

The influence of a Cr-dopant on the properties of α -FeOOH particles precipitated in highly alkaline media

Stjepko Krehula*, Svetozar Musić

Division of Materials Chemistry, Ruđer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia

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Abstract

The effects of a Cr-dopant on the precipitation of acicular α -FeOOH particles, the formation of solid solutions, particle size and shape were investigated using X-ray powder diffraction (XRD), Mössbauer and Fourier transform infrared (FT-IR) spectroscopies and field emission scanning electron microscopy (FE-SEM). Acicular and monodisperse α -FeOOH particles were precipitated at a very high pH by heating the suspension obtained by adding a tetramethylammonium hydroxide solution to an aqueous solution of FeCl_3 . The influence of the Cr-dopant was investigated by addition of various amounts of Cr^{3+} ions to the initial FeCl_3 solution, where $r = 100[\text{Cr}]/([\text{Cr}] + [\text{Fe}])$ stands for the added amount of Cr. XRD analysis of the obtained powders (with r values from 0 to 23.08) showed only the presence of the diffraction lines characteristic for α -FeOOH. Mössbauer spectroscopy showed a decrease in hyperfine magnetic field of α -FeOOH with an increase in Cr addition which indicates Cr incorporation into the α -FeOOH structure. The OH bending bands in the FT-IR spectra showed only a slight change in position with an increase in r , but the considerable increase in the lattice band wave number indicated a decrease in thickness of the lath-like α -FeOOH particles. This conclusion was confirmed by FE-SEM observations.

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1. Introduction

The incorporation of chromium into the crystal structure of minerals and other compounds can be important for practical application as well as from academic standpoint. The red colour of ruby is due to the presence of the trivalent Cr ions substitutionally incorporated into the structure of the mineral corundum (Al_2O_3). Cr is also a necessary constituent of stainless steel. It improves resistance to atmospheric corrosion as well as strength, hardenability and abrasion resistance.

Due to their similar ionic radii ($r(\text{Fe}^{3+}) = 0.645 \text{ \AA}$, $r(\text{Cr}^{3+}) = 0.61 \text{ \AA}$) and the same charge, Cr for iron substitution in the crystal structure of iron oxyhydroxides and oxides seems expectable. Indeed, the incorporation of Cr into α -FeOOH [1–7], γ -FeOOH [5], α - Fe_2O_3 [8–10] and Fe_3O_4 [11,12] has been observed.

Schwertmann et al. [1] synthesized goethites containing up to 10 mol% Cr by aging mixed $\text{Fe}(\text{NO}_3)_3$ – $\text{Cr}(\text{NO}_3)_3$ or FeCl_2 – CrCl_3 solutions in an alkaline medium. The incorporation of Cr into the α -FeOOH structure reduced unit-cell edge lengths as well as particle length and thickness, and strongly stabilized goethite against dissolution. Sudakar et al. [2] observed a linear decrease of unit-cell parameters and particle lengths in Cr-substituted α -FeOOH. Sileo et al. [3] prepared series of Cr-substituted goethites with $[\text{Cr}]/[\text{Fe}]$ molar ratios up to 0.12 by aging at 70 °C mixtures of $\text{Fe}(\text{NO}_3)_3$ and $\text{Cr}(\text{NO}_3)_3$ in 0.3 M KOH. They observed a decrease in the unit-cell volume as well as in the particle length and improvement in stability towards thermal transformation to hematite as the Cr content increases. On the basis of Rietveld refinement and EXAFS data they concluded that polyhedron around Cr incorporated into the α -FeOOH structure can be described as $\text{Cr}(\text{OH}_{0.5})_6$ in contrast to the Fe-polyhedron, $\text{FeO}_3(\text{OH})_3$. Cr inclusions in goethite are important for the formation of a nanophase oxide layer which may help to protect the weathering steel from further corrosion [13].

* Corresponding author. Tel.: +385 1 4561094; fax: +385 1 4680098.
E-mail address: krehul@irb.hr (S. Krehula).

