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Neutron Powder Diffraction Study of the Dehydration of Zeolite N

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Zeolite N is pseudo-tetragonal with an EDI-type structure. The orthorhombic cell at 293 K has $a=989.8(2)$, $b=989.1(2)$, $c=1308.5(1)$ pm, space group $I222$ and $Z=1$, for the composition $K_{12}Al_{10}Si_{10}O_{40}Cl_2 \cdot 8H_2O$. Neutron diffraction powder patterns were analyzed for data collected at 5 K and in the temperature range 293–623 K. Thermal analysis shows that complete dehydration takes place in the temperature range 373–623 K, which is consistent with the observed reduction of background from incoherent scattering reduction and changes in occupation numbers. The removal of water is connected with rearrangement of the chlorine and potassium atoms, the driving force probably being the strive for acceptable coordination of the salt-like components.

The crystal structure of zeolite N was recently reinvestigated using high-resolution synchrotron X-ray powder diffraction data.[1] The structure is pseudo-tetragonal, but an orthorhombic distortion was observed as a slight line-broadening in the synchrotron powder pattern, and the structure was thus described using the space group $I222$. The content of the unit cell was $K_{12}Al_{10}Si_{10}O_{40}Cl_2 \cdot 8H_2O$. Zeolite N is thus a KCl-bearing compound which also contains some water molecules. The AlO_4 and SiO_4 tetrahedra form an ordered arrangement, and the topology of the framework structure is of the edingtonite type, EDI.[2] The potassium and chlorine atoms form deformed ClK_6 octahedra positioned in the channels of the structure. Oxygen atoms of the water molecules were also located in the structure, however with positions less precise than those of the potassium and chlorine atoms.

A thermogravimetric analysis of zeolite N shows a 5.2% loss of weight during heating to 873 K, due to loss of water in the temperature range 373–623 K. Real-time X-ray synchrotron powder diffraction studies of the dehydration processes of the zeolites mesolite and scolecite were recently reported by Ståhl and Hanson,[3] using a position-sensitive detector. In a similar way neutron powder diffraction has for two decades been used in studies of dehydration processes and of chemical reactions.[4–6] In addition to changes in positions and intensities of Bragg reflections, neutron diffraction powder patterns show significant changes in the background levels of the patterns when H_2O is released in the dehydration process.

A preliminary real-time X-ray synchrotron powder diffraction investigation of the dehydration of zeolite N in the temperature range 300–573 K showed only minor changes in intensities and positions of the Bragg reflections of the powder patterns. For this reason it was decided to persue the study of the dehydration process of zeolite N using neutron powder diffraction.

Experimental

The sample of zeolite N was made in a hydrothermal synthesis[1] and was from the same batch as the sample used in the earlier structure investigation.[1] A thermogravimetric analysis made on a Stanton Redcroft TG–TGA simultaneous thermal analyser STA 1000/1500 using a heating rate of 10 K min^{-1} and a 150 ml min^{-1} flow of Ar gas showed a weight loss of 4.5% during heating to 673 K, which was assumed to reflect loss of water (Fig. 1).

Neutron powder diffraction patterns of zeolite N were measured at 5 K and in the temperature range 293–623 K on the neutron powder diffractometer D2B at Institut Max von Laue – Paul Langevin,[7] using neutrons with $\lambda=159.38$ pm. The recorded patterns in the 2θ range 10.0–150.0° with $\Delta 2\theta=0.05°$ were used for refining the structure of zeolite N according to the procedure described by Rietveld[8] and the GSAS program system.[9]

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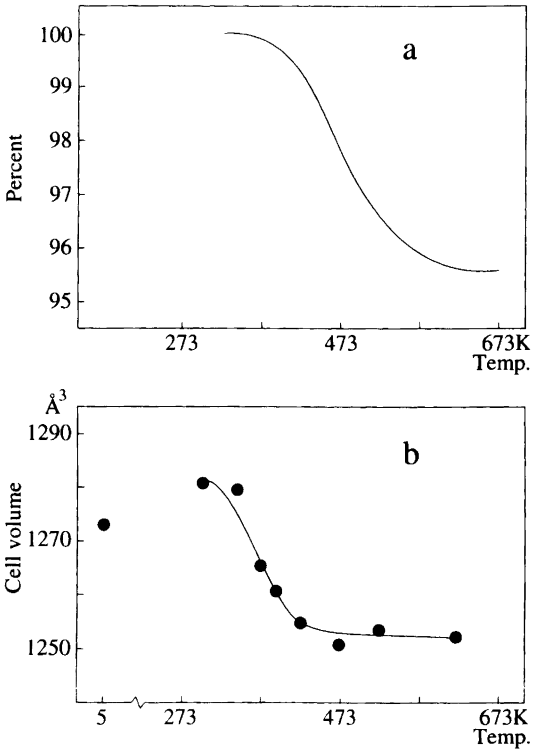

