Journal of Thermal Analysis, Vol. 32 (1987) 797–805

TEMPERATURE EFFECTS ON COPRECIPITATED Al, Fe-HYDROXIDES DURING HYDROTHERMAL TRANSFORMATIONS

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(Received May 21, 1986)

Studies of the hydrothermal behaviour of coprecipitated Al, Fe-hydroxides with aluminium contents from 5 to 50 mol% reveal that the temperature of the hydrothermal process strongly affects the reciprocal influence of Al(III) and Fe(III) ions on the direction of transformation of the initially amorphous gels.

It has been found by X-ray diffraction analysis and IR spectroscopic investigations that at 373 K, up to 10 mol% Al, well-crystallized Al-substituted hydrohematite is formed; at 15–25 mol% Al the crystallinity falls off and the products are amorphous; and at 27.5–50 mol% Al the poorly-crystallized hydrohematite appears, accompanied by different crystalline aluminium trihydroxides, the equilibria of which depend essentially on the Al : Fe ratio and on the pH of the medium.

The hydrothermal process carried out at 413 K yields the Al-substituted protohematite for samples with 15–50 mol% Al, whereas the unique crystalline phase of Al-hydroxide is a well-crystallized boehmite.

The coexistence of different crystalline or amorphous Al and Fe oxides and hydroxides is commonly encountered in nature, for example in soils and clays, as well as in bauxites and other sediments. Moreover, Al, Fe-oxide and hydroxide systems are of great interest with respect to such technological problems as ore mining, soil research, corrosion studies, and the preparation of catalysts and other materials [1, 2]. Although these compounds are mostly isostructural, for instance corundum-hematite, diaspore-goethite, boehmite.-lepidocrocite, γ-Al_2O_3-γ-Fe_2O_3, the isomorphous replacement of iron by aluminium is very limited. In spite of many investigations, the data on the concentration limits of solubility are very contradictory. The $(Al, Fe)_2O_3$ solid solutions with the hematite structure are relatively well known. The degree of aluminium substitution reported in the literature for the hematite lattice is 10–16 mol% Al [3–7], though the variation of the lattice parameters with the aluminium content is observable up to 20 mol% Al [6]. The effect of Al-substitution on the crystallinity, the magnetic Morin transition

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in hematite and the inhibition of goethite formation have been the subjects of many investigations [6–10].

Increase of the aluminium concentration ($Al:Fe > 0.2$) yields not only alumohydrohematite, but also amorphous or crystalline aluminium hydroxides [6, 7]. The formation of these phases, and their coexistence depending on the hydrothermal conditions, is a result of the specific interaction of Fe^{3+} ions present in the system. The kinds and quantities of the Al-hydroxide phases produced are strongly dependent on the temperature and the hydrogen ion concentration of the medium.

Detailed investigations on the coexistence of crystalline phases of aluminium hydroxides, and on the effects of small deviations in stoichiometry on the direction of aging of the coprecipitated $Al_{0.5}Fe_{0.5}(OH)_3$ system have been described earlier [11–13]. The present study was initiated to determine the effect of the temperature of hydrothermal treatment on the equilibria between crystalline phases of aluminium and iron hydroxides and oxides in coprecipitated Al,Fe-hydroxides, with the Al : Fe molar ratio changing from 0.05 to 0.5.

Experimental

Samples of Al, Fe-hydroxides were obtained by adding 1 M sodium hydroxide solution to 1 M Fe^{3+} and Al^{3+} nitrate solutions mixed in proportions of from 0.95 : 0.05 to 0.5 : 0.5, until a pH of 9.5 to 10.5 was reached in the mother liquor. The suspensions were then put in palladium vessels and kept in an autoclave at 373 ± 0.5 K or 413 ± 0.5 K for 8 h. The products were washed with distilled water to remove nitrates, and dried at room temperature for 72 h. The use of palladium containers allowed avoidance of the effect of silica from laboratory glass.

Crystalline phase analysis and reflection intensity measurements were performed with a TUR–61 X-ray diffractometer, employing CoK_α radiation, with an HZG–3 proportional counter spectrometer.

The infrared spectra of the samples were recorded in the range 200–4000 cm^{-1}, from CsBr discs, using a Perkin–Elmer 580 spectrophotometer.

Results and discussion

The results of our experiments are presented in the form of X-ray powder patterns and infrared absorption spectra of samples obtained by hydrothermal treatment of originally amorphous Al,Fe-hydroxides. These complementary identification methods allow clear establishment of the coexisting crystalline phases.

