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# An X-ray diffraction and Mössbauer study of nano-crystalline $Fe_2O_3$–$Cr_2O_3$ solid solutions

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A series of gels with nominal composition $Fe_{2-x}Cr_xO_3$ ($x = 0$–2) was prepared at room temperature by an inorganic sol–gel route and studied by X-ray diffraction and Mössbauer spectroscopy. The gels dried at 105 °C were found to be X-ray amorphous, but Mössbauer studies revealed the gels to be nano-crystalline solid-solution particles of the composition above, with super-paramagnetic properties. Further heating to 600 °C gave crystalline X-ray patterns which allowed lattice parameter and crystallite size calculations to be made. It was found that lattice parameters and crystallite sizes decreased with increasing chromia content, and that at the higher chromia/iron ratios, a partially collapsed Mössbauer pattern results, indicating reductions in crystallite size and hyperfine field with increasing chromia content.

## 1. Introduction

Nano-crystalline materials are of current interest due to their novel physical properties and technological applications. Gleiter [1, 2] has shown that nano-crystals possess properties that are drastically different from that of the corresponding bulk material, and can be treated as a new phase. In a previous publication [3], nano-crystalline mixed oxide compounds were produced at low temperatures and seen to have novel properties over their conventional counterparts. In the same fashion, nano-crystalline composites of these mixed oxides with synthetic silica have been produced, giving novel properties over bulk mixed oxide preparations [4].

In this paper, therefore, we report X-ray diffraction and Mössbauer results on various nano-crystalline $Fe_2O_3$–$Cr_2O_3$ solid solutions. Mössbauer spectrometry has been used here as a means of nano-crystallite characterization, by probing their unique magnetic properties and thereby gaining valuable information on the Fe–Cr interactions within these crystallites.

## 2. Experimental procedure

### 2.1. Sample preparation

Requisite quantities of $Cr(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (Aldrich chemical company 99%), were dissolved in distilled water to give a solution with a total metal concentration of 2M. The solution was vigorously stirred at room temperature and 100 ml of an immiscible base, diluted with suitable solvent, was added to remove some of the anions. The suspension was allowed to separate and the organic layer decanted and discarded. The extraction was repeated twice further to leave a polymeric sol with $[NO_3^-]:[Fe/Cr] = 0.9$. The sols produced were analysed thermogavimetrically to give an accurate oxide residue and crystallization temperature. Samples were then oven dried at 105 °C to give glassy black re-dispersible gels, or calcined to 600 °C for 2 h to give crystalline solid solutions.

### 2.2. Sample characterization

### 2.2.1. *X-ray powder diffraction measurement (XRD)*

X-ray powder diffraction (XRD) patterns for samples treated at various temperatures were recorded in the region of $2\theta = 5°$–$120°$ with a step scan of 0.1 deg $min^{-1}$ on a Philips diffractometer (Model PW1710) using $CuK_\alpha$ radiation. Cell parameters were calculated and further refined using linear regression procedures (Philips APD 1700 software) applied to the measured peak positions of all major reflections up to $2\theta = 90°$. Line broadening analysis was also performed on crystalline patterns using the Scherrer equation on the highest intensity (1 0 4) peak, to ascertain average crystallite size.

### *2.2.2. Mössbauer measurements*

Mössbauer spectra were recorded at room temperature in transmission geometry with a PC-based Mössbauer spectrometer operating in constant acceleration mode. A 25 mCi $^{57}$Co source in a rhodium matrix was used as the incident radiation. The spectrometer was calibrated with a high-purity natural iron foil of 25 μm thickness. Mössbauer data were fitted with a least squares programme assuming lorentzian line width.

## 3. Results and discussion

XRD patterns of the gels dried at 105 °C are amorphous, indicating that long-range crystallization of the solid solutions has not yet commenced.

