

^{57}Fe Mössbauer study of $\beta\text{-FeOOH}$ obtained in presence of Al^{3+} and Ti^{4+} ions

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Abstract

This paper deals with the influence of Al^{3+} and Ti^{4+} ions on the formation of akaganeite when prepared by hydrolysis of FeCl_3 solutions. The products were characterized by X-ray diffraction (XRD) using Rietveld refinement, Infrared spectroscopy (FTIR) and 300 and 77 K Mössbauer spectrometry (MS). Akaganeite is the only phase being formed independent upon the type and concentration of the metallic cations. No significant variations in the hyperfine and crystallographic parameters on the akaganeite prepared in the presence of Al^{3+} ions with concentrations lower than or equal to 10 mol% were observed. One does conclude that the present chemical route allows only rather small amounts of Al to enter in the structure of akaganeite. On the other hand, Ti^{4+} affects the physical properties of akaganeite: its presence favors the decrease of the average grain sizes, the reduction of both the unit cells and the magnitude of all average hyperfine parameters and the formation of structural defects.

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1. Introduction

Akaganeite, $\beta\text{-FeOOH}$, is an iron oxyhydroxide, commonly found in chloride-rich environments, which has recently been the subject of numerous investigations specially related with the effect of the foreign cations upon its formation. In that respect, Holm [1] has reported incorporation of small amounts of Cr, Mn, Co, Ni and Zn on akaganeite structure, when equal concentrations of metallic cations as well as Fe cations are used. Schwertmann and Cornell [2,3] reported a method to prepare akaganeite containing 2.3 mol% Si. Cai et al. [4] prepared akaganeite from hydrolysis of FeCl_3 solutions in the presence of manganese. They found that manganese appears to impede crystallization at low pH but improves it at high pH. Ishikawa et al. [5–7] studied the influences of cations, such as Ti^{4+} , Cr^{3+} , Cu^{2+} and Ni^{2+} , and anions, such as SO_4^{2-} , HPO_4^{2-} , NO_3^- , and SiO_3^{2-} , upon the

formation of akaganeite. This research group concluded that among the cations, Ti^{4+} is the one that more drastically affects both the size of structural domains and the crystalline state of akaganeite. To explain the results for the cations, Ishikawa et al. [5–7] used the fact that Cr^{3+} , Cu^{2+} and Ni^{2+} exhibit larger hydrolysis constants, $-\log K$, in comparison to Fe^{3+} . Additionally and because they do not have at hand the value of $-\log K$ for Ti^{4+} , they assumed that it should be similar to or less than that of Fe^{3+} . However, a table of hydrolysis constants has been reported in Ref. [8], where the value of $-\log K$ for Ti^{4+} is equal to -4 . It is worth mentioning that Ishikawa et al. [5–7] neither used Mössbauer spectrometry nor reported the lattice parameters for the obtained akaganeites. On the other hand, Ishikawa et al. [5–7] showed that the crystallinity of akaganeite was appreciably reduced by adding SO_4^{2-} and HPO_4^{2-} , improved by adding SiO_3^{2-} , but it was slightly influenced by NO_3^- [7]. Kamimura et al. [9] have also studied the influence of cations (Cr^{3+} , Cu^{2+} and Ni^{2+}) and anions (SO_4^{2-} and NO_3^-) upon the formation of akaganeite. An important result is that the crystallinity of

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the powdered materials depends upon the combination of cations and anions. For example, the XRD peaks of akaganeite are broadened when the sulfates are added as anions, but, on the contrary, there is no significant change in the XRD peaks when the nitrates are added.

