

Nano size crystals of goethite, α -FeOOH: Synthesis and thermal transformation

Axel Nørlund Christensen^a, Torben R. Jensen^{b,*}, Christian R.H. Bahl^c, Elaine DiMasi^d

^aCrystal Chemistry, Højkolvej 7, DK-8210 Århus V, Denmark

^bInterdisciplinary Nanoscience Centre (iNANO), Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

^cMaterials Research Department, Riso National Laboratory, P.O. Box 49, DK-4000 Roskilde, Denmark

^dNational Synchrotron Light Source Department, Brookhaven National Laboratory, Upton, NY 11973, USA

Received 26 October 2006; received in revised form 22 December 2006; accepted 30 January 2007

Available online 16 February 2007

Abstract

An aqueous suspension of amorphous iron(III) hydroxide was kept at room temperature (298 K) for 23 years. During this period of time the pH of the liquid phase changed from 4.3 to 2.85, and nano size crystals of goethite, α -FeOOH crystallised from the amorphous iron(III) hydroxide. Transmission electron microscopy (TEM) investigations, Mössbauer spectra, and powder X-ray diffraction using Co K α radiation showed that the only iron containing crystalline phase present in the recovered product was α -FeOOH. The size of these nano particles range from 10 to 100 nm measured by TEM. The thermal decomposition of α -FeOOH was investigated by time-resolved *in situ* synchrotron radiation powder X-ray diffraction and the data showed that the sample of α -FeOOH transformed to α -Fe₂O₃ in the temperature range 444–584 K. A quantitative phase analysis shows the increase in scattered X-ray intensity from α -Fe₂O₃ to follow the decrease of intensity from α -FeOOH in agreement with the topotactic phase transition.

© 2007 Elsevier Inc. All rights reserved.

Keywords: Iron(III) hydroxide; α -FeOOH; α -Fe₂O₃; X-ray powder diffraction; Rietveld refinement; TEM

1. Introduction

In a previous investigation, the experimental conditions for the crystallization of amorphous precipitates of oxides and hydroxides were studied at hydrothermal temperatures. Special attention was paid to transition metals forming compounds from M(II) and M(III) ions [1]. Iron is one of these elements, known for its corrosion in contact with the atmosphere and its formation of rust [2], which has a more complex composition than given in the formula FeOOH, and also for its formation of red–brown “rust-coloured” amorphous precipitates in hydrolysis of iron(III) aqueous solutions. In aqueous systems in nature, iron is known to precipitate to form ochre, which is a complex mixture of iron(III) oxides or hydroxides and clay minerals.

The formation of the iron(III) oxide hydroxide α -, γ - and δ -FeOOH from iron(II) and (III) aqueous solutions has been studied for decades [3–5], and has attracted interest due to the compounds magnetic properties and their technological application [6–8]. Of special interest is development of synthetic methods for the formation of the compounds as pure phases with well defined crystal size distribution.

Hydrolysis of iron(III) solutions at ambient temperatures results in an amorphous precipitate of iron(III) hydroxide. This amorphous compound is, as all other amorphous precipitates, thermodynamically unstable and may gradually transform to goethite, α -FeOOH, and hematite, α -Fe₂O₃. Time, temperature and in particular, pH are the main parameters governing the rates of transformation to the crystalline phases [9–12]. The main results are that goethite is formed at high pH values, and hematite at medium to low pH values, but goethite can also be obtained at low pH values at ambient conditions [11,13].

*Corresponding author. Fax: +45 8619 6199.

E-mail address: trj@chem.au.dk (T.R. Jensen).

The hydrothermal preparation of goethite and hematite from amorphous iron(III) hydroxide was studied at various pH values in the temperature range 373–473 K. In the pH range 8.0–10.0, goethite and hematite were formed. In the range 10.5–10.8 only goethite was formed, and in the pH range 0.8–2.6 hematite was the only reaction product [14]. The decomposition of α -FeOOH to α -Fe₂O₃ in neutral and weakly alkaline hydrothermal solution was observed at 423 ± 20 K, and this temperature was suggested to be the upper temperature for the formation of the α -FeOOH minerals [15]. However, the transformation is also strongly pH dependent so that the transformation temperature increased by 25 K per pH unit [16].