Mössbauer spectra of the dried gels are shown in Fig. 1. All of them show a single quadrupole doublet. The computed isomer shifts (IS) and quadrupole splittings (QS) corresponding to these spectra are shown in Table I. The isomer shifts of the samples confirm that iron is in the $Fe^{3+}$ state. Also, IS of the $Cr^{3+}$ substituted samples are clearly more than that of the $Fe_2O_3$ alone, implying that the S electron density at the $Fe^{3+}$ site has been modified by the presence of $Cr^{3+}$ as a substituent. The sharpness of the doublets is also indicative that the iron in each gel is unique in its environment and thus homogeneously distributed. This data indicates that $Fe_2O_3$–$Cr_2O_3$ solid solutions have formed at the gel stage and for all compositions in the present study.

It is known that in Mössbauer spectroscopy, collapse of the magnetic ordering occurs when nanosized particles are present, due to their superparamagnetic relaxation, resulting in a collapsed spectrum. Such spectra resulting from iron oxide-based compounds exhibit doublets with large quadrupole splitting, rather than the more usual sextet patterns. Thus the presence of quadropole doublets throughout the composition range in the present study, shows that the

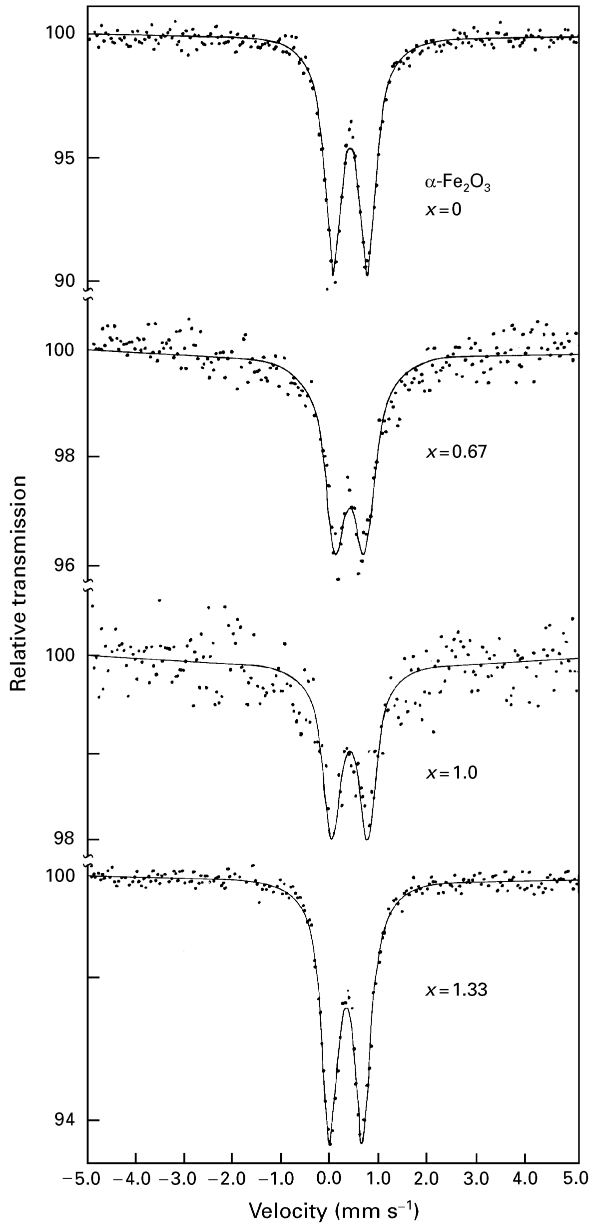

*Figure 1* Mössbauer spectra of the gels dried at 105 °C.