Fig. 1. (a) TGA curve for dehydration of zeolite N in the temperature range 293–673 K. (b) Unit-cell volume of zeolite N vs. temperature.

Results and discussion

The model of the structure of zeolite N found in the synchrotron X-ray powder diffraction investigations[1] had a statistical distribution of the water molecules with oxygen atoms in 8*k* sites at 0.424(2), 0.346(2), 0.425(1) and at 0.361(1), 0.476(2), 0.441(1) for OW1 and OW2, respectively. The potassium atoms were in site 4*i* for K1 at 0, 0, 0.2499(3) and in site 8*k* for K2 at 0.2115(4), 0.2121(4), 0.4363(2). The two water molecules have contacts to the potassium atoms K1 and K2. Assuming tetrahedral bond directions for the oxygen atoms OW1 and OW2, the following possible hydrogen atom positions of the water molecules can be calculated: H1 at 0.41, 0.44, 0.41 and H2 at 0.48, 0.34, 0.48 bonded to OW1 and H3 at 0.30, 0.55, 0.45 and H4 at 0.43, 0.48, 0.49 bonded to OW2. OW1 has a weak hydrogen-bond contact with the framework atom O2 at 0.60, 0.10, 0.44, and OW2 has a weak hydrogen-bond contact with the framework atom O1 at 0.10, 0.60, 0.42. A sketch of this model is displayed in Fig. 2. In the synchrotron X-ray powder diffraction pattern[1] investigation of the peak widths, FWHM, of the reflections clearly indicated that the symmetry was orthorhombic rather than tetragonal. The *a*- and *b*-axes were of different lengths; however, the distortion was too small to provoke line splittings in the powder pattern. In the space group *I*222 the *a*- and *b*-directions are alike with respect to symmetry, but owing to the quality of the synchrotron X-ray pattern it was

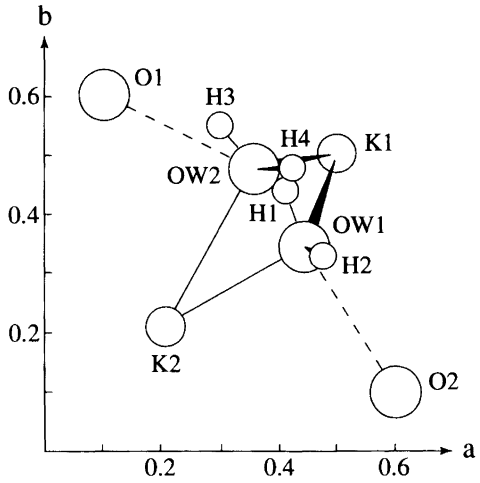

Fig. 2. Sketch of water molecules arranged statistically between the two potassium atoms K1 and K2, and with contacts to the framework oxygen atoms O1 and O2.

possible to derive a model with statistical distribution of the water molecules over two sites.

In the neutron diffraction powder pattern the reflections are broad owing to the low instrumental resolution, and it was not possible to extract as detailed information as in the case with the synchrotron X-ray powder pattern. The profile fits did thus not show significant improvements in using two water molecule positions arranged statistically as suggested in the model mentioned above, instead of one water molecule in one of the two possible positions. The calculations were for this reason made using the latter model.

Figure 3 displays the observed, calculated and difference pattern of the neutron diffraction powder profile of zeolite N measured at 5 K, and Table 1 lists the derived positional parameters. As a result of the hydrogen content of the sample, the background of the pattern is high and declines with increasing scattering angle. The model arrived at in the profile refinement is in acceptable agreement with the model from profile analysis of the synchrotron X-ray powder pattern.[1]

Figure 4 displays the observed, calculated and difference pattern of the neutron diffraction powder profile of zeolite N measured at 623 K. Table 2 lists derived positional parameters. According to the TGA data in Fig. 1, the sample should be dehydrated at 623 K. The release of H_2O from the sample is immediately evident from the much lower background at 623 than at 5 K, cf. Figs. 3 and 4.