The first *in situ* investigation of the rate of crystallization of amorphous iron(III) hydroxide to α -Fe₂O₃ and α -FeOOD was made at hydrothermal conditions using neutron powder diffraction [17]. The amorphous iron(III) hydroxide precipitated at pH = 10.0 was converted very fast to a mixture of α -Fe₂O₃ and α -FeOOD at temperatures from 377 to 394 K. The rate of crystallization of samples precipitated at pH = 4.5 was slower, and the product was pure α -Fe₂O₃. The acidity of the hydrothermal solution increased during the hydrothermal treatment, due to complete hydrolysis.

The aging of amorphous iron(III) hydroxide to α -FeOOH and α -Fe₂O₃ was studied by small angle neutron scattering techniques in the temperature range from room temperature to 373 K. The amorphous particles had a poly disperse size distribution, which changed with time. The scattering density of the particles increased with time and each particle of the amorphous samples produced a particle of α -Fe₂O₃ in acid medium. There was no indication of a process where the particles dissolved and re-precipitated [18]. The solid state transformation of α -FeOOH to α -Fe₂O₃ was studied and showed an ordered structural translation between the two crystalline lattices [19]. This is a topotactic transformation between the two compounds where the solids have structural relationships [20,21].

The present study is a continuation of investigations and synthesis started 4 decades ago [1,14,17]. A minor ambiguity exists concerning the results of the crystallization processes at low pH values at room temperature: the product can be pure α -Fe₂O₃, pure α -FeOOH, or a mixture of the two compounds. Results from a long-term crystallization experiment are reported below, which illustrates that one of these alternatives is possible, namely formation of nano size crystals of goethite.

2. Experimental

The reaction mixtures used were prepared in the following way: to 200 mL of a 0.75 M Fe(NO₃)₃·9H₂O solution was added dropwise to a 2.25 M NaOH solution under stirring. The pH of the liquid suspension was monitored with a pH meter, and the precipitation of iron(III) hydroxide ended at pH = 4.3. After this observation, the addition of the sodium hydroxide solution was

stopped. The suspension was stored in two 250 mL pyrex flasks, closed with rubber stoppers. The suspension had a red–brown colour, which over the years gradually changed to a yellow–red colour. The pH was measured occasionally and showed decreasing values. After 23 years at room temperature, the pH of the suspensions was 2.85. The suspensions were centrifuged, and the wet paste was dried on paper at approximately, 323 K. The chemicals used in the synthesis were Fe(NO₃)₃·9H₂O (Merck) and NaOH (Merck). The presence of NaNO₃ as an impurity, see below, is derived from the reactions using these chemicals.

Powder X-ray diffraction patterns were recorded on a Stoe Stadi powder diffractometer using Ni-filtered CuK α radiation, $\lambda = 1.54060$ Å. A position sensitive linear detector was used in a step scan mode. The patterns showed that the sample was goethite, with NaNO₃ as an impurity phase. In order to reduce fluorescence from the sample, X-ray patterns were additionally recorded on a Bruker powder diffractometer using CoK α radiation, $\lambda = 1.78897$ Å. This pattern is displayed in Fig. 1.

The time-resolved synchrotron radiation powder X-ray diffraction data were collected on beam line X6B of the National Synchrotron Light Source (NSLS) using a CCD area detector with a resolution of 512×512 pixels. The samples were placed in 0.4 mm diameter quartz glass capillaries and heated in a hot air stream. A temperature range from 298 to 673 K was used with a heating rate of 5.00 K/min, corresponding to 2.75 K/pattern, and using an exposure time of 0.5 min/pattern. The selected X-ray wavelength was $\lambda = 0.65255$ Å, refined with a powder pattern of LaB₆ ($a = 4.1570$ Å). The capillary was oscillated 5° to randomise the orientations of the crystallites in the samples. The diffraction data frames from the area detector were converted to powder patterns with the software FIT2D [22], giving a 2θ range of 2.0–34.6°. Full profile Rietveld refinement was performed with the