Figures 1 and 2 show the diffractograms of preparations with 5–20 mol% of aluminium, obtained at 373 K and 413 K, respectively. The unique crystalline phase occurring there reveals the hematite structure. Although at 373 K the increase of Al leads to a progressive fall in crystallinity, resulting in an amorphous phase for 15–20 mol% Al (Fig. 1), the hydrothermal process carried out at 413 K, even at higher Al content, gives rise to a crystalline product with the hematite structure (Fig. 2). The character of this hematite phase may be established by comparison of the relative intensities, as well as on the basis of the nonuniform broadening of the X-ray reflections [14], but primarily on the basis of the infrared spectra (Fig. 3). The positions of the IR absorption bands observed here result from both Al- and OH-substitution in the hematite lattice. Aluminium substitution causes a shift to higher absorption values in comparison with pure hematite [15, 16], whereas an increasing hydroxyl group content in the hematite anion sublattice displaces the absorption bands towards lower frequencies [17]. From the infrared spectra presented in Fig. 3 we can draw the conclusion that the increase of temperature from 373 K to 413 K leads to the formation of a crystalline species with protohematite features [18] instead of an amorphous phase. Although the limit

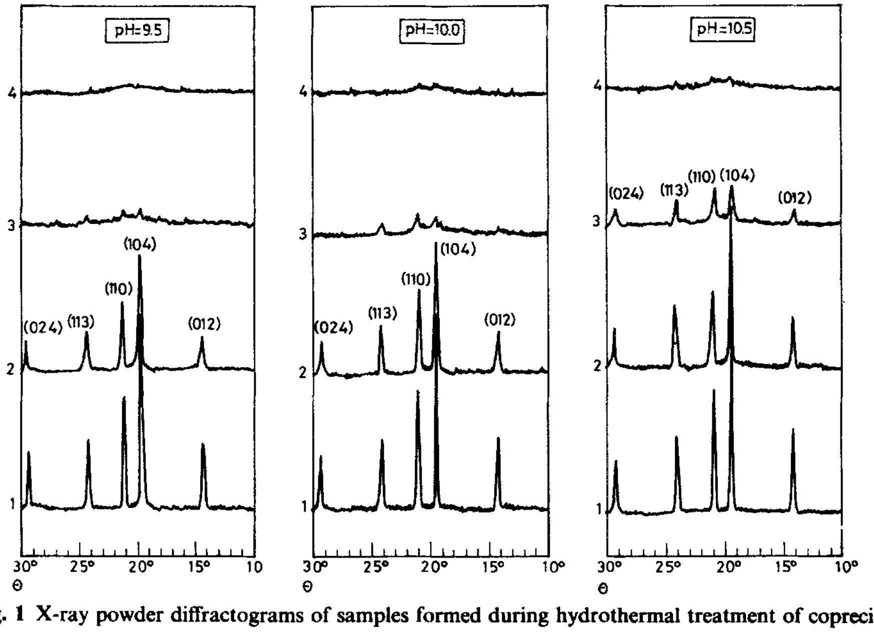

Fig. 1 X-ray powder diffractograms of samples formed during hydrothermal treatment of coprecipitated Al, Fe-hydroxides with 5 (1), 10 (2), 15 (3) and 20 mol% Al (4) at 373 K