Balasubramanian et al. [4] investigated by X-ray diffraction and Mössbauer spectroscopy the magnetic and crystalline properties of Cr-substituted α -FeOOH produced from a solution of $\text{Fe}(\text{NO}_3)_3$ and $\text{Cr}(\text{NO}_3)_3$, (with $\text{Cr}/(\text{Cr} + \text{Fe})$ up to 0.25 M), stored in 0.3 M KOH at 70 °C. The mean crystallite size, as measured by X-ray diffraction, decreased with increasing Cr concentration. Mössbauer spectroscopy showed that the value of the mean hyperfine field at 77 K decreased from 49.6 T for pure goethite to 44.9 T for 10.14 wt.% Cr-substituted goethite. This decrease was attributed to both decreasing particle size and increasing Cr incorporation. For Cr concentrations greater than 3.00 wt.%, room temperature Mössbauer spectra showed a collapse in the magnetic field to a broadened asymmetric doublet. In a similar way as in α -FeOOH, the incorporation of Cr at the octahedral (B) sites of Fe_3O_4 led to a decrease in the hyperfine field of iron at octahedral (B) as well as tetrahedral (A) sites [11].

In view of the results of earlier investigations into Cr-substituted goethites, we have carried out a new investigation by X-ray powder diffraction (XRD), Mössbauer and Fourier transform infrared (FT-IR) spectroscopies and field emission scanning electron microscopy (FE-SEM) to obtain additional data about the properties of α -FeOOH formed in the presence of Cr ions. Data obtained in the previous investigations are somewhat scanty, especially those obtained by Mössbauer, FT-IR and SEM. The objective of the present study was to systematically investigate the influence of varying amounts of Cr ions on the properties of goethite particles formed in highly alkaline media. Acicular and monodisperse goethite particles prepared in our previous work [14] were used as a reference material.

2. Experimental

2.1. Preparation of samples

Chemicals of analytical purity, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, supplied by Kemika, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, supplied by Aldrich, were used. A tetramethylammonium hydroxide (TMAH) solution (25% w/w, electronic grade 99.9999%) supplied by Alfa Aesar® was used. Twice-distilled water prepared in our own laboratory was used in all experiments. Predetermined volumes of FeCl_3 and $\text{Cr}(\text{NO}_3)_3$ solutions and twice-distilled water were mixed, then TMAH was added as a precipitating agent. The exact experimental conditions for the preparation of samples are given in Table 1, where $r = 100[\text{Cr}]/([\text{Cr}] + [\text{Fe}])$ represents the degree of Cr addition. Thus formed suspensions were vigorously shaken for ~10 min, then heated at 160 °C, using the Parr general-purpose bomb (model

4744), comprising a Teflon vessel and cup. After 2 h of heating the precipitates were cooled to RT (mother liquor pH ~ 13.5) and subsequently washed with twice-distilled water using the ultraspeed Sorvall RC2-B centrifuge. Upon drying, all precipitates were characterised by X-ray powder diffraction (XRD), Mössbauer and FT-IR spectroscopies, as well as high-resolution scanning electron microscopy (FE-SEM).

2.2. Instrumentation

X-ray powder diffractometer APD 2000 (Cu $K\alpha$ radiation, graphite monochromator, NaI-Tl detector) manufactured by ItalStructures (Riva Del Garda, Italy) was used. ^{57}Fe Mössbauer spectra were recorded in the transmission mode using a standard WissEl (Starnberg, Germany) instrumental configuration. A $^{57}\text{Co}/\text{Rh}$ Mössbauer source was used. The velocity scale and all the data refer to the metallic α -Fe absorber at RT. A quantitative analysis of the recorded spectra was made using the MossWinn program.

Fourier transform infrared (FT-IR) spectra were recorded at RT using a PerkinElmer spectrometer (model 2000). The FT-IR spectrometer was linked to a PC with an installed IRDM (IR data manager) program to process the recorded spectra. The specimens were pressed into small discs using a spectroscopically pure KBr matrix.

A thermal field emission scanning electron microscope (FE-SEM, model JSM-7000F, manufactured by JEOL Ltd.) was used. The specimens were not coated with electrically conductive surface layer.

3. Results

3.1. X-ray powder diffraction

The X-ray powder diffraction analysis revealed only the presence of the diffraction lines corresponding to α -FeOOH phase (PDF card 29-0713) in all prepared samples. The corresponding Miller indices were marked above the diffraction lines. The diffraction patterns of four characteristic samples were shown in Fig. 1. In addition to the diffraction lines characteristic of α -FeOOH, the diffraction pattern of sample CrG11 contained a clearly visible broad line at about $2\theta \approx 36^\circ$ ($d \approx 2.5 \text{ \AA}$), corresponding to ferrihydrite [15,16].