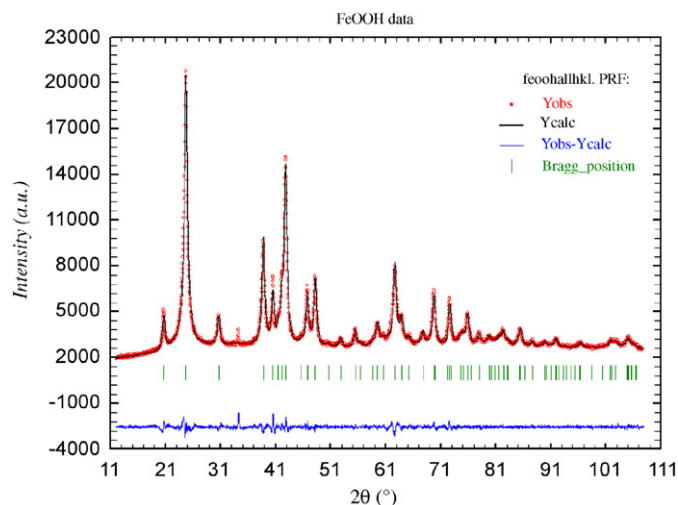


Fig. 1. Powder X-ray diffraction pattern of α -FeOOH recorded with CoK α radiation, $\lambda = 1.78897$ Å. A Lorentzian function was used to describe the line profiles with the parameters $U = 0.5740$, $V = -0.2937$, and $W = 0.3351$ [23]. The lower curve is a difference plot.

program FULLPROF [23]. Parameters refined were three unit cell parameters, three profile parameters, and typically 57 background parameters. The background was defined in interpolation between the selected background points.

TEM measurements of the sample were performed using a JEM 3000F microscope operated at 300 kV. The sample of α -FeOOH was investigated by ^{57}Fe Mössbauer spectroscopy at the temperatures 80, 160, 200, 250 and 295 K. A constant acceleration Mössbauer spectrometer with a source of ^{57}Co in rhodium was used, calibrated with a 12.5 μm α -Fe foil at room temperature.

3. Results and discussions

Fig. 2 shows an image obtained from the sample. The crystals are found to be either elongated or rhombohedral. The sizes range from a thickness of less than 5 nm to a length of above 100 nm. The micrograph of needles and a few rhombohedrally formed crystallites of α -FeOOH is in contrast to the micrographs reported previously [9,10] showing micro crystal needles of α -FeOOH and larger hexagonal crystals of α -Fe₂O₃. These latter crystals of

