Colombia.

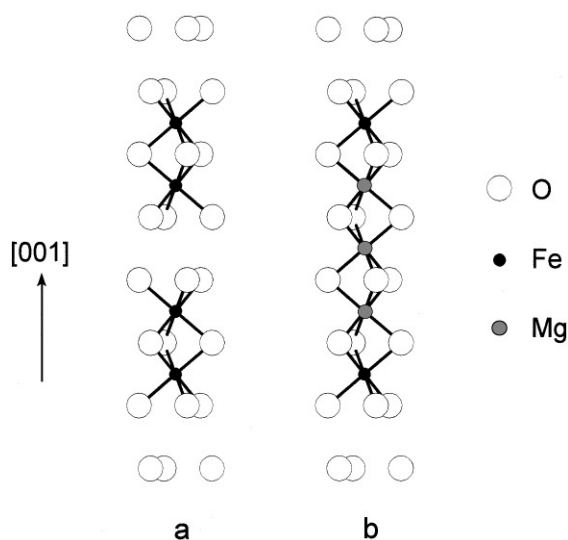


FIG. 1. a) Pairs of face-sharing octahedra in α -Fe₂O₃; b) The proposed defect model in which three Mg²⁺ ions replace two Fe³⁺ ions to form chains of five face-sharing octahedra.

influenced by such repulsive interactions, and charge considerations support a simple substitution mechanism with charge balance being achieved by partial occupancy of the interstitial octahedral sites. In this way, the substitution of two Fe³⁺ ions by two Mg²⁺ ions would be balanced by an additional Mg²⁺ ion in an interstitial position. For local charge neutrality, short-range order to form linear clusters of three Mg²⁺ ions seems probable, as shown in Fig. 1b. This model was found to provide a sound basis for Rietveld

TABLE 1
Refined Atomic Parameters

Atom	Position	x/a	y/b	z/c	$B_{\text{iso}}/\text{\AA}^2$	Cell occupancy
Fe	12c	0	0	0.3544(1)	1.88(6)	11.38(12)
Mg1	12c	0	0	0.3544(1)	1.88(6)	0.62(12)
Mg2	6b	0	0	0	1.88(6)	0.31(6)
O	18e	0.3089(11)	0	0.25	1.3(1)	18

Unit Cell

$$R-3c; a = 5.0489(3) \text{ \AA}, c = 13.7885(8) \text{ \AA}$$

Constraints

$$B_{\text{iso}}: \text{Fe} = \text{Mg1} = \text{Mg2} \quad \text{Occupancy: Mg1} = 2\text{Mg2}, \text{Fe} = 12-\text{Mg1}$$

$$z/c: \text{Fe} = \text{Mg1}$$

R-factors

$R_{\text{wp}} = 17.8$, $R_{\text{exp}} = 13.1$, $R_1 = 3.4\%$. R_{wp} and R_{exp} have their normal significance and relate to regions of the profile at which Bragg peaks contribute; R_1 is the residual based on observed and calculated integrated intensities.

refinement, and the fitted profiles are shown in Fig. 2. Refined structural parameters are shown in Table 1, together with the appropriate constraints applied during the refinement. Final analysis allowed for preferred orientation, but the correction was very small.

The unit cell is slightly expanded (Table 1) relative to pure α -Fe₂O₃ ($a = 5.035 \text{ \AA}$, $c = 13.751 \text{ \AA}$) (5), which is consistent with substitution of the larger cation Mg²⁺ on the Fe³⁺ sites (octahedral radii 0.72 and 0.645 \AA , respectively) (6). The partial occupancy of the interstitial octahedral sites would