3.2. ^{57}Fe Mössbauer spectroscopy

^{57}Fe Mössbauer spectra of characteristic samples are shown in Fig. 2. The corresponding Mössbauer parameters obtained by the fitting procedure and the identification of phases are given in Table 2. The Mössbauer spectrum of reference sam-

Table 1

Concentration conditions of the reaction mixtures (40 ml) for the preparation of the samples by autoclaving at 160 °C for 2 h

Sample	$[\text{FeCl}_3]$ (mol dm ⁻³)	$[\text{Cr}(\text{NO}_3)_3]$ (mol dm ⁻³)	$r = 100[\text{Cr}]/([\text{Cr}] + [\text{Fe}])$	Volume 25% w/w TMAH (ml)
G	0.1	0	0	10
CrG1	0.1	0.001	0.99	10
CrG2	0.1	0.002	1.96	10
CrG3	0.1	0.003	2.91	10
CrG4	0.1	0.004	3.85	10
CrG5	0.1	0.005	4.76	10
CrG6	0.1	0.006	5.66	10
CrG7	0.1	0.0075	6.98	10
CrG8	0.1	0.0100	9.09	10
CrG9	0.1	0.0150	13.04	10
CrG10	0.1	0.0200	16.66	10
CrG11	0.1	0.0300	23.08	10

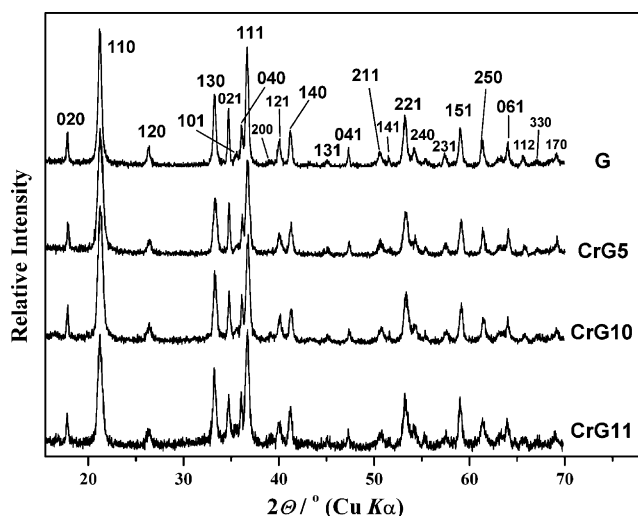


Fig. 1. XRD patterns of samples G, CrG5, CrG10 and CrG11, recorded at RT.

ple G, as well as the spectra of samples synthesized in the presence of a lower Cr concentration (up to $r=9.09$, sample CrG8), showed just the sextet characteristic of α -FeOOH. The α -FeOOH component was fitted taking into account the hyperfine magnetic field (HMF) distribution. HMF distributions in these samples were gradually broadened and their maxima were shifted toward lower HMF values with an increasing Cr concentration in the precipitation systems (Fig. 3). The average values of the hyperfine magnetic field ($\langle B_{\text{hf}} \rangle$) were also gradually decreased (Table 2). Fig. 4 shows a dependence of the average hyperfine magnetic field in the synthesized samples on the $100[\text{Cr}]/([\text{Cr}] + [\text{Fe}])$ ratio (r). For lower Cr concentrations the value of the average hyperfine field decreases steeply up to $r \approx 3$, then decreases slowly. At $r = 13.04$ and 16.66 the $\langle B_{\text{hf}} \rangle$ value remained constant, then increased slightly for sample synthesized at $r = 23.08$.

In addition to the typical α -FeOOH sextet, the Mössbauer spectra of samples synthesized at $r \geq 13.04$ showed an additional

