DETERMINATION OF SOLID SOLUTION LIMITS BASED ON THE THERMAL BEHAVIOUR OF ALUNINIUM SUBSTITUTED IRON HYDROXIDES AND OXIDES

E.Wolska, W. Szajda and P. Piszora

DEPARTMENT OF MAGNETOCHEMISTRY, A.MICKIEWICZ UNIVERSITY, POZNAN
UL.GRUNWALDZKA 6, PL-60780 POZNAN, POLAND

The formation of substitutional solid solutions of the isostructural oxyhydroxides α-FeOOH-α-AlOOH (goethite-diaspore and γ-FeOOH-γ-AlOOH (lepidocrocite-boehmite) was investigated by X-ray powder diffraction technique and by thermal analysis.

The unit cell parameters of both orthorhombic structures of α-Fe$_{1-x}$Al$_x$OOH (Pbnm) and γ-Fe$_{1-x}$Al$_x$OOH (Cmcm) decrease clearly with the increase of aluminium content up to $x \approx 0.10$.

Thermal analysis reveals the sensitivity of DTA and DTG effects to the composition of solid solutions. The temperatures of topotactic formation of rhombohedral α-(Fe, Al)$_2$O$_3$ and of the defect-spinel γ-(Fe, Al)$_2$O$_3$ during the dehydroxylation of α-(Fe, Al)OOH and γ-(Fe, Al)OOH respectively increase as the aluminium concentration rises up to 10 mol%. The dehydration curves of samples with greater aluminium content exhibits the same maximum $\Delta m/\Delta T$ as for the 10 mol% Al-preparation, indicating indirectly the end-members of the solid solution ranges.

Keywords: goethite-diaspore, lepidocrocite-boehmite, thermal analysis, X-ray powder diffraction

Introduction

The incorporation of aluminium into the iron oxide and hydroxide crystal lattice plays an important role in geological processes. The formation of substitutional solid solutions between the isostructural oxyhydroxides of iron and aluminium such as goethite-diaspore (α-Fe$_{1-x}$Al$_x$OOH) and lepidocrocite-boehmite (γ-Fe$_{1-x}$Al$_x$OOH) has been the subject of numerous studies. The syntheses of a series of α-Fe$_{1-x}$Al$_x$OOH samples with Al content up to 33 mol% were reported [1] and the existence of the Al-lepidocrocites (γ-Fe$_{1-x}$Al$_x$OOH) was recognized [2]. Although it has been proved that in both cases limited ranges of solid solution are formed, data on the aluminium concentration limits are contradictory. X-ray

powder diffraction measurements do not allow to fix the end-members of solid solution because of the decreasing crystallinity of samples with increasing Al content [3]. The dehydration reactions and the polymorphic phase transitions, however, may be studied easily and accurately by differential thermal analysis and thermogravimetry. The temperatures of both the DTA and DTG peaks varying with the aluminium content provide a very sensitive monitor of the composition of solid solutions.

In this paper some X-ray powder diffraction data are combined with thermo-analytical results in order to establish the limits of solid solution formation in the α-$Fe_{1-x}Al_xOOH$ and γ-$Fe_{1-x}Al_xOOH$ series.

Experimental

The α-(Fe, Al)OOH samples were obtained by two different modified methods:

1/ by storing coprecipitated amorphous (Fe,Al)-hydroxides in alkaline media (*pH* 13) and

2/ by storing the mixtures of separately precipitated $Al(OH)_3$ and $Fe(OH)_3$ gels at *pH* 13 in NaOH solutions. The method of preparation of γ-(Fe, Al)OOH samples was described previously [4].

The samples were characterized by X-ray powder diffraction using CoK_α radiation on the TUR-61 unit equipped with an HZG-3 proportional counter spectrometer. The unit cell dimensions were determined on a Philips PW1050 instrument with graphite/monochromator. The XRD patterns were obtained by step-scanning at 0.02°C increments and counting time of 10s per increment. Angles were corrected using Si as the internal standard.