TABLE I. Mössbauer parameters for dried gel samples 105 °C. Error in IS and QS is ± 0.02 mm s$^{-1}$

| Sample $Fe_{2-x}Cr_xO_3$ | Isomer shift, δ (mm s$^{-1}$) | Quadrupole splitting, 2ε (kOe) |
|---|---|---|
| $x = 0$ | 0.32 | 0.70 |
| $x = 0.67$ | 0.35 | 0.60 |
| $x = 1$ | 0.36 | 0.72 |
| $x = 1.33$ | 0.35 | 0.67 |

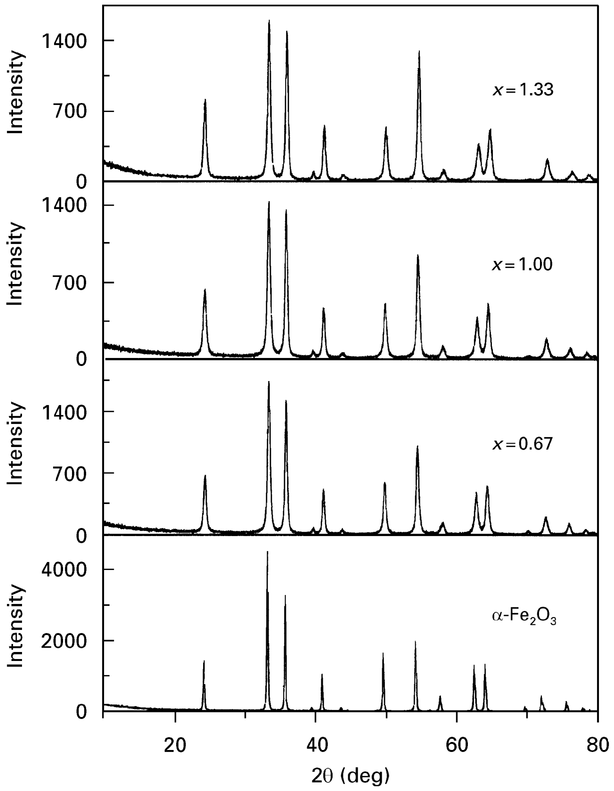

*Figure 2* XRD patterns of the samples $Fe_{2-x}Cr_xO_3$ calcined to 600 °C.

solid-solution particles are nanometre sized. The large quadrupole splitting observed for the dried gel samples is also indicative that nano-sized crystallites are present, as these are known to create electric field gradients and thus large QS [5].

XRD patterns of the gels calcined to 600 °C are shown in Fig. 2. This clearly shows crystallization of all solid solutions prepared in the present investigation, with the absence of any $Fe_2O_3$ or $Cr_2O_3$ as a separate phase. Lattice parameter measurements of the crystalline solid solutions are shown in Table II. Here we see that as chromia substitution increases, both lattice parameter and cell volume decrease as expected, because the $Cr^{3+}$ ion is smaller than the $Fe^{3+}$ ion (61.5 and 64.5 pm, respectively). A plot of the cell parameters, $a/c$, against the degree of substitution, $x$, is shown in Fig. 3. The non-linear nature of this curve indicates some lattice distrortion in the gradual replacement of $Fe^{3+}$ with $Cr^{3+}$ in the haematite lattice.

Line broadening measurements on the solid solutions was performed using the 100% intensity (1 0 4) plane of diffraction to ascertain crystallite size as a function of chromia substitution. The results are shown in Fig. 4. Here we clearly see a reduction in the average crystallite size as the amount of $Cr^{3+}$ substitution increases. This could be due to the prevention of crystallite growth/sintering by the chromia in the haematite lattice, which has a much higher melting point than $Fe_2O_3$. It can also be seen in this diagram, the shift in $2\theta$ values that accompanies the systematic substitution of iron oxide with chromia and hence the change in lattice parameters.

TABLE II. Lattice parameters from X-ray diffraction patterns of 600 °C heated samples

| Composition $Fe_{2-x}Cr_xO_3$ | $a$ (nm) | $c$ (nm) | $c/a$ (nm) | Cell volume ($10^{-3}$ nm$^3$) |
|---|---|---|---|---|
| JCPDS $Fe_2O_3$ | 0.5035(6) | 1.3748(9) | 0.2730 | 301.93 |
| $x = 0$ | 0.5040(5) | 1.3745(9) | 0.2727 | 302.44 |
| $x = 0.67$ | 0.5022(5) | 1.3660(7) | 0.2720 | 298.43 |
| $x = 1$ | 0.5006(1) | 1.3638(5) | 0.2720 | 296.00 |
| $x = 1.33$ | 0.4986(3) | 1.3618(0) | 0.2731 | 293.22 |