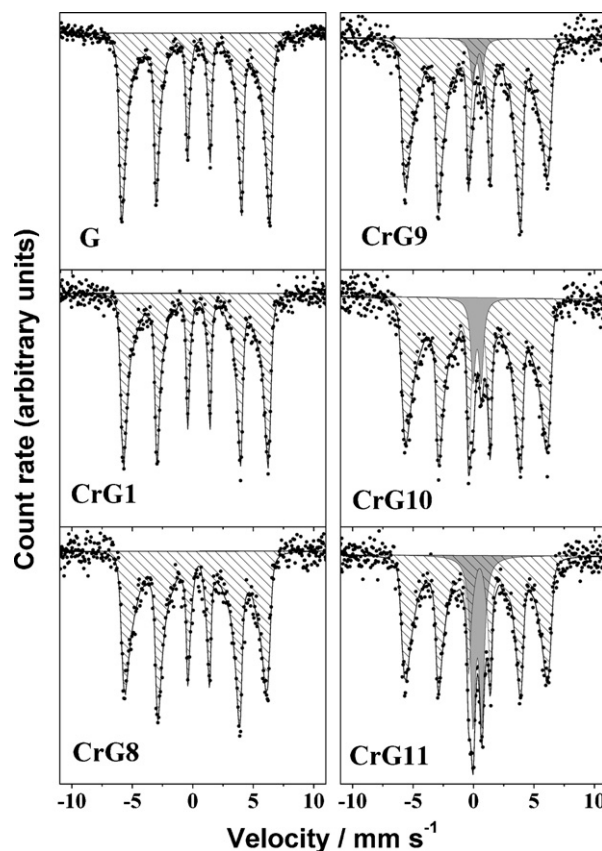


Fig. 2. ^{57}Fe Mössbauer spectra of samples G, CrG1 and CrG8 to CrG11, recorded at RT.

quadrupole doublet of area increasing with the increase in Cr concentration (Fig. 2, Table 2). Since the XRD patterns did not show any additional diffraction lines besides those of α -FeOOH (Fig. 1) and the broad line in the diffraction pattern of sample CrG11 which can be assigned to ferrihydrite, it can be concluded that this doublet corresponds to a low-crystalline Cr-ferrihydrite or mixed Fe–Cr hydroxide.

Table 2
 ^{57}Fe Mössbauer parameters calculated for samples G and CrG1 to CrG11 and identification

Sample	Spectral line	δ (mm s $^{-1}$)	2ϵ (mm s $^{-1}$)	$\langle B_{\text{hf}} \rangle$ (T)	Γ (mm s $^{-1}$)	Area (%)	Identification
G	M	0.37	−0.26	34.9	0.28	100	α -FeOOH
CrG1	M	0.38	−0.25	33.8	0.23	100	α -(Fe,Cr)OOH
CrG2	M	0.38	−0.26	33.0	0.26	100	α -(Fe,Cr)OOH
CrG3	M	0.38	−0.26	32.5	0.25	100	α -(Fe,Cr)OOH
CrG4	M	0.37	−0.25	32.4	0.23	100	α -(Fe,Cr)OOH
CrG5	M	0.37	−0.27	32.6	0.25	100	α -(Fe,Cr)OOH
CrG6	M	0.38	−0.24	32.2	0.27	100	α -(Fe,Cr)OOH
CrG7	M	0.37	−0.26	31.9	0.24	100	α -(Fe,Cr)OOH
CrG8	M	0.37	−0.25	31.4	0.25	100	α -(Fe,Cr)OOH
CrG9	M	0.36	−0.24	31.2	0.23	94.3	α -(Fe,Cr)OOH
	Q	0.29	0.70		0.43	5.7	Cr-ferrihydrite
CrG10	M	0.36	−0.27	31.2	0.26	90.2	α -(Fe,Cr)OOH
	Q	0.30	0.67		0.47	9.8	Cr-ferrihydrite
CrG11	M	0.37	−0.26	32.0	0.27	76.6	α -(Fe,Cr)OOH
	Q	0.32	0.72		0.50	23.4	Cr-ferrihydrite

Errors: $\delta = \pm 0.01$ mm s $^{-1}$, $2\epsilon = \pm 0.01$ mm s $^{-1}$, $B_{\text{hf}} = \pm 0.2$ T, isomer shift is given relative to α -Fe.

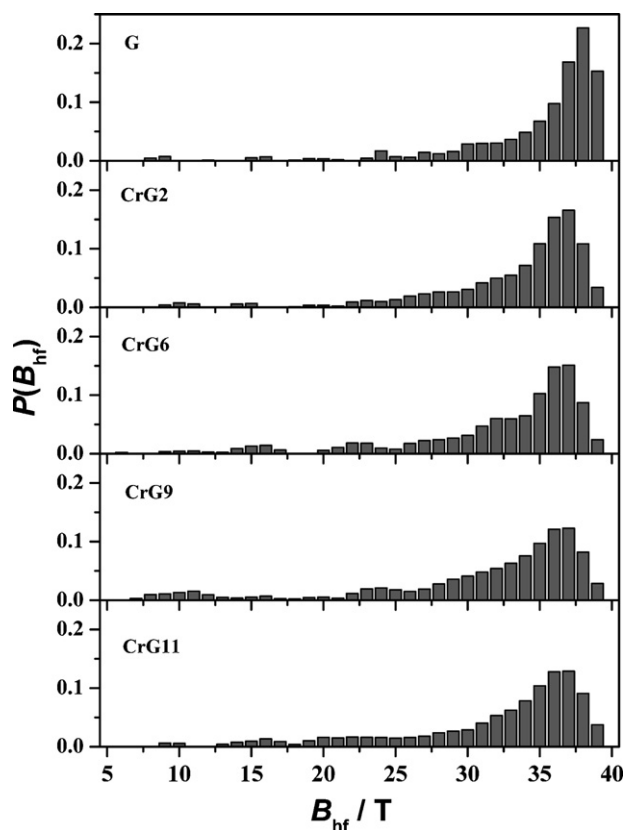


Fig. 3. Hyperfine magnetic field distributions in goethite calculated for chosen samples.