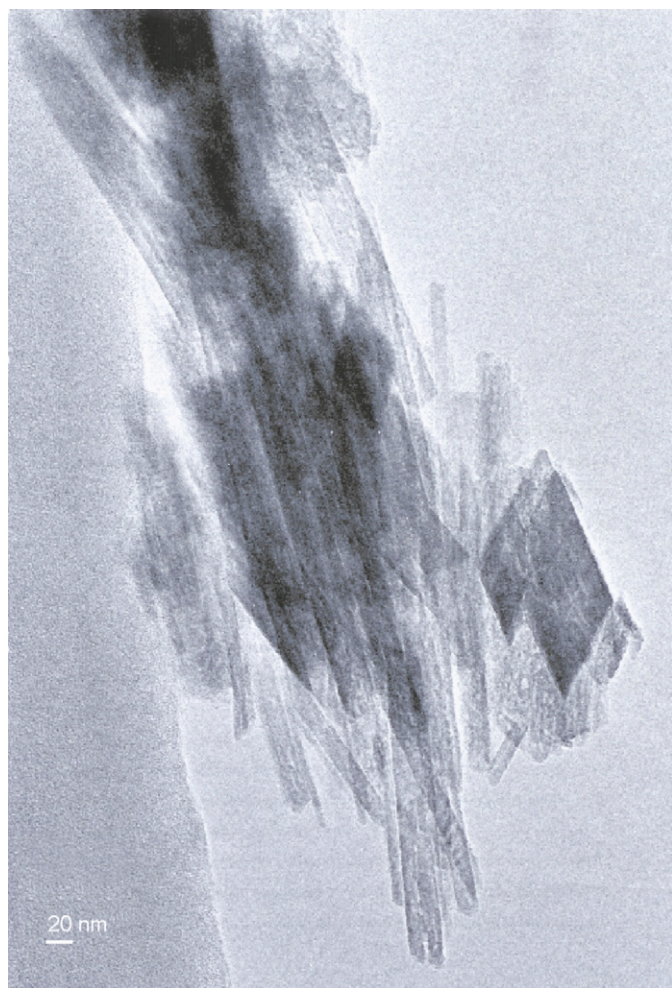


Fig. 2. TEM photograph of the investigated sample of goethite, α -FeOOH.

α -Fe₂O₃ had a characteristic look in the previous works, and were not observed in the present investigation. This is the first indication that only α -FeOOH was formed in this long time synthesis at room temperature.

The Mössbauer spectra displayed in Fig. 3 show only α -FeOOH with decreasing hyperfine field splitting with increasing temperature. The broadened asymmetrical lines at elevated temperatures indicate some degree of particle aggregation. The spectrum, recorded at 295 K has a doublet in the middle of the spectrum, which indicates fast super-paramagnetic relaxation of the smallest particles of goethite. The growth of the doublet component without the collapse of the sextets indicates a broad size distribution of the particles.

The powder X-ray diffraction pattern recorded with CoK α radiation was used in a profile refinement, see Fig. 1. The pattern showed, that the only crystalline iron containing phase in the sample was α -FeOOH, but the sample had a minor impurity of NaNO₃. The refined unit cell

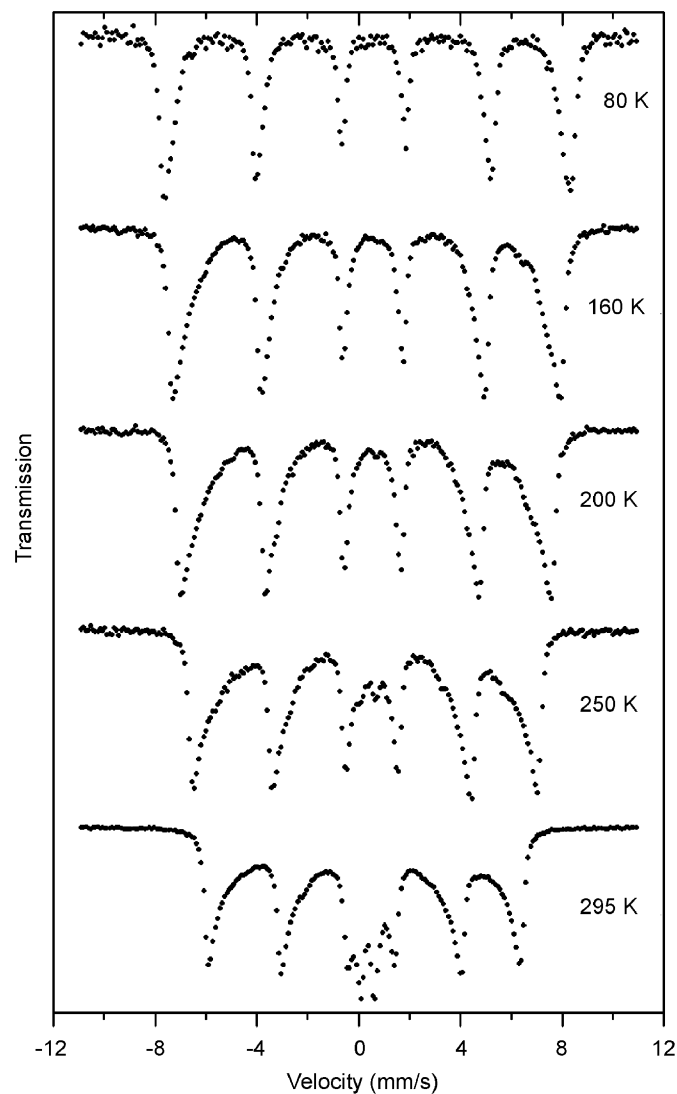


Fig. 3. Mössbauer spectra of goethite, α -FeOOH, measured at temperatures in the range 80–295 K.