It is noticed that in none of the previous investigations, the effect of Al^{3+} ions upon the formation of akaganeite is reported. Al^{3+} is diamagnetic and its ionic radius is smaller than that of Fe^{3+} . These two features do originate changes in both the crystallographic and the magnetic properties of akaganeite when incorporated into the lattice. Cheng et al. [10] were able to prepare Al-substituted iron dextrans in which the core structure is similar to that of a cell contracted akaganeite. These results are very interesting for medical applications in oral and injectable iron therapy. The synthesis of these types of samples requires the use of polyols and polysaccharides to stabilize nanoscale iron (III) oxides as colloidal materials at pH near 7. However, to the best of our knowledge, there is no published work in which Al^{3+} substitutes Fe^{3+} in the akaganeite structure when it is obtained from the hydrolysis of Fe^{3+} ions. One possible explanation is that Al^{3+} requires perhaps higher pH values to be co-precipitated with iron in the solutions. The pH values for the normal hydrolysis of Fe^{3+} ions to precipitate akaganeite lies between 1.2 and 1.7 [2–3]. One possibility to incorporate Al into the structure is thus to increase the concentration of Al ions in the solution.

This paper deals with the influence of Al^{3+} and Ti^{4+} ions on the formation of akaganeite when it is obtained from hydrolysis of FeCl_3 solutions. The main techniques used to retrieve information about physical, chemical and structural properties of the samples are Mössbauer spectrometry, X-ray diffraction, and Infrared spectroscopy.

2. Experimental

Akaganeite samples were obtained by hydrolysis at 70 °C for 48 h of solutions containing mixtures of 0.1 M FeCl_3 , and varying concentrations of AlCl_3 and TiCl_4 salts. The samples were code-named as MeAkX, in which Me represents the metal cation (Al, Ti) and X the mole percentage calculated as $X = [Y_{\text{dop}}/Y_{\text{Fe}}] \times 100$, where Y_{dop} and Y_{Fe} are the amount in moles of the dopant and iron, respectively. Values for X of 0%, 1%, 5%, 10% and 30% were used for Al. For Ti only X = 10% was used.

All products were characterized by X-ray diffraction (XRD), Mössbauer spectrometry (MS), and Fourier transformed Infrared spectroscopy (FTIR). XRD patterns were obtained using a D500 Siemens diffractometer equipped with a Cu ($K\alpha$) radiation. Data were collected in the 9–100° 2θ range with a 0.04° step and a counting time of 3 s per point. XRD patterns were analyzed using MAUD, a program which combines the Rietveld method and a Fourier transform analysis, well-adapted especially in the presence of broadened Bragg peaks [11]. This program allows thus to derive crystalline cell parameters, average crystallite size as well as microstrains. The initial

structural model (monoclinic space group (C2/m:b3)) used was that reported by Post and Buchwald [12]. The scale factor, sample displacement, incident intensity, unit cell parameters, five-order polynomial background, chloride site occupancy, and the average crystallite size were refined [13]. The average crystallite size and the texture were assumed to be isotropic and arbitrary, respectively, in the present study. Mössbauer spectra of 300 and 77 K were collected in a time-mode spectrometer working in the transmission geometry using a constant acceleration drive with triangular reference signal. Calibration was achieved from a standard α -iron foil at 300 K. The spectra were analyzed using the program MOSFIT which is based on non-linear least-squares fitting procedures assuming lorentzian Mössbauer lines. All isomer shift values are quoted with reference to α -Fe at 300 K. The infrared measurements were taken in a Hewlett Packard instrument with a LiTaO_3 detector and without the use of KBr for making the pellets, in the range from 4000 to 500 cm^{-1} .

3. Results

Fig. 1 shows the XRD patterns for the samples formed in the presence of aluminum ions at different concentrations.