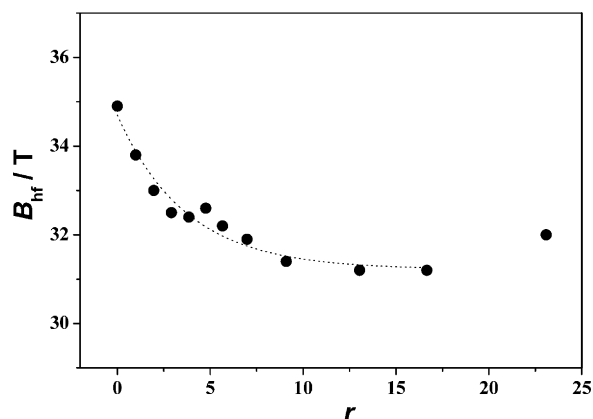


Fig. 4. Dependence of the average hyperfine magnetic field in goethite on the Cr content in the initial solutions.

3.3. FT-IR spectroscopy

Characteristic parts of the FT-IR spectra of prepared samples are shown in Fig. 5. The FT-IR spectrum of reference sample G corresponds to a pure α -FeOOH [17–19]. The IR bands at 3421 and 3157 cm^{-1} corresponds to the stretching vibrations of adsorbed H_2O molecules and structural OH groups, respectively. Intensive bands at 892 and 797 cm^{-1} are assigned to Fe–O–H bending vibrations, while the bands at lower wave numbers correspond to Fe–O and Fe–OH stretching vibrations or lattice vibration bands [17,18]. The position of the IR absorption band corresponding to the O–H stretching vibration of structural OH groups showed a tendency of gradual shift toward lower wave numbers with an increasing concentration of Cr

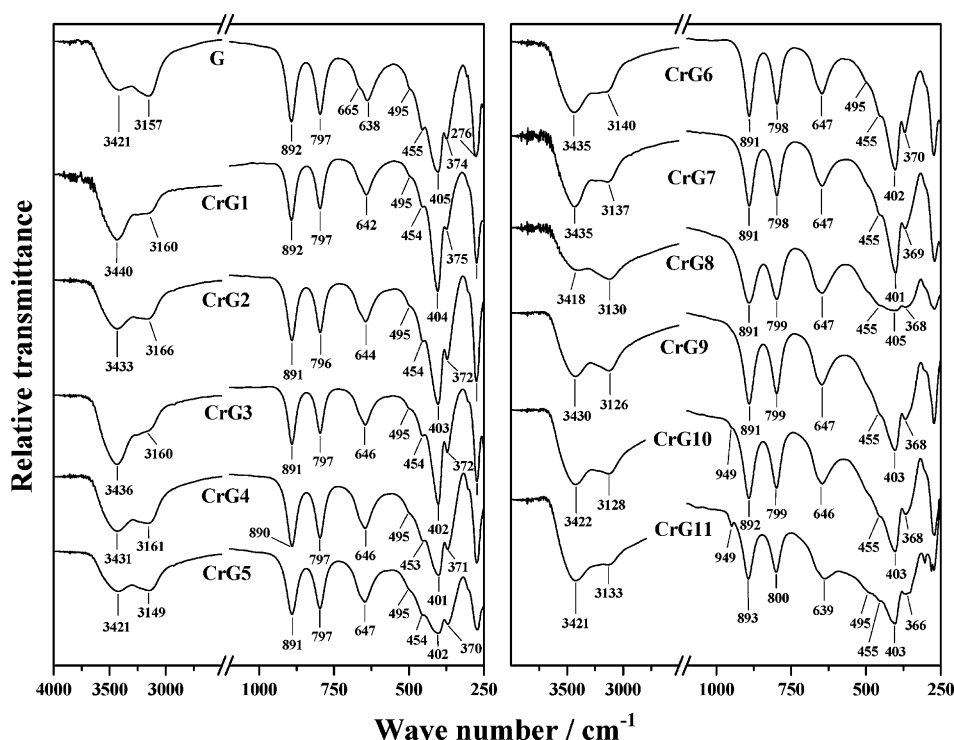


Fig. 5. FT-IR spectra of samples G and CrG1 to CrG11, recorded at RT.