parameters of α -FeOOH were $a = 9.9553(5)$, $b = 3.0219(1)$ and $c = 4.6092(4)$ Å, using the space group $Pnma$. The line width full-width at half-maximum (FWHM) of the 101 reflection at $2\theta = 24.70^\circ$ was 0.653° .

A stack of powder patterns showing the 2θ range 5 – 25° , and covering the temperature range 298 – 673 K is displayed in Fig. 4. In the thermal decomposition, the patterns up to 584 K showed the reflections of α -FeOOH. However, the decomposition starts at 444 K. Decomposition to α -Fe₂O₃ thus took place in the relatively broad temperature range 444 – 584 K, showing increasing intensity from the reflections of α -Fe₂O₃. The transformation was followed quantitatively in structure refinements of the two structures using the program FULLPROF [23]. Atomic coordinates for the known structures of α -FeOOH [24] and α -Fe₂O₃ [25] were used as start values in the refinements. The results of this quantitative phase analysis are displayed in Fig. 5. The coexistence of two crystalline phases are not observed in first order phase transitions, as in the transitions of calcite to lime [26], or in the transformation of ettringite to monosulfate [27]. The goethite to hematite phase transition was previously observed at approximately 600 K in susceptibility measurements on α -FeOOH studies in the temperature interval 273 – 673 K [28].

Selected patterns were used in profile refinements [23] to determine the values of the unit cell parameters and FWHM values of selected reflections. The unit cell volume of α -FeOOH increased from 139.0 Å³ at 306 K to 139.7 Å³ at 491 K due to thermal expansion. The line width FWHM of the 101 α -FeOOH reflection at $2\theta = 8.93^\circ$ decreased from 0.445° at 306 K to 0.410° FWHM at 463 K, indicating

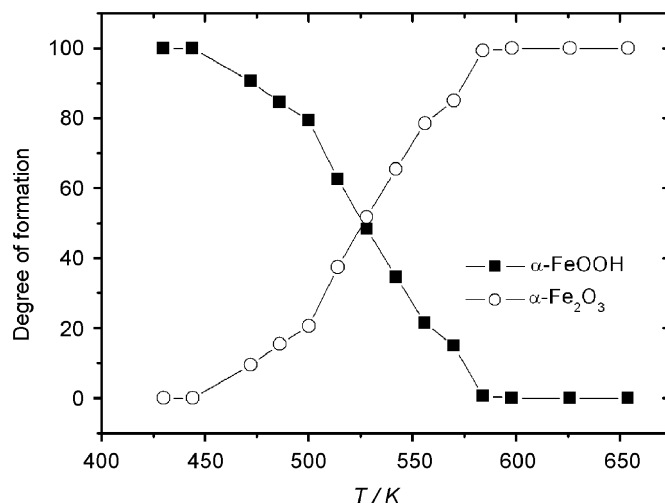


Fig. 5. The degree of transformation of α -FeOOH to α -Fe₂O₃ versus temperature is extracted by quantitative phase analysis by full profile Rietveld from the *in situ* powder X-ray diffraction data.

a modest growth of the crystallites during the heat treatment. The unit cell volume of α -Fe₂O₃ increases from 305.3 Å³ at 573 K to 306.0 Å³ at 673 K. FWHM of the 104 α -Fe₂O₃ reflection at $2\theta = 13.82^\circ$ decreased from 0.686° at 518 K to 0.417° at 673 K, also indicating a slight growth of the crystallites during the heat treatment.