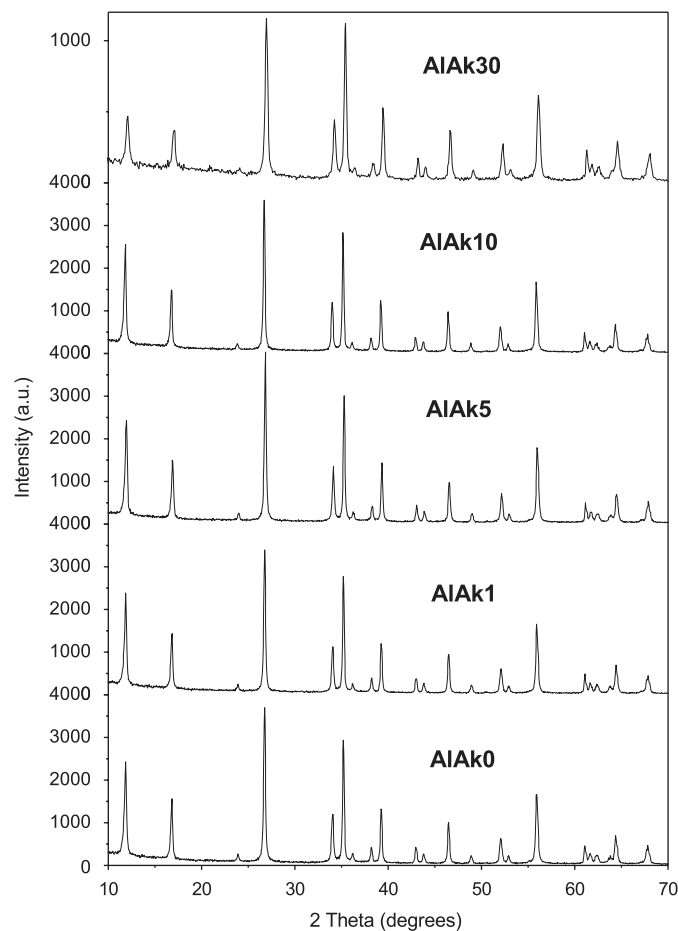


Fig. 1. XRD patterns for those samples obtained in the presence of 0, 1, 5, 10 and 30 mol% of Al.

Only Bragg peaks corresponding to the akaganeite phase are observed in all samples (PDF: 80-1770) [14]. No indication on the formation of other phases was detected. Additionally, the shape and intensity of the Bragg peaks are not drastically affected for Al concentrations lower than or equal to 10 mol% (see Fig. 1). However, the Bragg peaks of AlAk30 are more broadened, less intense and shifted in comparison to the Bragg peaks of the other samples. The structural parameters derived from the Rietveld refinement of the patterns for the different samples are drawn in Fig. 2. It is noticed that there is no clear tendency in the a - and b -lattice constants as well as in the average grain size with increasing Al content up to 10 mol%. However, by comparing the parameters of the pure sample (AlAk0) with those obtained for AlAk30, it is observed an expansion of the a - and c -lattice constants, a slight decrease of the b -parameter, and a drastic reduction in the coherent structural domain grain size. These results suggest that small amount of Fe^{3+} might be substituted by Al^{3+} .