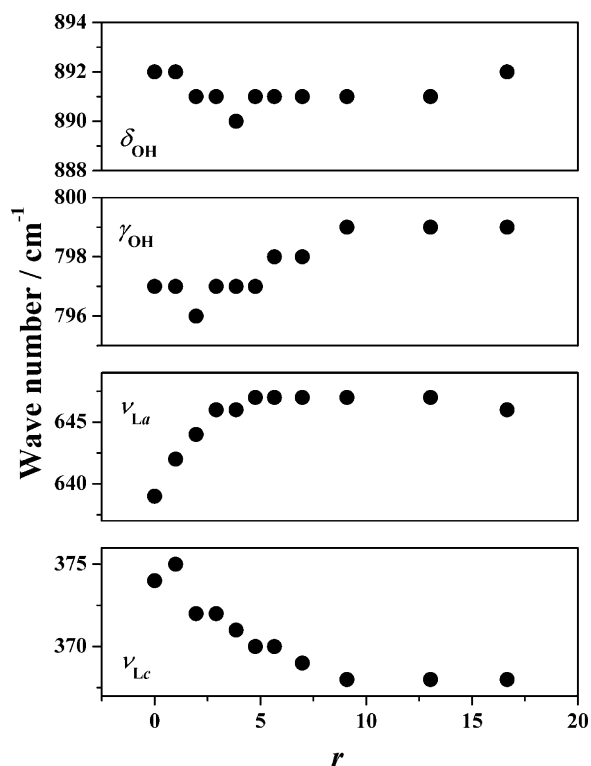


Fig. 6. Dependence of the position of IR bands on the Cr content in the initial solutions.

ions in the precipitation system. In reference literature the shift of this band toward lower wave numbers was explained mainly by an increase in strength of the OH ··· O hydrogen bond [20].

The presence of Cr ions (at high pH values in the form of Cr(OH)₄⁻) in the precipitation system induced only slight changes in the position of Fe–O–H bending bands. In the FT-IR spectra of all samples the in-plane bending band (δ_{OH}) was in the range of 891 to 893 cm⁻¹ and the out-of-plane bending band (γ_{OH}) was in the range of 796 to 800 cm⁻¹ (Fig. 6). These observations are consistent with data obtained by Schwertmann et al. [1] who explained shifts in the position of Fe–O–H bending bands by the shortening of M–OH as a consequence of Cr incorporation.

However, the lattice band at 638 cm⁻¹ (ν_{La}) in the spectrum of reference sample shifted gradually to 647 cm⁻¹ (Fig. 6) in the spectra of samples obtained in the presence of higher amounts of Cr ions (*r* ≥ 4.76). This band has a transition moment parallel to the *a*-axis and its position is affected by the particle shape [18].

The lattice band corresponds to the vibration parallel to the *c*-axis (ν_{Lc}) shifted slightly from 405 cm⁻¹ in the spectrum of reference sample to 401 or 402 cm⁻¹ in the spectra of samples obtained at *r* values between 2.91 and 6.98. Also, the lattice band at 374 cm⁻¹ (reference sample) shifted gradually to 366 cm⁻¹ (sample with *r* = 23.08).