Differential thermal analysis was performed in air at a heating rate of 10 deg/min, with Al_2O_3 as a reference material, on a Derivatograph OD102 (MOM Budapest). The TG and DTG curves were obtained using a Shimadzu TGA50 instrument. Thermal dehydroxylation processes were followed by keeping the samples at the given temperatures for 24 hours.

Results and discussion

The accurate determination of unit cell parameters of the orthorhombic (Pbmn) goethite structure reveals the decrease of lattice constants a, b, and c with the increase of the aluminium content in the range of about $0 < x < 0,1$ (Fig.1). A significant deviation from Vegard's rule for higher Al contents indicates the
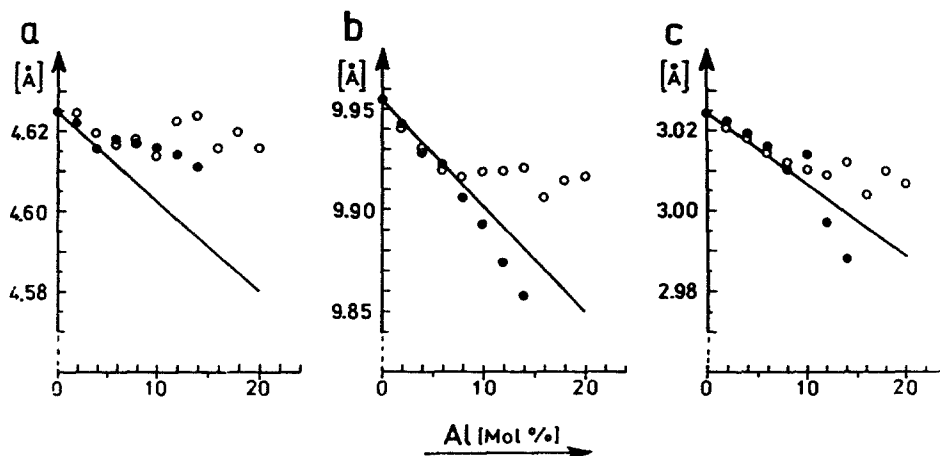
Fig. 1 Lattice constants a, b and c of the aluminium substituted goethite phases α-Fe$_{1-x}$Al$_x$OOH as a function of the Al content in relation to the Vegard's rule dependence. • samples obtained from coprecipitated gels; o samples from separately precipitated and mixed hydroxides
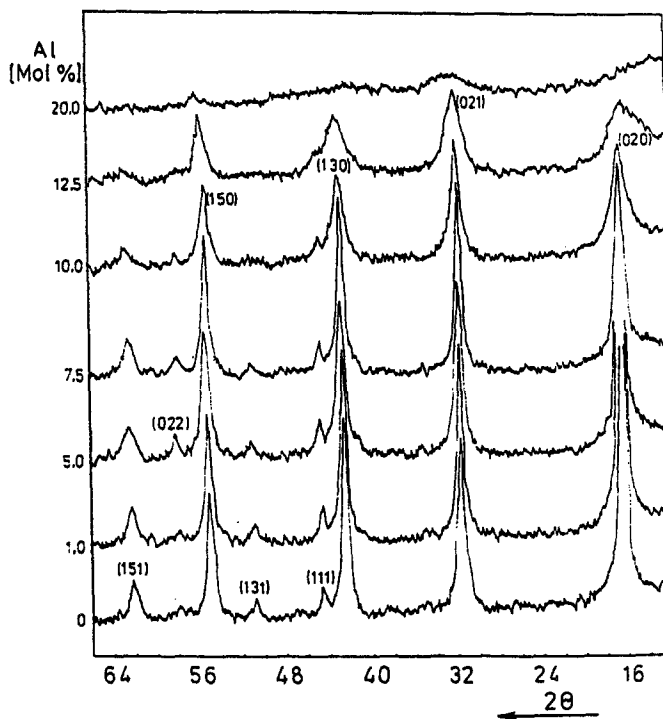
Fig. 2 X-ray powder diffraction patterns of the aluminium substituted lepidocrocites, γ-Fe$_{1-x}$Al$_x$OOH