4. Conclusion

The electron micrograph, the Mössbauer spectra and the X-ray powder diffraction analysis showed that the sample of α -FeOOH did not have any impurity of α -Fe₂O₃ or of other iron containing phases. Therefore, this long time crystallisation experiment shows that pure α -FeOOH can be formed in moderately acid aqueous media. However, the sample contained an impurity of NaNO₃ from the reactants. The *in situ* synchrotron radiation X-ray powder diffraction data showed the thermal decomposition of nano size particles of α -FeOOH to α -Fe₂O₃ over a relatively broad temperature range 444 – 584 K. A modest crystallite growth can be deduced for the two compounds from the FWHM of the diffraction lines at $2\theta = 8.93^\circ$ and 13.82° for α -FeOOH and α -Fe₂O₃, respectively. The size of the crystallites of α -FeOOH and α -Fe₂O₃ obtained in this study are larger than those of the particles of γ -Fe₂O₃ of 12 – 13 nm, formed in an *in situ* X-ray diffraction investigation using an amorphous precursor [29].

Moderately acid aqueous media occur more frequently in nature than strongly alkaline aqueous media. The observation in this work that crystalline goethite can be formed from amorphous iron(III) hydroxide in a moderately acid aqueous medium thus suggests that this could be one of the routes of formation of goethite mineral deposits in nature. The results are different from the long-term transformation of ferrihydrite investigated in the temperature range 277 – 298 K and the pH range 2.5 – 12 [13]. At time

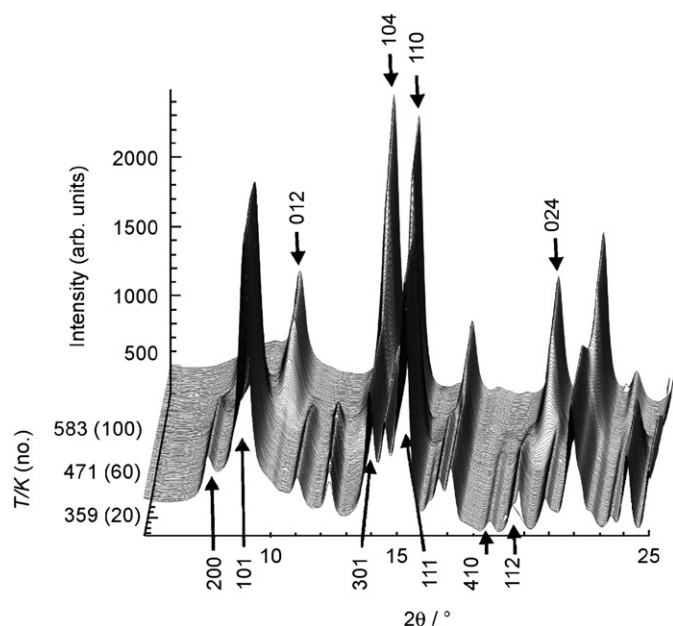


Fig. 4. Stack of *in situ* powder X-ray diffraction patterns recorded in the temperature range from 298 to 673 K using synchrotron radiation, $\lambda = 0.65255$ Å. Only the 2θ range of 5 – 25° is displayed. Miller indices of selected reflections are indicated for α -FeOOH (below the curves) and for α -Fe₂O₃ (above the curves).

periods up to 12 yr, α -FeOOH and α -Fe₂O₃ were observed at all temperatures and pH values [13]. The synthesis of ferrihydrite was different from the synthesis of the iron(III) hydroxide samples used in the present investigation. However, acceleration of the crystallization process by an increase in temperature to 373 K [30], or to hydrothermal conditions [17], results in formation of mixtures of goethite and hematite, or in formation of pure hematite, respectively.

Acknowledgments

The Danish Natural Science Research Council has supported this investigation with grants under the program DANSYK, and Carlsberg Fondet with a stipend to Torben R. Jensen. The synchrotron X-ray measurements were carried out at Brookhaven National Laboratory, supported under Contract DE-AC02-98CH10886 with the US Department of Energy, Office of Basic Energy Sciences.