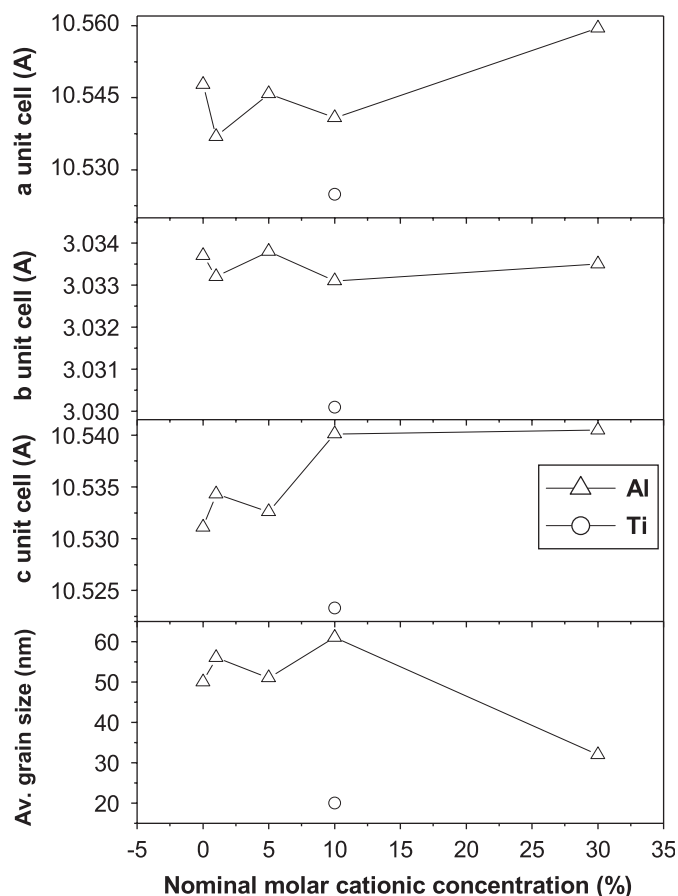


Fig. 2. Unit cell parameters and average grain sizes versus molar cationic concentration for all samples. The up triangles and circles represent the data derived from the XRD fit for samples with aluminum and titanium, respectively. The error bars for the lattice parameters are so small that they are hidden by the size of the symbols. The solid lines, that are connecting the Al data points, are put to guide the naked eye. Estimated errors are of about $\pm 6 \times 10^{-4}$ Å, $\pm 2 \times 10^{-4}$ Å, $\pm 6 \times 10^{-4}$ Å, and, ± 5 nm for the a , b , c unit cell parameters and the average grain sizes, respectively.

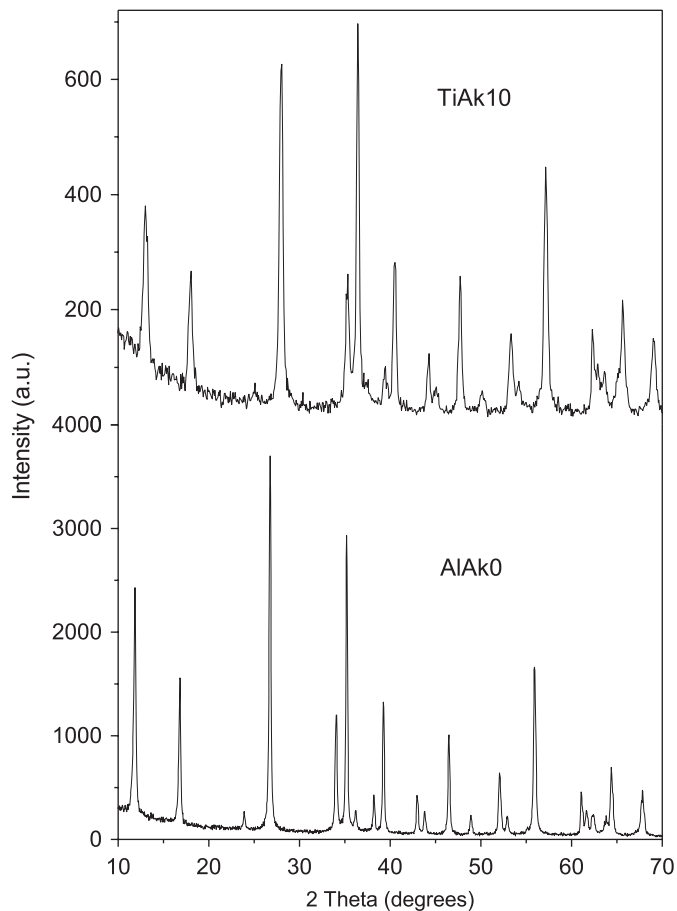


Fig. 3. XRD patterns for the pure and the sample obtained in the presence of 10 mol% of Ti.