limited substitution of Al^{3+}- for Fe^{3+}-ions in the α-$Fe_{1-x}Al_xOOH$ lattice. The inconsistency with Vegard's law which appears for the a-parameter at lower Al contents might be explained in terms of the involvement of supplementary hydroxyl groups in the goethite lattice and the resulting cation deficiency [5, 6].The results presented in Fig. 1 are similar for the goethite samples obtained from coprecipitated (Al,Fe)-hydroxides and from separately precipitated and mixed $Al(OH)_3$ and $Fe(OH)_3$ gels.
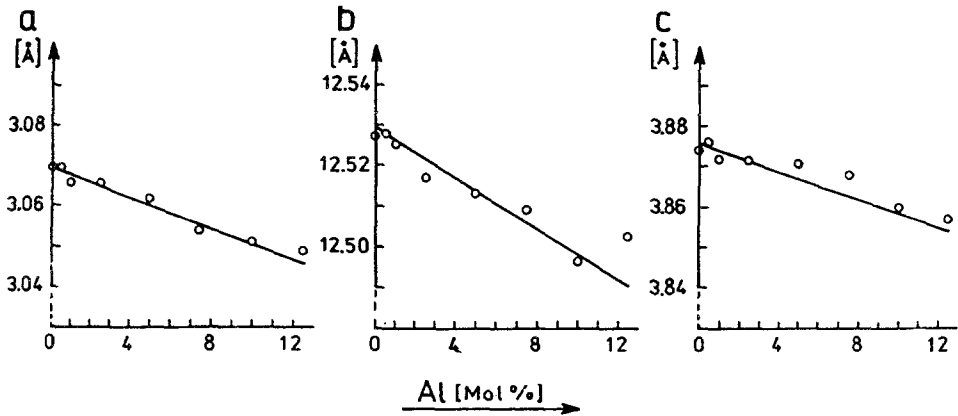

Fig. 3 Lattice parameters of the Al-substituted lepidocrocites in relation to the Vegard's rule dependence

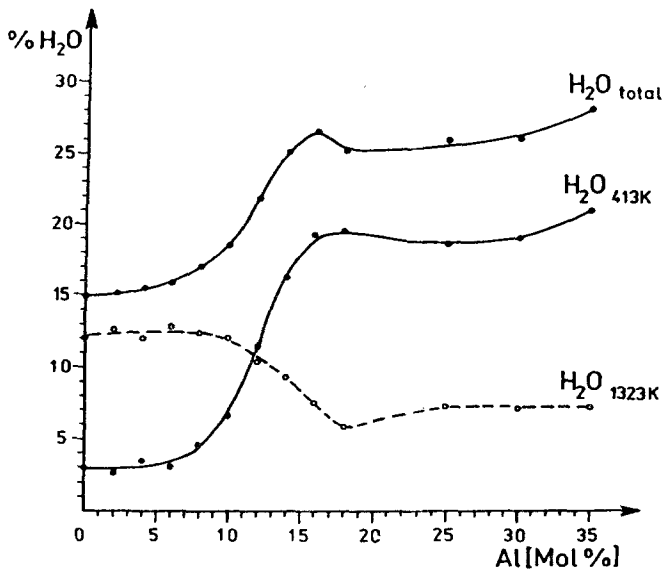**Fig. 4** Water content in the α-$Fe_{1-x}Al_xOOH$ samples obtained from coprecipitated (Al, Fe)-hydroxides, plotted as a function of the aluminium content