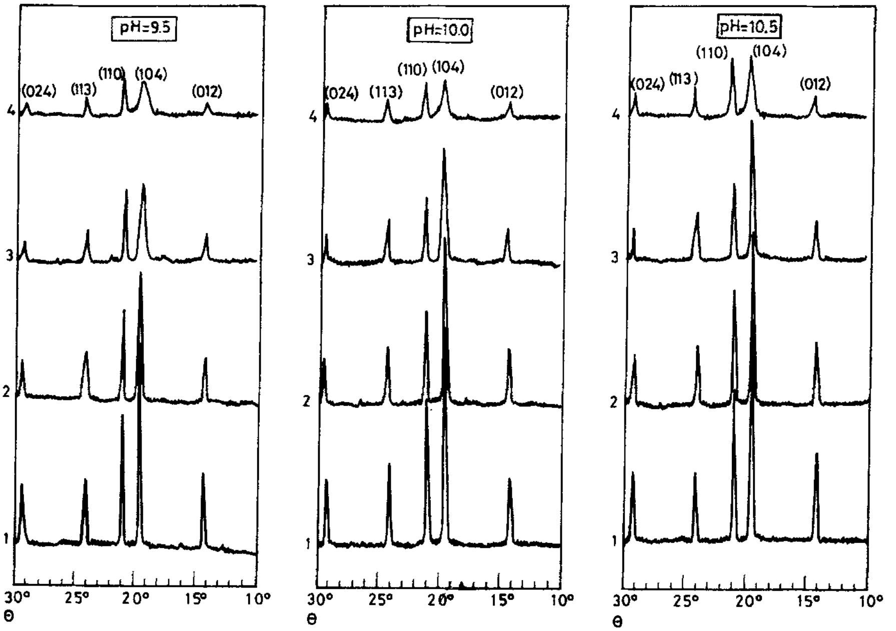

Fig. 2 X-ray powder diffractograms of samples with 5–20 mol% Al obtained at 413 K (notations as in Fig. 1)

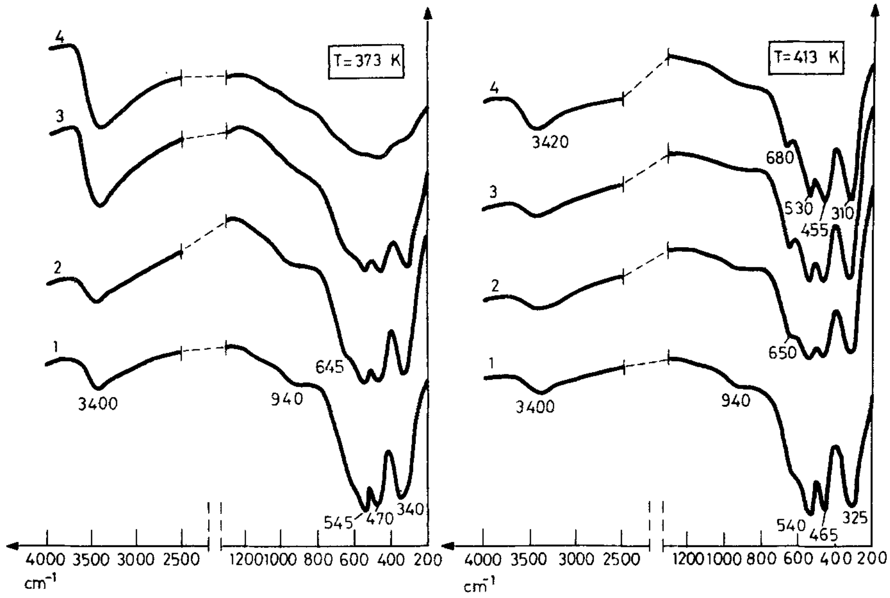

Fig. 3 Infrared spectra of samples with aluminium content 5–20 mol% after hydrothermal treatment (pH 10.5) at different temperatures (notations as in Fig. 1)

of aluminium substitution in the hematite lattice is well overrun, no separate aluminium hydroxide phase could be detected by X-ray analysis.

The effect of the temperature of the hydrothermal process on the amorphous Al, Fe-hydroxides with 20–30 mol% Al is shown in Fig. 4. After heating at 373 K, the samples containing > 15 mol% Al of aluminium are completely amorphous. Only from 27.5 mol% Al on the X-ray patterns of the preparations obtained at pH 10 and 10.5 exhibit weak reflections of the hematite phase and of an aluminium trihydroxide. At 413 K, the crystalline protohematite is still present in samples with 20–30 mol% Al. The unique crystalline phase of aluminium hydroxide is a well-crystallized boehmite, which occurs from 22.5 mol% Al on at pH 9.5 and 10.

Since the infrared spectra (Fig. 5) of the hematite phase formed at 413 K do not change with increase in Al (no displacement of the absorption band position occurs), we presume that the degree of aluminium substitution and the content of structural OH groups in the hematite lattice remain approximately constant. The infrared spectra in Fig. 5 further allow identification of the aluminium hydroxide formed at 373 K as gibbsite [19], and that at 413 K as crystalline boehmite [12].