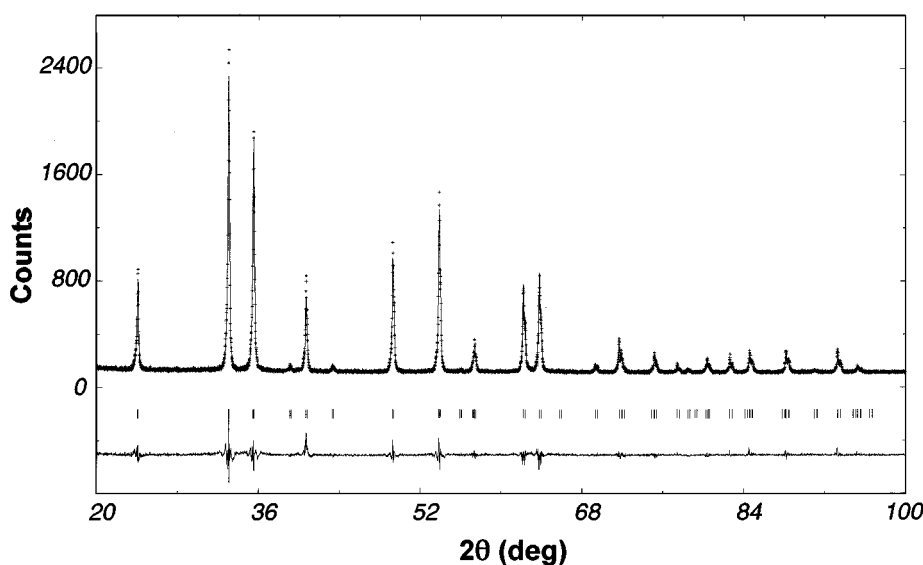


FIG. 2. Observed (+), calculated and difference X-ray powder diffraction profiles. The reflection positions are marked by small vertical lines.

TABLE 2
Shell–Shell Potentials

Interaction	A/eV	$\rho/\text{\AA}$	$C/\text{eV \AA}^6$	Core charge/e	Shell charge/e
$\text{Fe}^{3+}\text{-O}^{2-}$	3219.335	0.2641	0	1.971	1.029
$\text{Mg}^{2+}\text{-O}^{2-}$	2457.243	0.2610	0	1.58	0.42
$\text{O}^{2-}\text{-O}^{2-}$	25.41	0.6937	32.32	0.513	-2.513

be expected to further increase the expansion. The Mg:Fe atomic ratio determined from the XRD analysis is 8.2(1.7)%, which is in satisfactory agreement with the expected 11.1% (difference less than twice the esd) of the nominal composition $\text{Fe}_{1.8}\text{Mg}_{0.2}\text{O}_3$. It should be noted that an alternative model in which Mg^{2+} ions in interstitial octahedral sites are electrostatically balanced by vacancies on the octahedral Fe^{3+} sites also provides satisfactory agreement between observed and calculated XRD profiles. However, this model was rejected because of the unacceptably low value of 2.9(5)% for the Mg:Fe ratio.

Interatomic Potential Calculations

The values of the shell–shell and core–shell potentials which were used are given in Tables 2 and 3, respectively. The region which is explicitly relaxed, region 1, was given a radius of 8 Å in all defect calculations. The radius of region 2, where only the effect of the defect is considered, was set at 12 Å.

A model involving the Mg^{2+} ions occupying an empty octahedral interstitial site together with substituting on the two adjacent octahedral Fe^{3+} sites in the corundum-related $\alpha\text{-Fe}_2\text{O}_3$ structure gave a defect energy of +0.94 eV per dopant ion. Alternative models whereby the occupation by Mg^{2+} of three interstitial sites was accompanied by the creation of two Fe^{3+} vacancies, or the substitution of two Fe^{3+} ions by two Mg^{2+} ions and the creation of an oxygen

TABLE 3
Core–Shell Potentials

Interaction	$k_2/\text{eV \AA}^{-2}$
Fe^{3+} core– Fe^{3+} shell	179.58
Mg^{2+} core– Mg^{2+} shell	349.95
O^{2-} core– O^{2-} shell	20.53

vacancy, or the occupation by one Mg^{2+} of an interstitial site with the creation of two Fe^{3+} vacancies and two oxygen vacancies gave the significantly less favorable defect energies of +1.10, +1.87, and +4.76 eV, respectively. Hence, the defect structure of Mg^{2+} -doped $\alpha\text{-Fe}_2\text{O}_3$ as determined by Rietveld structure refinement of the X-ray powder diffraction pattern corresponds to the most energetically favorable defect cluster for the system as found by interatomic potential calculations.

ACKNOWLEDGMENTS

We thank the EPSRC for the award of a studentship (J.M.) and Colciencias and the Universidad del Valle for financial support (A.B.).

REFERENCES

1. F. J. Berry, C. Greaves, J. G. McManus, M. Mortimer, and G. Oates, *J. Solid State Chem.* **130**, 272 (1997).
2. J. Rodriguez-Carajal, "FULLPROF V.2., 6.1" (ILL, France), 1994. Based on the original code by R. A. Young, *J. Appl. Crystallogr.* **14**, 149 (1981).
3. J. D. Gale, *J. Chem. Soc. Faraday Trans.* **93**, 629 (1997). [J. D. Gale, "General Utility Lattice Program (GULP)," 1992–1994, London, The Royal Institution and Imperial College]
4. T. S. Bush, J. D. Gale, C. R. A. Catlow, and P. D. Battle, *J. Mater. Chem.* **4**, 831 (1994).
5. L. W. Finger and R. M. Hazen, *J. Appl. Phys.* **51**, 5362 (1980).
6. R. D. Shannon, *Acta Crystallogr. A* **32**, 751 (1976).