Fig. 3 shows the XRD patterns of TiAk10 and AlAk0. All the Bragg peaks correspond to only one phase: akaganeite. Three features are clearly observed in Fig. 3: decrease in the intensities, broadening and displacement to higher angles of all the Bragg peaks of TiAk10 with respect to those of the pure akaganeite (AlAk0). The a -, b - and c -lattice constants and the average grain size derived from the fits (see Fig. 2) drastically decrease with the presence of Ti.

The FTIR spectra (not shown) of AlAkX samples are characterized by different bands located at 1639, 1383, 839, 814, 658, and 641 cm^{-1} , all of them typical of akaganeite. There is no appreciable change in the positions, broadening and relative intensities of these bands. These results are in good agreement with the XRD findings.

The 300 K Mössbauer spectra all samples which exhibit a quadrupolar structure, were adjusted by using two quadrupolar doublets and the derived parameters are similar to those reported for pure akaganeite [2,3,13,15]. The origin of these two sites is probably related to the two symmetrically different iron sites required by the monoclinic structure [12].

Fig. 4 shows the Mössbauer spectra collected at 77 K for those samples prepared in the presence of aluminum. These magnetic spectra were well described considering at least three sextets and the derived parameters are listed in

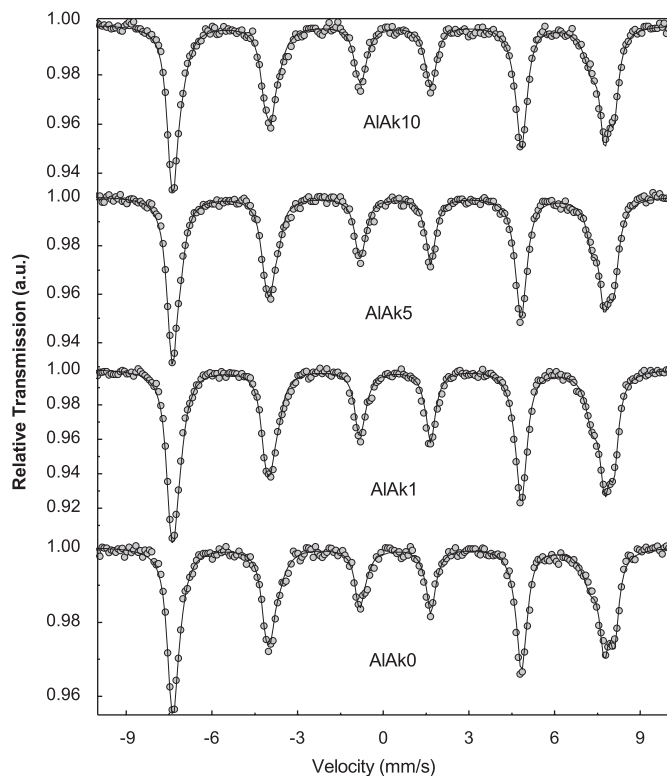


Fig. 4. 77 K Mössbauer spectra for those samples obtained in the presence of 0, 1, 5, and 10 mol% of Al.

Table 1

Average hyperfine parameters obtained from the fit of the 77 K Mössbauer spectra for all samples

Sample	$\langle \delta \rangle$ (mm/s)	$\langle 2\epsilon \rangle$ (mm/s)	$\langle B \rangle$ (T)
AlAk0	0.49	-0.24	46.5
AlAk1	0.48	-0.23	46.6
AlAk5	0.48	-0.22	46.6
AlAk10	0.49	-0.23	46.4
AlAk30	0.44	-0.18	46.6
TiAk10	0.42	-0.21	43.9
	0.37*	1.06*	0

Estimated errors are of about ± 0.01 mm/s for the average isomer shift, $\langle \delta \rangle$, and the average quadrupole shift, $\langle 2\epsilon \rangle$, and of about ± 0.1 T for the average magnetic hyperfine field, $\langle B \rangle$.

*Those parameters correspond to the doublet component.