Figures 6 and 7, containing X-ray patterns and IR spectra of samples obtained during the hydrothermal treatment of hydroxides with the compositions

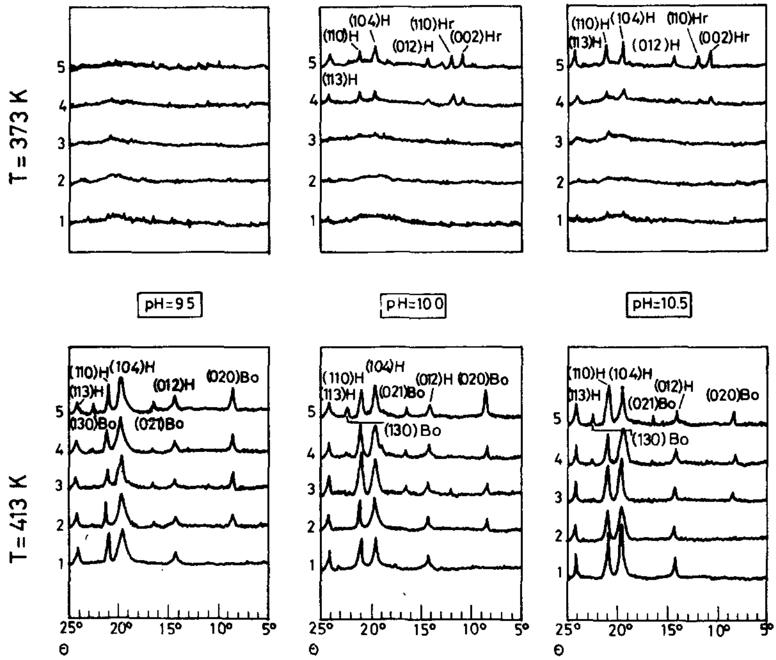

Fig. 4 X-ray powder diffractograms of samples containing 20 (1), 22.5 (2), 25 (3), 27.5 (4) and 30 mol% Al (5) after hydrothermal treatment at 373 K and 413 K. Hr-gibbsite, Bo-boehmite, H-hematite

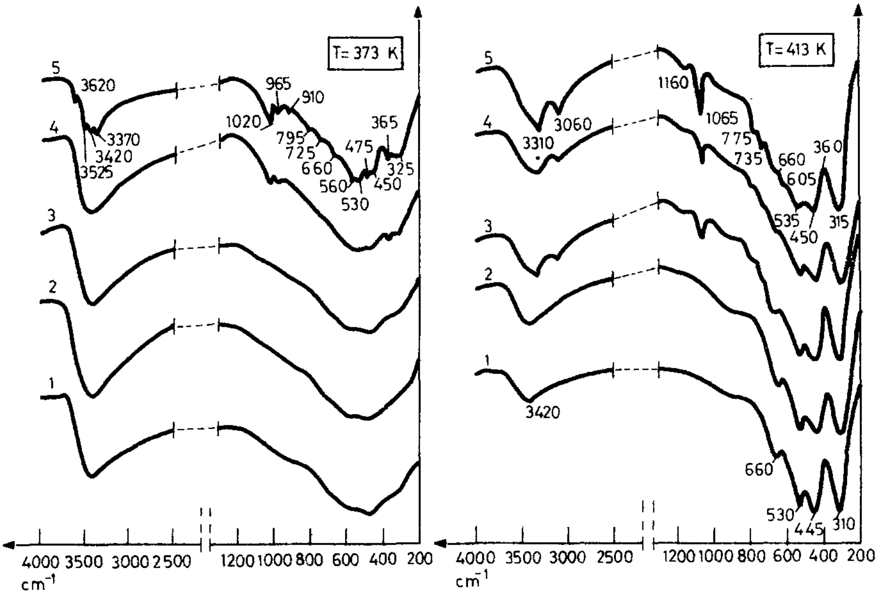

Fig. 5 Infrared spectra of samples with aluminium content 20–30 mol% obtained at pH 10.5 (notations as in Fig. 4)