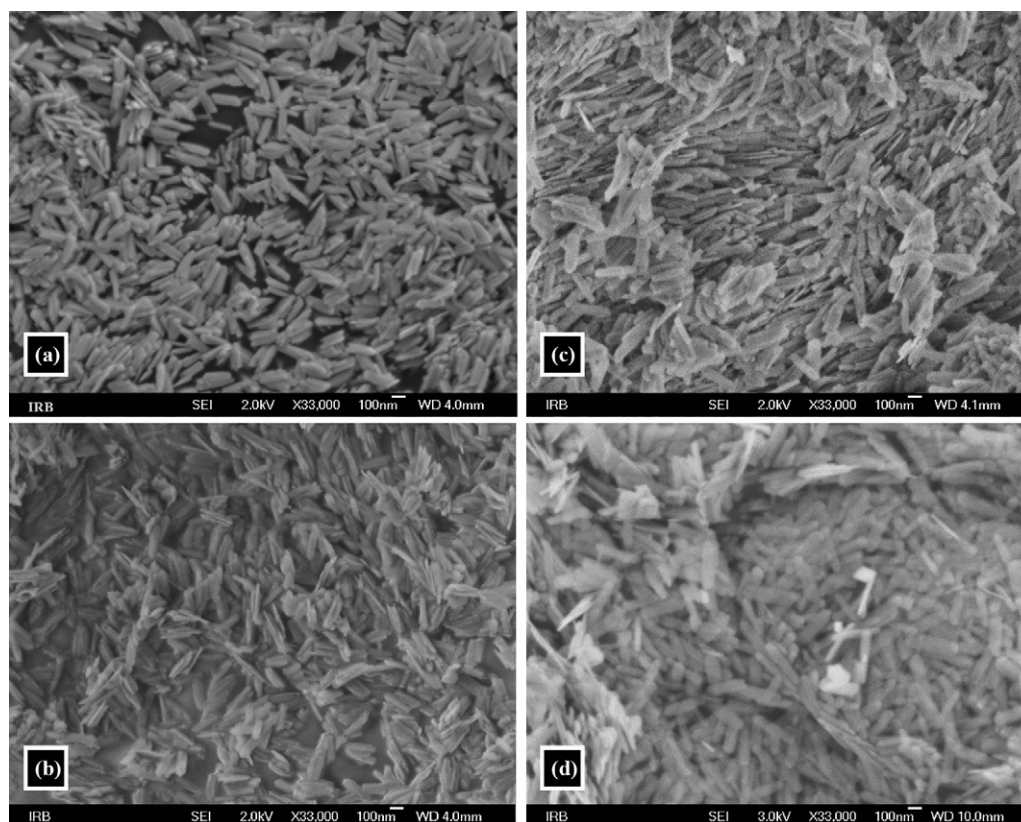


Fig. 7. FE-SEM micrographs of samples: (a) G, (b) CrG2, (c) CrG7, (d) CrG11.

The band at 949 cm^{-1} in the spectra of samples CrG10 and CrG11 corresponds to tetramethylammonium cation adsorbed on the surface of solid phases.

3.4. FE-SEM

All samples were characterized by FE-SEM and selected images are shown in Fig. 7. Reference sample G, mainly consisting of lath-like α -FeOOH particles of 150–200 nm in length (c -axis direction), 40–60 nm in width (b -axis direction) and 10–20 nm in thickness (a -axis direction), is shown in Fig. 7a. The presence of Cr ions in the precipitation system induced a slight increase in length (c -axis direction) of α -FeOOH particles (200–300 nm; Fig. 7b and c), but not as much as observed in the case of some other cations [21–25]. At the same time, width (b -axis direction) was increased to 80–120 nm. However, lath-like α -FeOOH particles formed in the presence of Cr ions (samples CrG2 to CrG11) showed clearly a decrease in thickness (a -axis direction) compared with reference particles (sample G; Fig. 7a). These Cr-doped α -FeOOH particles are extremely thin (up to 5–10 nm) and in contact with each other form aggregates of thin laths by their largest surface perpendicular to the a -axis direction (Fig. 7b and c). Fig. 7d shows an FE-SEM image of the sample CrG11 which contain Cr-substituted α -FeOOH particles as well as the amorphous-like aggregates of Cr-substituted ferrihydrite.

4. Discussion

The lattice band corresponding to the vibration parallel to the a -axis in α -FeOOH (ν_{La}) showed an unusual shift towards higher wave numbers with an increase in the initial concentration of Cr ions. Such tendency was not noticed in studies of the influence of some other cations on the formation of α -FeOOH [21–25]. In these studies the position of that lattice band remained the same or has been shifted slightly to lower wave numbers with an increase in the initial concentration of metal ions. The lattice band corresponding to the vibration parallel to the c -axis in α -FeOOH (ν_{Lc}), positioned at 405 cm^{-1} in the spectrum of reference sample G, also showed a gradual shift towards 401 or 402 cm^{-1} in the spectra of samples obtained at r values between 2.91 and 6.98. Furthermore, the lattice band positioned at 374 cm^{-1} in the spectrum of reference sample G showed a shift towards lower wave numbers with an increase in the initial concentration of Cr ions, which is unlike the behaviour of this band in the spectra of α -FeOOH samples synthesised in the presence of some other cations [21–25]. These observations could be explained by a specific influence of Cr ions compared with other cations on the shape of α -FeOOH particles, as observed by FE-SEM (Fig. 7). Lath-like α -FeOOH particles become thinner (width and length increased slightly) with the incorporation of Cr into the α -FeOOH structure, unlike, for example, Zn-, Ru-, Cu- or Cd-doped α -FeOOH particles which grow considerably (to 500–1000 nm) in length (c -axis direction) with a suppressed growth in width and thickness (a - and b -axis direction, respectively).