Table 1 (A fit with four sextets is also possible [13]). Because of the different fitting models describing the spectra, we restricted here to compare the mean values, which are the weighted mean values, weighted according to the area value for each component. It is seen that the shape of the spectra did not change appreciably from one sample to another. Within the error bars, there are no appreciable differences in the hyperfine parameters for the akaganeites prepared in the presence of the Al ions at concentrations below 10 mol % to those parameters for the pure one. However, there is a decrease in both the average isomer $\langle \delta \rangle$ and the average quadrupole $\langle 2\epsilon \rangle$ shifts for AlAk30

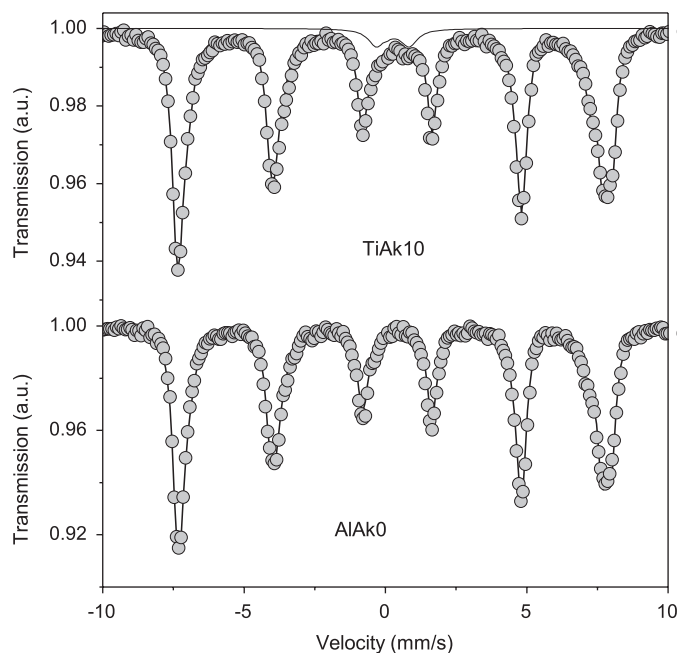


Fig. 5. 77 K Mössbauer spectra for the pure and the sample obtained in the presence of 10 mol% of Ti.

in comparison to AlAk0. These results well support XRD and FTIR findings. It is also important to emphasize that some Mössbauer spectra were recorded versus temperature in the close vicinity of the magnetic ordering temperature: it is concluded that the magnetic ordering temperature remains rather independent of the Al content. Fig. 5 shows the 77 K Mössbauer spectra for that sample prepared in the presence of Ti. An important difference in the spectrum of this akaganeite in comparison to the pure one is the presence of a quadrupolar doublet. The derived parameters from the fits are listed in Table 1. It is possible to observe a decrease in the magnitude of the three hyperfine parameters for this sample in comparison to AlAk0, especially for the average magnetic hyperfine field.

4. Discussion

No significant variations in the hyperfine and crystallographic parameters of akaganeite prepared in the presence of Al^{3+} ions at concentrations lower than 10 mol% were observed. These results suggest a rather small Al^{3+} for Fe^{3+} substitution, if any, in the crystallographic structure of akaganeite. A first possible explanation to this result is perhaps that in aqueous media with chloride content, Al^{3+} requires higher pH values than the ones investigated here (greater than 2) to be co-precipitated with iron in the solutions. In fact, the final pH values here for the normal hydrolysis of Fe^{3+} ions lies between 0.65 and 1.26. A second possible explanation lies in the fact that the hydrolysis constant, $-\log K$, for Al^{3+} ($-\log K = 5.0$) is higher than that for Fe^{3+} ($-\log K = 2.2$) in the hydrolysis reaction. The increment of Al concentration up to