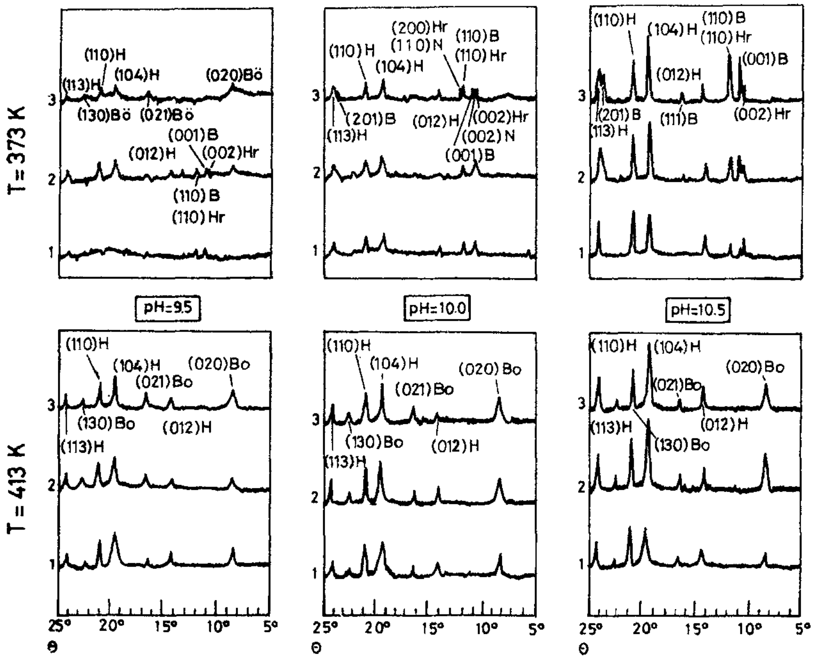

Fig. 6 X-ray diffractograms of samples obtained by hydrothermal treatment at 373 K and 413 K, containing 30 mol% (1), 40 mol% (2) and 50 mol% (3) of aluminium. B-bayerite, N-nordstrandite

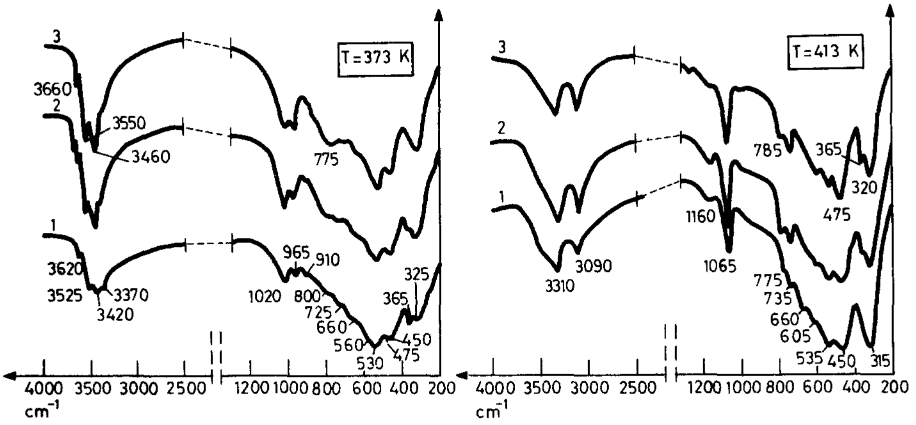

Fig. 7 Infrared spectra of samples presented on Fig. 6, obtained at pH 10.5

$Al_{0.3}Fe_{0.7}(OH)_3$ (1), $Al_{0.4}Fe_{0.6}(OH)_3$ (2) and $Al_{0.5}Fe_{0.5}(OH)_3$ (3), reveal the differences in coexistence of the crystalline phases of aluminium and iron oxides caused by changes of the Al : Fe ratio in the preparations and by the temperature of the hydrothermal process. At 373 K, the products of the hydrothermal transformation are the trihydroxides of aluminium ($Al(OH)_3$) and pseudoboehmite (AlOOH). The differentiation of the $Al(OH)_3$ phases was based on the positions and intensities of the OH vibration bands in the IR absorption spectra, as the X-ray reflections from all three crystalline aluminium trihydroxides (gibbsite, bayerite and nordstrandite) partially overlap [19]. It may be seen from Fig. 6 (373 K) that the equilibria between these phases are strongly dependent on both the pH of the hydrothermal process and the Al : Fe ratio in the preparations. The infrared spectra of the samples obtained at pH 10.5 (Fig. 7; 373 K) reveal the decrease of the gibbsite content and the increase of bayerite with increasing Al : Fe ratio. When the temperature is raised to 413 K, the direction of the aluminium hydroxide transformation changes and only well-crystallized boehmite is formed.