References

- [1] A.N. Christensen, Studier over nogle hydrotermalt fremstillede oxider og hydroxider, Dr. Phil. Thesis, Aarhus Universitets Kemiske Institut, 1967.
- [2] A.F. Holleman, E. Wiberg, Inorganic Chemistry, Academic Press, Berlin, 2001, p. 1438.
- [3] C.M. Flynn, Chem. Rev. 84 (1984) 31–41.
- [4] W. Schneider, Commun. Inorg. Chem. 3 (1984) 205–223.
- [5] W. Schneider, B. Schwyn, in: W. Stumm (Ed.), Aquatic Surface Chemistry. Wiley, New York, 1987, pp. 167–196.
- [6] T. Ishikawa, T. Takeda, R.K. Kandori, J. Mater. Sci. 27 (1992) 4531–4535.
- [7] B.R.V. Narasimban, S. Prebhakar, Mater. Lett. 52 (2002) 295–300.
- [8] M.P. Morales, M.A. Verges, J. Magn. Mater. 203 (1999) 146–148.
- [9] R.C. Mackenzie, R. Meldau, Mineral. Mag. London 32 (1959) 153–165.
- [10] U. Schwertmann, Z. Pflanz. Bodenkunde 108 (1965) 37–45.
- [11] U. Schwertmann, E. Murad, Clays Clay Miner. 31 (1983) 277–284.
- [12] R.M. Cornell, R. Giovanoli, W. Schneider, J. Chem. Tech. Biotechnol. 46 (1989) 115–134.
- [13] U. Schwertmann, H. Stanjek, H.-H. Becher, Clay Miner. 39 (2004) 433–438.
- [14] A.N. Christensen, Acta Chem. Scand. 22 (1968) 1487–1490.
- [15] F.G. Smith, D.J. Kidd, Am. Mineral. 34 (1949) 403–412.
- [16] R.G. Robins, J. Inorg. Nucl. Chem. 29 (1967) 431–435.
- [17] A.N. Christensen, P. Convert, M.S. Lehmann, Acta Chem. Scand. A 34 (1980) 771–776.
- [18] A.N. Christensen, M.S. Lehmann A. Wright, Acta Chem. Scand. A 37 (1983) 63–69.
- [19] H.P. Rooksby, Silic. Ind. XXV (7/8) (1960) 335–339.
- [20] Y. Cudennec, A. Lecerf, Solid State Sci. 7 (2005) 520–529.
- [21] Y. Cudennec, A. Lecerf, J. Solid State Chem. 179 (2006) 716–722.
- [22] A.P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, D. Hausermann, High Pressure Res. 14 (1996) 235–248.
- [23] J. Rodríguez-Carvajal, Physica B 192 (1993) 55–69.
- [24] A. Szytula, A. Burewicz, Z. Dimitrijewic, S. Krasnicki, H. Rzany, J. Todorovic, A. Wanic, W. Wolski, Physica Status Solidi 26 (1998) 429–434.
- [25] R.L. Blake, R.E. Hessevick, T. Zoltai, L.W. Finger, Am. Mineral. 51 (1966) 123–129.
- [26] N.V.Y. Scarlett, I.C. Madsen, M.I. Pownceby, A.N. Christensen, J. Appl. Crystallogr. 37 (2004) 362–368.
- [27] A.N. Christensen, T.R. Jensen, J.C. Hanson, J. Solid State Chem. 177 (2004) 1944–1951.
- [28] J.B. Forsyth, I.G. Hedley, C.E. Johanson, J. Phys. C (Proc. Phys. Soc.) Ser. 2. 1 (1968) 179–188.
- [29] J.-E. Jørgensen, L. Mosegaard, L.E. Thomsen, T.R. Jensen, J.C. Hanson, J. Solid State Chem. 180 (2006) 179–184.
- [30] U. Schwertmann, W.R. Fischer, Z. Anorg. Allg. Chem. 346 (1966) 137–142.