30 mol%, do not promote appreciable Al for Fe substitution, but it interfere with the grain growth. Additionally, we find a lattice expansion for AlAk30 where one should expect a lattice contraction due to the smaller ionic radius of Al^{3+} (0.053 nm) in comparison to that of Fe^{3+} (0.064 nm). It is well documented in the literature that lattice constant changes, contraction or expansion, are expected when the size of particles decreases [16–18] as compared to the bulk values. In the case of AlAk30 we have a nanostructured material and since substitution is very low we may argue that the lattice is not disturbed too much with respect to the bulk case. As a consequence of the small crystalline grain size, both the grain boundary and the surface contribution are enhanced with respect to those of the bulk, the number of atoms close to and in the grain boundary or at the surface is larger as compared to the bulk. This leads to smaller coordination for these atoms, i.e., the attractive and repulsive forces are imbalanced driving the particles away from each other and increasing the lattice constant. Finally, the diamagnetic character of Al^{3+} cations has to favor a reduction of the magnetic ordering temperature, but it remains: because it is rather independent of the Al content. One concludes that very small amount of Al substitutes Fe within the akaganeite structure in AlAk30.

In the case of Ti containing akaganeite, we found a drastic lattice contraction and a drastic grain size reduction, accompanied also by a reduction in the three hyperfine parameters. Moreover, the quadrupolar doublet in the 77 K Mössbauer spectrum of this sample could suggest the presence of ultra fine akaganeite grains. These results can be related to the fact that Ti^{4+} exhibits a negative hydrolysis constant ($-\log K = -4.0$) in comparison to the positive one of Fe^{3+} ($-\log K = 2.2$). This implies that Ti^{4+} is many orders of magnitude more easily hydrolysable than Fe^{3+} , and this great difference can cause that some Fe^{3+} species cannot be completely precipitated and remained in the solution in agreement with the low final pH values measured [5]. Now, because the ionic radius of Ti^{4+} (0.068 nm) is slightly larger than that of Fe^{3+} (0.064 nm), thus a lattice expansion is expected. However, our results show that, on the contrary, there is a drastic lattice contraction. Additionally, one must think how to compensate the extra charge due to the Ti^{4+} for Fe^{3+} substitution, which could be done either by introducing more Cl^- ions, more OH^- groups, more Fe^{3+} vacancies or a combination of the three. The possibility to replace two Fe^{3+} ions by one Fe^{2+} and one Ti^{4+} is rejected here, otherwise, we should expect an important Fe^{2+} signal in the Mössbauer spectra, which is not observed. Assuming more Cl^- ions requires precaution due to the fact that Cl^- has the largest ionic radius among the ions present in the akaganeite lattice. Thus its presence does introduce an important expansion in the lattice, which is not observed. Now, because the ionic radius of OH^- is less than that of Cl^- , the presence of Ti^{4+} is expected to introduce more OH^- than Cl^- ions, and thus a contraction in the lattice. It

is also probable that there are iron vacancies in the lattice. Another possibility to explain the observed results may be due to an inhomogeneous distribution of the dopant in the akaganeite host, forming a kind of core-shell structure for the substituted particles, e.g., we may have a larger Ti for Fe substitution at the surface. This will produce a lattice misfit at the interface between the two differently doped systems producing compressive stresses on the core and as a consequence reducing the lattice parameter. All these observations require further investigation.

5. Conclusions

Akaganeite was prepared by hydrolysis of FeCl_3 solutions in the presence of Al^{3+} and Ti^{4+} ions at different concentrations. XRD, FTIR and Mössbauer spectrometry show that akaganeite is the only phase being formed, i.e. they do not promote the formation of another phase. Very small differences in some of the crystallographic and hyperfine parameters for samples obtained in the presence of Al ions at concentrations lower than 10 mol% were observed. However at 30 mol%, the presence of Al is able to reduce the average grain size and the magnitude of some hyperfine parameters of the final products. On the other hand, Ti^{4+} drastically affects the physical properties of the akaganeite: its presence decreases the grain sizes, reduces all the unit cell parameters and introduces defects into the crystallographic structure. The types of defects presented in the samples require further investigation.

Acknowledgments

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