However, it is to be stressed that the data presented here, indicating the very strong effects of the temperature and the pH of the hydrothermal process on the coexistence of crystalline aluminium and iron oxides and hydroxides, relate exclusively to the coprecipitated gels of Al, Fe-hydroxides. The behaviour of separately precipitated hydroxides exposed to hydrothermal treatment is different: amorphous aluminium hydroxide is transformed to pseudoboehmite [12], whereas amorphous iron hydroxide undergoes conversion to a mixture of hydrohematite and goethite [20, 21]. During the hydrothermal treatment of amorphous $Al(OH)_3$ and $Fe(OH)_3$ gels mixed after separate precipitation, it is observed that Al^{3+} ions do influence the course of the iron hydroxide transformation and prevent goethite formation, but the aluminium hydroxide is transformed into pseudoboehmite, as if it were pure $Al(OH)_3$ [11].

We can summarize the results of this investigation by stating that:

1. The reciprocal effects of Al^{3+} ions on the phase transitions of iron hydroxide, and of Fe^{3+} ions on the equilibria between the different crystalline aluminium hydroxides, are particularly pronounced in the coprecipitated gels, where very small deviations in the Al : Fe ratio bring about substantial changes in the phase composition of the aluminium hydroxides.

2. An increase in the temperature of the hydrothermal transformation enhances the effect of Al^{3+} ions on the "hydroxylation" of the hematite phase. Instead of an amorphous phase at 15–30 mol% Al content, a crystalline "hydrated" iron oxide with the hematite structure and protohematite features, i.e. with a degree of hydroxylation corresponding to $0.5 > x > 1$ in $(Al, Fe)_{2-x/3}(OH)_xO_{3-x}$, is formed [14]. The decrease of the unit cell dimensions of hematite with more than 10 mol% Al is presumably caused by the increasing cation deficiency in the hematite lattice.

3. As regards the formation of crystalline aluminium hydroxides, the influence of the temperature of the hydrothermal process is still more distinct: at 373 K, changes of the pH and the Al : Fe ratio cause differences in the phase equilibria of the aluminium trihydroxides, whereas at 413 K the unique phase formed is the well-crystallized boehmite.

An important consequence of this behaviour may be the very differentiated phase compositions observed for bauxites, laterites and other sedimentary minerals with different Al : Fe ratios.

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Zusammenfassung — Untersuchungen des hydrothermalen Verhaltens von kopräzipierten Al, Fe-Hydroxiden mit Aluminiumgehalten von 5–50 mol% haben ergeben, daß die Temperatur des hydrothermalen Prozesses den gegenteiligen Effekt von Al(III)- und Fe(III)-Ionen auf die Richtung der Umwandlung der anfänglich amorphen Gele wesentlich beeinflußt. Durch Röntgendiffraktion und IR-Spektroskopie wurde ermittelt, daß bei 373 K bis zu 10 mol% Al gut kristallisierter, Al-substitutierter Hydrohämatit gebildet wird. Bei 15–25 mol% Al sind die Produkte amorph und bei 27,5–50 mol% Al liegt schlecht kristallisierter Hydrohämetit vor, begleitet von verschiedenen kristallinen Aluminiumtrihydroxiden, deren Gleichgewicht im wesentlichen vom Al/Fe-Verhältnis und vom pH des Mediums abhängt. Der bei 413 K ausgeführte hydrothermale Prozeß ergibt Al-substituiertes Protohämatit für Proben mit 15–50 mol% Al, während ein gut kristallisierter Boehmit die einzige kristalline Al-Hydroxidphase ist.

Резюме — Исследование гидротермического поведения соосажденных гидроокисей алюминия и железа при содержании алюминия от 5 до 50 мольных процента показало, что температура гидротермического превращения исходных аморфных гелей в значительной мере затрагивается взаимным влиянием ионов железа и алюминия. На основе ИК спектроскопии и рентгенофазового анализа найдено, что при 373 К и при содержании алюминия до 10 мольных процента, образуется хорошо кристаллизующийся алюмозамещенный оксигематит. При содержании алюминия от 15 до 25 мольных процента, кристалличность уменьшается и продукты образуются аморфными, тогда как при 27,5–50 мольных процентах алюминия — образуется слабокристалличный оксигематит. Этот процесс сопровождается образованием различных кристаллических гидроокисей алюминия, равновесие которых зависит, в основном, от соотношения Al:Fe и pH среды. Гидротермический процесс, проведенный при 413 К с образцами содержащими 15–50 мольных процентов алюминия, дает алюмозамещенный протогематит, тогда как единственная кристаллическая фаза гидроокиси алюминия является кристаллическим боэмитом.