The isomorphous character of Al-incorporation in the lepidocrocite (Cmcm) structure could be confirmed due to the well crystallized single phase Al-lepidocrocite samples obtained for $0 < x < 0.125$ (Fig.2). We were now able to determine all three lattice parameters from a large set of X-ray reflections up to that limit. The relation between the experimental values of the lattice constants a, b and c and the Vegard's law behaviour for the γ-$Fe_{1-x}Al_xOOH$ system is presented in Fig.3. It allows to admit a linear fall in all three unit cell dimensions with the increase of the Al content, a rather expected effect of the substitution of a cation with smaller radius and with the electronic configuration retaining the octahedral coordination unaffected. Although the lattice constants of the sample with $x = 0.125$ could not be determined with sufficient accuracy, the X-ray examination permits to assume that the end member of γ-$Fe_{1-x}Al_xOOH$ solid solution has a formula of $Fe_{0.9}Al_{0.1}OOH$.

Another evidence for the limited range of solid solutions of both α- and γ-polymorphs of $Fe_{1-x}Al_xOOH$ is given by studying their thermal dehydroxylation processes. The ultimate product of heating of all the iron oxides and hydroxides is hematite.
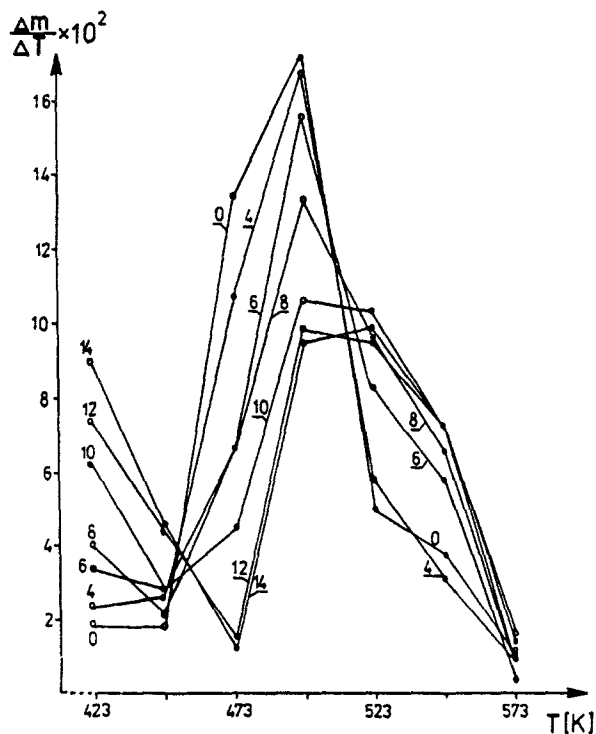

Fig. 5 Thermal hydroxylation of aluminium-substituted goethites during the goethite → protohematite transition (figures refer to the aluminium content in mol%)