Generally, the position of the IR absorption lattice bands of small particles (smaller than the wavelength of incident IR radiation) depends on the particle shape and size [26]. Change in the size of one-particle dimension influences a shift in the position of the particular lattice band to either higher or lower wave numbers depending on the nature of the band [27–29]. For example, IR absorption bands corresponding to the lattice vibrations with transition moments parallel to the c -axis are positioned at 650 and 400 cm^{-1} in the spectrum of lath-shaped α -Fe₂O₃ particles elongated in the a -axis direction. These bands were shifted to 580 and 385 cm^{-1} in the spectrum of spherical α -Fe₂O₃ particles (without elongation in any direction) and to 538 and 322 cm^{-1} in the spectrum of spindle-type α -Fe₂O₃ particles (elongation in the c -axis direction) [30].

By analogy, one can expect a shift in the position of the α -FeOOH lattice band with a transition moment parallel to the a -axis to higher wave numbers with a decrease in particle dimension in the a -axis direction and a simultaneous increase in the b - and c -axis direction. Thus, it can be concluded that the shift in position of the α -FeOOH lattice band with a transition moment parallel to the a -axis from 638 cm^{-1} in the spectrum of reference sample to 647 cm^{-1} in the spectra of samples obtained in the presence of higher amounts of Cr ions ($r \geq 4.76$) arise as a result of changes in the correlation between the α -FeOOH particle dimensions, i.e., a decrease in particle thickness along with an increase in particle width and length as a result of the incorporation of Cr ions into the α -FeOOH structure. Shifts in the positions of other lattice bands can be explained in the same way.

Generally, the value of the hyperfine magnetic field in α -FeOOH is influenced by the size and crystallinity of the particles, as well as by the degree of incorporation of foreign atoms into the α -FeOOH structure. A steep decrease in the $\langle B_{\text{hf}} \rangle$ value of α -FeOOH sextet in the spectra of samples synthesized at lower Cr concentrations (Fig. 4) can be explained by a combined effect of Cr ions incorporation into the α -FeOOH structure and a decrease in thickness of α -FeOOH particles (as observed by FE-SEM; Fig. 7). A slower decrease in the $\langle B_{\text{hf}} \rangle$ value at r between about 3 and 10 is a consequence of cessation of decrease in thickness of α -FeOOH particles, as can be concluded from FE-SEM observations of these samples and from their FT-IR spectra, where the position of the lattice band corresponding to vibration parallel to the a -axis in α -FeOOH is practically unchanged (646 or 647 cm^{-1}). An almost constant $\langle B_{\text{hf}} \rangle$ value of the α -FeOOH sextet in the spectra of samples synthesized at r between 9.09 and 16.66 indicates a maximum solubility of Cr ions in the α -FeOOH structure at about $r=10$, which is in good agreement with the results by Schwertmann et al. [1].

The effect of a decrease in thickness of α -FeOOH particles in the presence of Cr ions can be explained by a preferential absorption of Cr ions on the surface of growing crystals at the plane perpendicular to the crystallographic a -axis. The absorption of Cr ions retards the growth in the a -axis direction and therefore the favoured development of α -FeOOH laths is an elongation in the b - and c -axis directions.

5. Conclusions

- A strong effect of Cr ions on the precipitation of goethite particles in highly alkaline media by using tetramethylammonium hydroxide was observed.
- An α -(Fe,Cr) solid solution as a single phase was obtained at Cr ion concentrations up to 9.09 mol. In the presence of higher concentrations of Cr ions low-crystalline Cr-ferrihydrite or mixed Fe–Cr hydroxide was formed.
- The presence of Cr ions in the precipitation system influenced an increase in length (*c*-axis direction) of α -FeOOH particles (from 150–200 nm in reference sample to 200–300 nm), but not as much as was observed in the case of some other cations [21–25]. At the same time, width (*b*-axis direction) was increased from 40–60 nm to 80–120 nm.
- Lath-like α -FeOOH particles formed in the presence of Cr ions showed clearly a decrease in thickness (*a*-axis direction) compared with reference particles (from 10–20 nm to 5–10 nm). These Cr-doped α -FeOOH particles in contact with each other form aggregates of thin laths by their largest surface perpendicular to the *a*-axis direction.
- A change in the shape and size of α -FeOOH particles prepared in the presence of Cr ions influenced shifts in the positions of lattice bands in the FT-IR spectra of synthesized samples.

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