During the dehydration chlorine atoms move from site 2*c* 0, 0, 1/2 to site 2*a* 1/2, 1/2, 1/2. The position of the potassium atom K1 is almost unchanged, but K2 moves from the position 0.217(2), 0.207(2), 0.433(1) to the position 0.270(3), 0.282(3), 0.435(1). This fits well with a new contact between K2 and a chlorine atom at 1/2, 1/2, 1/2. In the analysis of the powder patterns measured in the temperature range 293–623 K, the adopted model used a distribution of chlorine atoms over the two

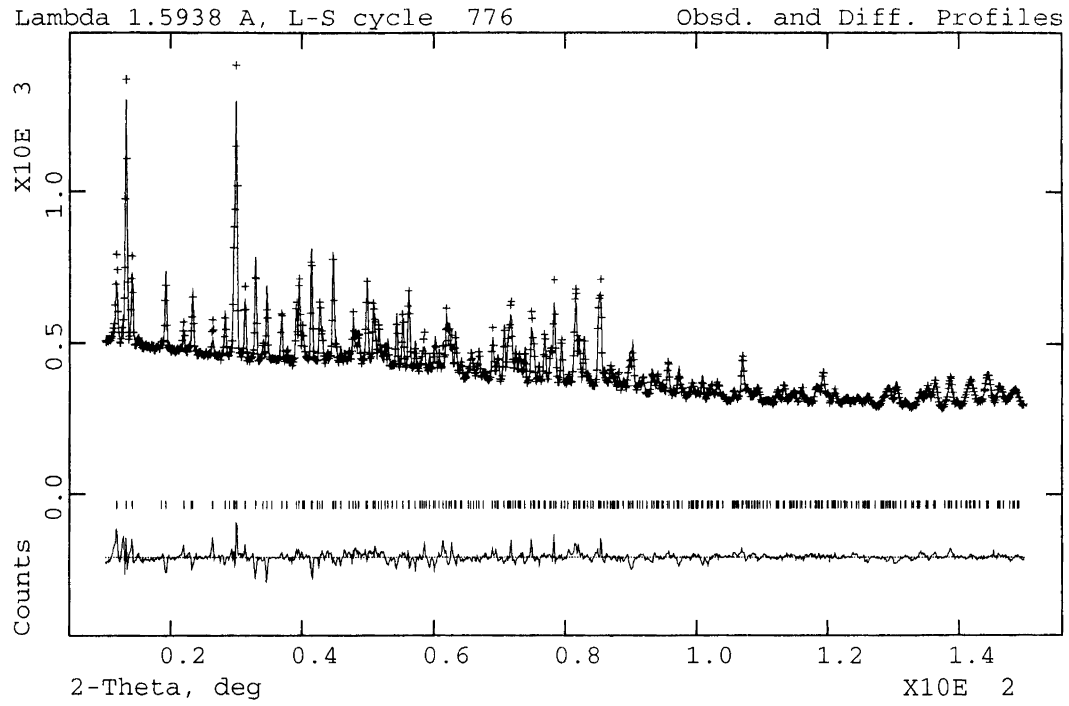

Fig. 3. Observed (+), calculated (line) and difference curves from Rietveld refinement of neutron powder diffraction data of zeolite N at 5 K, $\lambda = 159.38$ pm.

Table 1. Refined positional parameters for the structure of zeolite N. Neutron diffraction powder patterns recorded at 5 K.