The change from goethite to hematite is topotactic [7] and the dehydroxyla-
tion at about 520 K gives an intermediate, cation deficient, 'protohematite' phase
[5]. Goethite in which aluminium replaces some of the iron is thermally more
stable than the Al-free material and the disordered hematite first formed has
smaller unit cell dimensions than does the corresponding material produced from
Al-free goethite [8]. The degree of hydration of the Al-goethite samples rises with
the Al content independently of the method of sample preparation. Figure 4
presents the relation between the total H_2O content and the constitutional water
plotted against the Al content in the Al-goethites obtained from coprecipitated
(Al,Fe)-hydroxides. The changes in water content during the reaction, $\Delta H_2O/\Delta T$,
plotted as a function of temperature (Fig.5) show that the first loss of weakly
bound water, with maximum at 423 K is independent of the aluminium content.
However, the temperature of transition in the Al-protohematite is clearly depend-
ent on the composition of samples and increases from about 500 K to 525 K with
the increase of the Al content from 0 to 10 mol%, showing indirectly the limit of
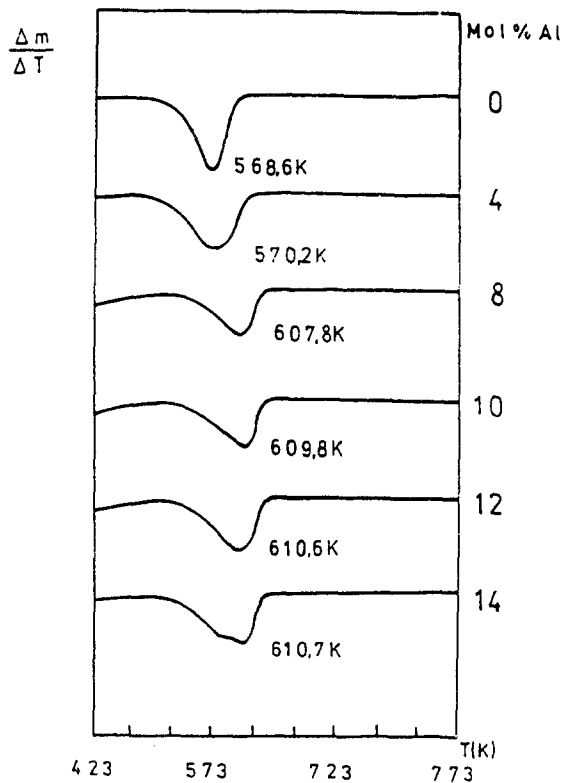solid solution formation at $x = 0.1$. The temperature of DTG peaks increases as

Fig. 6 DTG curves of Al-goethites obtained from mixtures of separately precipitated
         Al(OH)₃ and Fe(OH)₃ gels

well from 570 K to 610 K with increasing Al concentration in samples from 0 to 10 mol% for the Al-goethites obtained from a mixture of separately precipitated iron and aluminium hydroxides (Fig.6).

The γ-form of the oxyhydroxide, lepidocrocite, transforms during heating into the spinel γ-form of iron oxide by an oriented transformation [9]. The γ-Fe_2O_3 on further thermal treatment produces successively hydrohematite and hematite [10, 11]. The isomorphous incorporation of aluminium in the lattice of synthetic γ-FeOOH has been ascertained only recently [4]. The γ-$Fe_{1-x}Al_xOOH$ solid solution series was investigated by differential thermal analysis. Figure 7 shows the temperatures of the endothermic DTA effect accompanying the endothermic γ-(Fe, Al)OOH $\rightarrow \gamma$-(Fe, Al)$_2O_3$ transition and the exothermic γ-(Fe, Al)$_2O_3 \rightarrow$ α-(Fe, Al)$_2O_3$ phase transformation, plotted as a function of the aluminium con-
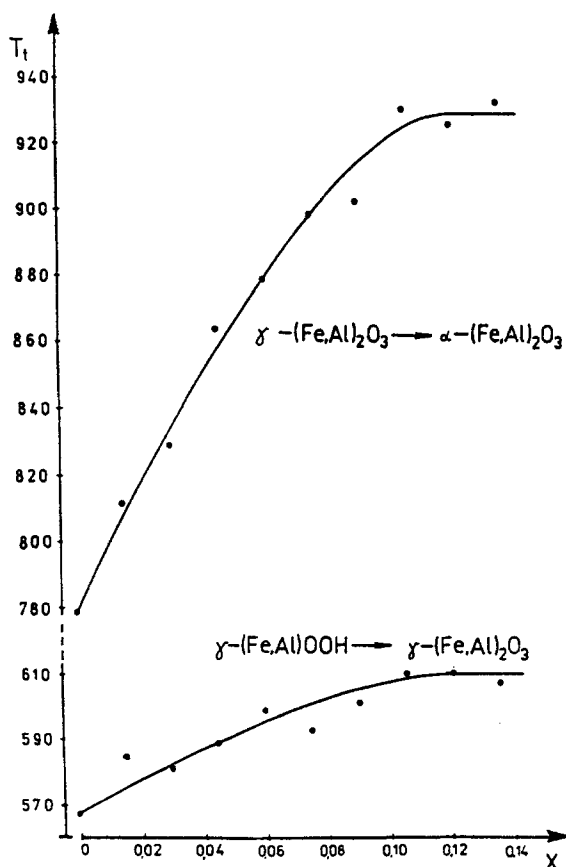