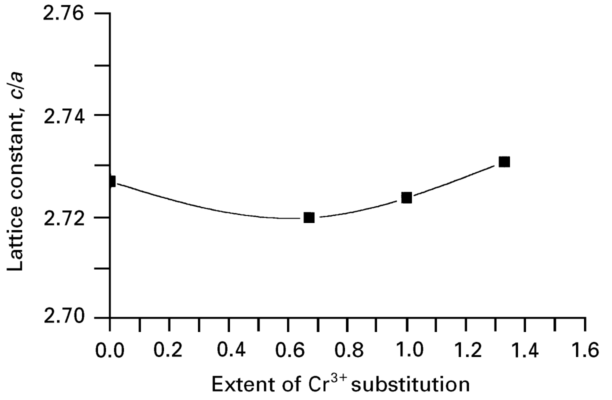

*Figure 3* Plot of cell parameter versus chromia substitution.

Fig. 5 shows the Mössbauer spectra of the heat-treated samples and Table III the parameters resulting from these patterns. $Fe_2O_3$ shows a clear sextet with IS $= 0.37$ mm s$^{-1}$, QS $= 0.16$ mm s$^{-1}$ and $H_{\text{int}} = 508$

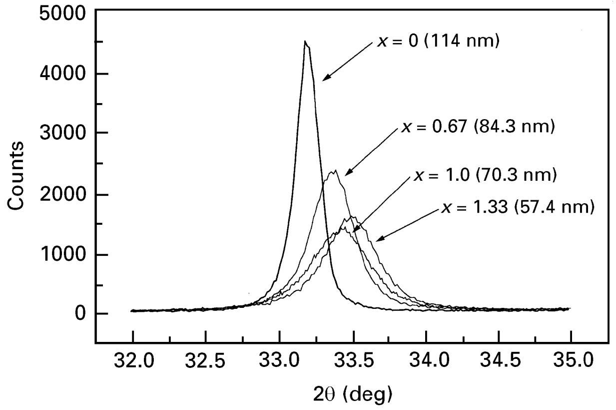

*Figure 4* XRD diagram showing the (1 0 4) diffraction peak with varying composition and crystallite size (in brackets).