Atom	Site	Occupancy factor	*x/a*	*y/b*	*z/c*
Al1	2*b*	1.0	1/2	0	0
Si1	2*d*	1.0	0	1/2	0
Al2	8*k*	1.0	0.339(1)	−0.109(1)	0.306(1)
Si2	8*k*	1.0	0.387(1)	0.167(1)	0.189(1)
O1	8*k*	1.0	0.392(1)	0.101(1)	0.073(1)
O2	8*k*	1.0	0.398(1)	0.907(1)	0.430(1)
O3	8*k*	1.0	0.307(1)	0.053(1)	0.259(1)
O4	8*k*	1.0	0.544(1)	0.190(1)	0.226(1)
O5	8*k*	1.0	0.309(1)	0.306(1)	0.188(1)
K1	4*i*	0.979	0	0	0.256(1)
K2	8*k*	0.979	0.217(2)	0.207(2)	0.433(1)
Cl	2*c*	0.918	0	0	1/2
OW1	8*k*	0.276(6)	0.426(4)	0.346(5)	0.428(4)
H1	8*k*	0.273(6)	0.459(3)	0.419(3)	0.515(3)
H2	8*k*	0.273(6)	0.463(4)	0.346(4)	0.429(4)

$a = 988.0(1)$, $b = 987.7(1)$, $c = 1306.4(1)$ pm. $R_P = 3.4\%$, $R_{WP} = 4.5\%$, $U = 287$, $V = -293$, $W = 278$, asymmetry parameter = 1.88.

positions 2*c* and 2*a*, and the potassium atom K2 distributed over the two 8*k* positions mentioned above. Only occupancy factors were refined for these statistically arranged atoms and for the three atoms of the water molecule. In addition, the positional parameters of the framework atoms and the potassium atom K1, the unit-cell parameters, scale factor, zero point and profile parameters were refined. The refinements show a reduction of the unit-cell volume which fits well with the loss in weight in the dehydration of zeolite N (see Fig. 1). The orthorhombic *a/b* ratio varied only slightly with temperature. The variation of the occupancies of the chlorine atoms and the K2 atoms are displayed in Fig. 5. No significant changes in the Al/Si–O framework were observed during the dehydration.

In the neutron powder diffraction experiment the degree of dehydration can be followed by evaluating the reduction in the background, since the incoherent scatterer H is released from the sample as H_2O and removed from the beam. The background variation of the patterns at $2\theta = 16°$ is displayed in Fig. 6. The lowering of the background fits very well the reduction in unit-cell volume displayed in Fig. 1b. The TGA data in Fig. 1a show the same trend, but the curve is shifted to higher temperatures. The sample sizes and timescales for the TGA and the neutron powder diffraction experiments are different, which may explain the above mentioned discrepancy. The dehydration in the neutron powder diffraction experiments is almost complete at 473 K. At this temperature the rearrangement of the chlorine atoms is well underway (Fig. 5a). The rearrangement of the potassium atom K2 starts around 473 K and appears hence to occur after rearrangement of the chlorine atom. The position of the potassium atom K1 is unchanged, which may explain that the rearrangement of the chlorine atoms must be faster than that of the potassium atom K2.

K1 has in the hydrated form of zeolite N contacts to six framework oxygen atoms with distances from 291 to 311 pm, to one chlorine atom at the distance 327 pm, and to the water molecules with the distances K1–OW2