Fig. 7 Temperatures of DTA peaks from the endothermic lepidocrocite → maghemite transition and exothermic maghemite → hematite transformation, plotted against the aluminium content x in γ-$Fe_{1-x}Al_xOOH$

tent. The positions of DTA peaks of the respective effects are almost linearly dependent on the Al content, but a significant relaxation in the temperature increase may be observed for $x > 0.1$ in γ-Fe$_{1-x}$Al$_x$OOH, which suggests the aluminium substitution limit.

Experimental data gathered during the present investigations on the formation of solid solutions caused by the aluminium-iron substitution in the isostructural α- and γ-forms of oxyhydroxides show clearly that only limited ranges of Fe$_{1-x}$ Al$_x$OOH solutions may be synthesized. In both polymorphic structures the solubility limit has been established at about $x = 0.1$ and seems to be independent of the method of sample preparation.

References

1 D.G.Schulze, Clays Clay Miner., 32 (1984) 36.
2 J.M.de Villiers and T.H.van Rooyen, Clay Miner., 7 (1967) 229.
3 E.Wolska, Mater.Sci., Forum, 62–64 (1990) 621.
4 U.Schwertmann and E.Wolska, Clays Clay Miner.,38 (1990) 209.
5 E.Wolska and U.Schwertmann, Z.Kristallogr.,189 (1989) 223.
6 E.Wolska and W.Szajda, Solid State Ionic,28–30 (1988) 1320.
7 M.H.Francombe and H.P.Rooksby, Clay Miner.Bull.,4 (1959) 1.
8 G.Brown, Associated Minerals, Crystal Structures of Clay Minerals and their X-ray Identi-
  fication (Eds. G. W. Brindley, G. Brown), Mineralogical Sociery, London 1984,
  pp. 361–407.
9 J.D.Bernal, D.R.Dasgupta and A.L.Mackay,Narure,180 (1957) 645.
10 E.Wolska and J.Baszynski, Phys.Stat.Sol.(a), 95 (1986) 87.
11 E.Wolska and W.Szajda, J.Thermal Anal., 32 (1987) 797.

Zusammenfassung — Mittels Röntgendiffraktion und Thermoanalyse wurde die Bildung von Substitutions-Mischkristallen der isostrukturellen Oxyhydroxide α-FeOOH-α-AlOOH (Goethit-Diaspor) und γ-FeOOH -γ-AlOOH (Lepidokrokit-Böhmit) untersucht.
Die Elementarzellenparameter beider rhombischer Strukturen von α-Fe$_{1-x}$Al$_x$OOH (Pbnm) und γ-Fe$_{1-x}$Al$_x$OOH (Cmcm) werden mit zunehmenden Aluminiumgehalt bis zu $x=0.10$ eindeutig kleiner.
Thermoanalyse zeigt die Empfindlichkeit von DTA- und DTG- Effekten gegenüber der Zusammensetzung der Mischkristalle. Steigt die Aluminiumkonzentration bis 10 mol% an, so erhöhen sich auch die Temperaturen für die topotaktische Bildung von rhomboedrischem α-(Fe,Al)$_2$O$_3$ und des Defekt-Spinells γ-(Fe,Al)$_2$O$_3$ bei der Dehydroxylierung von α-(Fe,Al)OOH und γ-(Fe,Al)OOH. Die Dehydratationskurven von Proben mit einem größeren Aluminiumgehalt zeigen dasselbe $\Delta m / \Delta T$-Maximum wie für die Proben mit 10 mol%, was indirekt auf die Grenze des Mischkristallbereiches deutet.