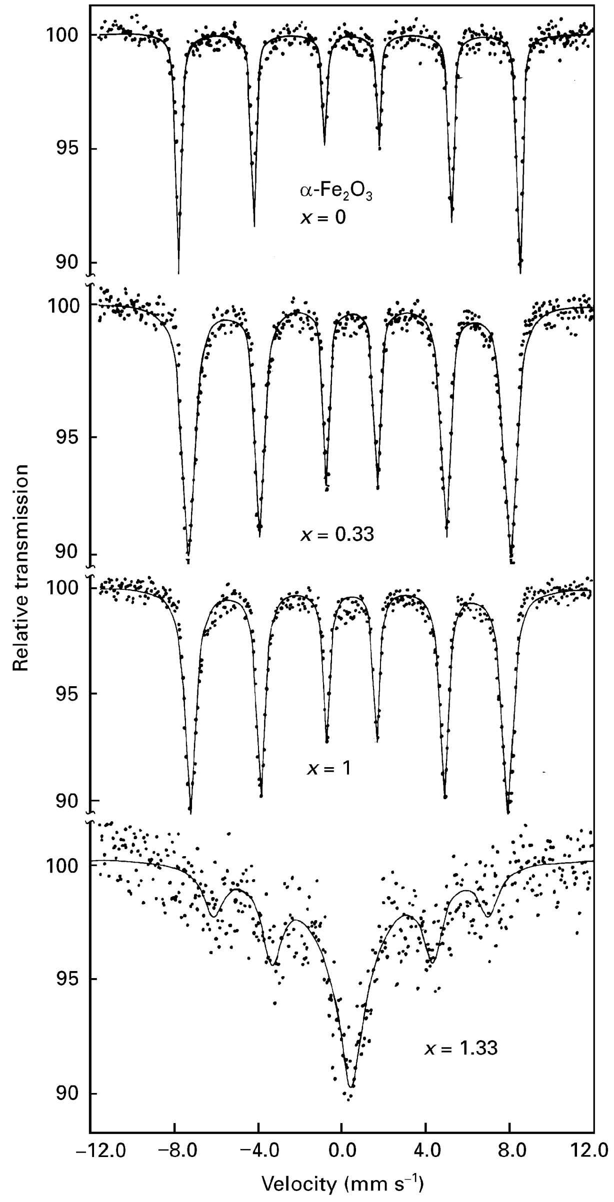

*Figure 5* Mössbauer spectra of the 600 °C calcined samples.

TABLE III. Mössbauer parameters for the 600 °C calcined samples. Error in IS and QS is ± 0.02 mm $s^{-1}$ and $H_{int}$ is ± 3 kOe

| Sample $Fe_{2-x}Cr_xO_3$ | Isomer shift, δ (mm $s^{-1}$) | Quadrupole splitting, 2ε (mm $s^{-1}$) | $H_{int}(H)$ kOe |
|---|---|---|---|
| $x = 0$ | 0.37 | 0.16 | 508 |
| $x = 0.67$ | 0.37 | 0.18 | 482 |
| $x = 1$ | 0.37 | 0.16 | 477 |
| $x = 1.33$ | Partially collapsed spectrum | | |

kOe. These values are very close to those parameters expected for crystalline haematite [6]. The samples $Fe_{2-x}Cr_xO_3$($x = 0.67$ and 1.00), also show sextet patterns, with hyperfine fields of 482 and 477 kOe, respectively. The sample with the highest chromia substitution, however, shows a partially collapsed sextet pattern. The development of sextets in the heat-treated samples is expected, because as the samples are heated, the particle size is expected to become larger due to sintering, causing a slowing down of the superparamagnetic relaxation. Thus magnetic splitting with the usual sextet pattern is seen in the heat-treated samples. As more $Cr^{3+}$ is introduced into the $Fe_2O_3$ system, the hyperfine field is being reduced until beyond a threshold value of crystallite size when the sextet becomes partially collapsed as in the Fe : Cr = 0.5 sample. This is consistent with the XRD data which show this lowest ratio sample as having the lowest crystallite size, approaching 50 nm.

## 4. Conclusion

By employing certain preparation methods, it is possible to produce homogeneous nano-crystalline gels of the $Fe_2O_3$–$Cr_2O_3$ system at room temperature. The gels at 105 °C are X-ray amorphous, but the use of Mössbauer spectroscopy has enabled the gels to be characterized as nanometre sized solid-solution particles, by exploiting the unusual magnetic properties of the gels nano-crystallites. The increased addition of chromia has also been seen to alter these magnetic properties. Also, the superparamagnetization effect which is dependent on crystallite size, appears to have a threshold of approximately 50 nm, around which size the sextet pattern collapses to a doublet. The effect of an increase in sintering temperature on chromia addition has been observed and could be of value in the prevention of grain growth at high temperatures, in iron oxide-based systems.

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## References

1. H. GLEITER, *Nanostruct. Mater.* **1** (1992) 1.
2. H. GLEITER, *J. Appl. Crystallogr.* **24** (1991) 29.
3. A. K. BHATTACHARYA, A. HARTRIDGE and K. K. MALLICK, *J. Mater. Sci.* **31** (1996) 5005.
4. A. K. BHATTACHARYA and A. HARTRIDGE, UK patent in application.
5. A. CHATTERJEE, D. DAS, D. CHAKRAVORTY and K. CHOUDHURY, *Appl. Phys. Lett.* **57** (1990) 1360.
6. N. N. GREENWOOD and T. C. GIBB, "Mössbauer spectroscopy" (Chapman and Hall, London, 1971) Ch. 10, p 241.

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