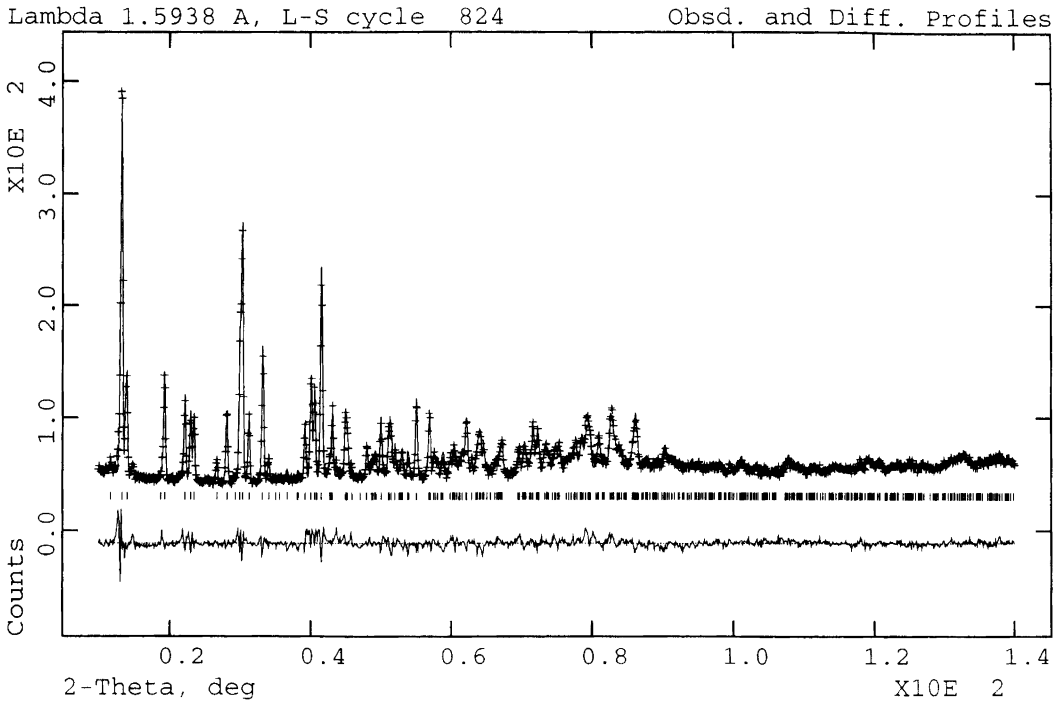

Fig. 4. Observed (+), calculated (line) and difference curves from Rietveld refinement of neutron powder diffraction data of zeolite N at 623 K, $\lambda = 159.38$ pm.

Table 2. Refined positional parameters for the structure of zeolite N. Neutron diffraction powder pattern recorded at 623 K.

Atom	Site	Occupancy factor	*x/a*	*y/b*	*z/c*
Al1	2*b*	1.0	1/2	0	0
Si1	2*d*	1.0	0	1/2	0
Al2	8*k*	1.0	0.335(1)	−0.111(1)	0.309(1)
Si2	8*k*	1.0	0.391(1)	0.163(1)	0.192(1)
O1	8*k*	1.0	0.396(1)	0.110(1)	0.071(1)
O2	8*k*	1.0	0.408(1)	0.899(1)	0.428(1)
O3	8*k*	1.0	0.318(1)	0.059(1)	0.275(1)
O4	8*k*	1.0	0.541(1)	0.200(1)	0.242(1)
O5	8*k*	1.0	0.312(1)	0.305(1)	0.191(1)
K1	4*i*	0.92(3)	0	0	0.242(2)
K21	8*k*	0.20(2)	0.216	0.206	0.432
K22	8*k*	0.68(3)	0.270(3)	0.282(3)	0.435(1)
Cl1	2*c*	0.06(2)	0	0	1/2
Cl2	2*a*	0.72(2)	1/2	1/2	1/2
OW1	8*k*	0.09(2)	0.424	0.341	0.425
H1	8*k*	0.09(2)	0.459	0.419	0.515
H2	8*k*	0.09(2)	0.463	0.346	0.429

$a = 977.9(1)$, $b = 974.3(1)$, $c = 1314.2(1)$ pm. $R_P = 4.2\%$, $R_{WP} = 5.7\%$, $U = 287$, $V = -293$, $W = 278$, asymmetry parameter = 1.88.

286 pm and K1–OW1 285 pm. K2 has contacts to four framework oxygen atoms with distances from 275 to 291 pm, to one chlorine atom at the distance 308 pm, and to the two water molecules with K2–OW1 249 pm and K2–OW2 300 pm. The chlorine atom has contact to six potassium atoms with four Cl–K2 308 pm and two Cl–K1 327 pm contacts.[1] The strive to maintain a high

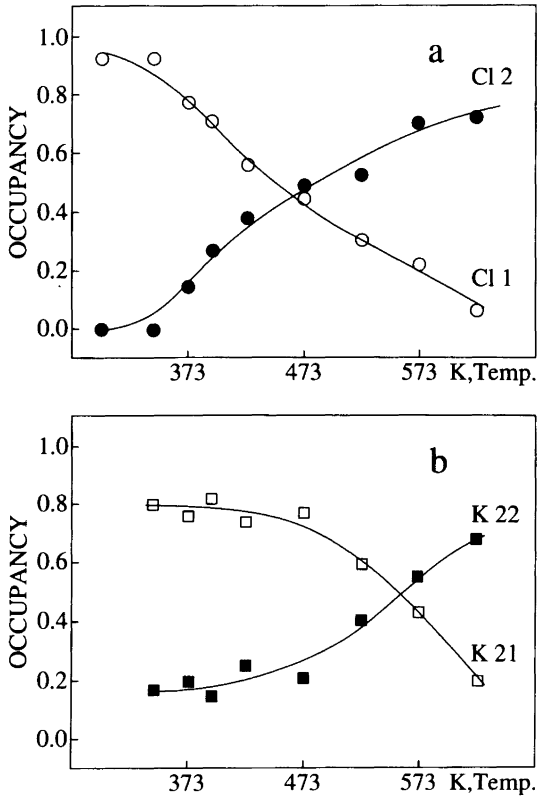

Fig. 5. (a) Occupancy of the chlorine atom in site 2*c* (Cl1) and site 2*a* (Cl2). (b) Occupancy of the potassium atom K2 in 0.217(2), 0.207(2), 0.433(1) (K21) and 0.270(3), 0.282(3), 0.435(1) (K22).

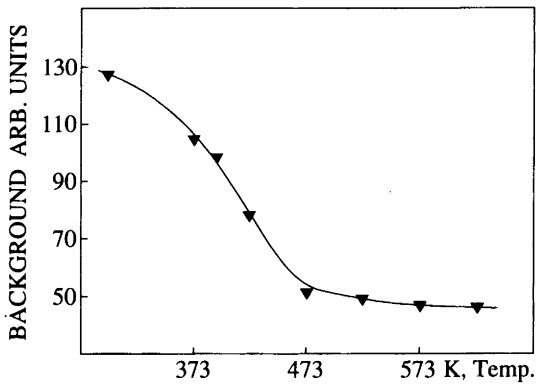

Fig. 6. Background of the neutron diffraction powder patterns at $2\theta = 16°$ plotted vs. temperature.

coordination number for the potassium and chlorine atoms is the reason for the movement of K2 and Cl when the water molecules leave the structure. In the dehydrated form K1 has contact to six framework atoms K1–O5 291 pm (×2), K1–O4 309 pm (×2), K1–O3 311 pm (×2), and to one chlorine atom K1–Cl 327 pm. The potassium atom K2 has contact to four framework atoms K2–O1 273 pm, K2–O2 279 pm, K2–O4 314 pm, K2–O5 324 pm, and to one chlorine atom K2–Cl 325 pm. The dehydration thus reduces the coordination number of K1 from nine to seven and that of K2 from seven to five. The chlorine atom has contact to six potassium atoms with Cl–K2 325 pm (×4) and with Cl–K1 327 pm (×2) in a distorted octahedral arrangement similar to that in the hydrated form of zeolite N, but with longer average Cl–K distances.

The dehydration of zeolite N is thus a process which is also combined with a rearrangement of the non-framework atoms chlorine and potassium. Many zeolites in the dehydrated form take up water readily. This is not the case for the dehydrated form of zeolite N. However, when dehydrated zeolite N is refluxed with D_2O for 5 h it is partly converted to the deuterated form. When a dry sample of this was used in a thermogravimetric analysis, it had a loss of weight of 6.3%. This is in good agreement with the formula $K_{12}Al_{10}Si_{10}O_{40}Cl_2 \cdot 7.2D_2O$, whereas the composition of a completely deuterated sample is $K_{12}Al_{10}Si_{10}O_{40}Cl_2 \cdot 8D_2O$.

The present neutron powder diffraction experiments demonstrate that the dehydration of the zeolite N is a complex process which involves major rearrangement of the 'salt' components in order to retain acceptable coordination environments.

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References

1. Christensen, A. N. and Fjellvåg, H. *Acta Chem. Scand. 51* (1997) 969.
2. Baerlocher, C. and Barrer, R. M. *Z. Kristallogr. 140* (1974) 10.
3. Ståhl, K. and Hanson, J. *J. Appl. Crystallogr. 27* (1994) 543.
4. Christensen, A. N. and Lehmann, M. S. *J. Solid State Chem. 51* (1984) 196.
5. Christensen, A. N., Lehmann, M. S. and Pannetier, J. *J. Appl. Crystallogr. 18* (1985) 170.
6. Christensen, A. N., Andersen, N. H. and Hoser, A. *Acta Chem. Scand. 52* (1998) 651.
7. Hewat, A. W. *Mater. Sci. Forum 9* (1986) 69.
8. Rietveld, H. M. *J. Appl. Crystallogr. 2* (1969) 65.
9. Larson, A. C. and von Dreele, R. B. GSAS, General Structure Analysis System, LANSCE, MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545 (1994).

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