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Analysis of Rietveld Method Application for Gyrolite Crystal Structure Refinement

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The several simulated X-ray diffraction patterns for calcium silicate hydrate – gyrolite were calculated with GSAS program using the structural model of natural mineral gyrolite and profile parameters values determined from refining crystal structure of real synthetic gyrolite. To determine the limits of the Rietveld method applicability for synthetic gyrolite crystal structure refinement, each simulated pattern was refined by using a biased starting structural model of gyrolite. The complete and precise refinement of all parameters of gyrolite crystal structure was achieved only using structural restraints on bond lengths in tetrahedral, octahedral and interlayer sheets of silicate.
Keywords: layered silicate, gyrolite, crystal structure, XRD, Rietveld refinement, bond restraints.

1. INTRODUCTION*

Natural mineral gyrolite is a layered calcium silicate hydrate (C–S–H where C = CaO; S = SiO_2; H = H_2O) with most likely chemical formula $NaCa_{16}Si_{24}O_{60}(OH)_8 \cdot 14H_2O$ [1]. This material could be a good substitute for polymeric flocculants, which widely were used for wastewater and industrial effluent treatment [2]. Particularly, the synthetic gyrolite recently has attracted attention as a sorbent for wastewater purification from hazardous heavy metals [3 – 6] and as a new generation chemically modified filler for polymeric nanocomposites [7]. In preparation of such filler the ion-exchange properties of gyrolite were adapted. In order to modify properly gyrolite the crystal structure peculiarities of this phylosilicate must to be known. X-ray diffraction analysis (XRD) and Rietveld refinement are the most suitable non-destructive techniques for this purpose [8, 9]. Especially useful feature is that the Rietveld refinement allows accurate determination of the occupancies of different crystallographic sites of various chemical elements [10]. Therefore, the Rietveld refinement of synthetic gyrolite crystal structure using the whole X-ray diffraction profile could help to study and to explain the phenomena of ion exchange taking place during synthesis and modification or application of gyrolite.

For a long period of time many scientists tried to solve crystal structure of natural mineral gyrolite [11 – 15]. Finally, the crystal structure of natural gyrolite has been solved by Merlino S. [1]. The structures of other natural minerals of the gyrolite-truscottite group have been solved with conventional single-crystal X-ray structural analysis too [16 – 18]. On the contrary there were few studies of synthetic gyrolite structure refinement using the Rietveld method however they were not completely clarified [19 – 21].

Stumm A., Garbev K. et al. [19] studying gyrolite as a storage material of heavy metals have used Rietveld method for refinement of the amount and position of Zn atoms incorporated into the X-sheet of gyrolite crystal lattice. During refinement the occupation degree of Na5 atom (notation according Merlino S. structure model) the authors equated to zero. In order to keep the number of the variable parameters as low as possible the atomic positions and temperature factors they did not refined.

Garbev K. [20] has developed a suitable strategy for crystalline C–S–H phase's refinement as well as possible sources of errors and specific problems has analyzed in detail. Also, many of C–S–H structural models author has confirmed by Rietveld refinement.

Renaudin G. et al. [21] performed Rietveld refinement of C–S–H and C–A–S–H phase's crystal structure of similar compositions to gyrolite. They have refined all (over 40) describing the structure and microstructure parameters. However, assuming that the amount of independent atomic sites (32) is too high and the diffraction peaks overlap to such an extent that it is impossible to separate them due to the low resolution of the X-ray powder patterns, the authors did not refined the atomic positions.

Literature examples show that it is important to establish a practical methodology for synthetic gyrolite crystal structure refinement using Rietveld method. The aim of this work is to study the conditions that determine the limits of Rietveld method application for refinement of all parameters of synthetic gyrolite crystal structure. These findings are expected could be suitable to adjust the methodology for refinement of complex crystal structures of other C–S–H, because many of those are composed of similar structural elements.

2. EXPERIMENTAL

Hydrothermal synthesis of gyrolite has been carried out in rotating autoclave (10 rpm) under the saturated steam pressure at 200 °C; the duration of isothermal curing was 72 hours. The molar ratio of primary mixture were $CaO/SiO_2 = 0.66$. These synthesis conditions were chosen according to previously published data [22].

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X-ray diffraction patterns of synthetic gyrolite and standards were recorded with a Brag-Brentano focusing geometry diffractometer DRON-6 at 35 kV and 20 mA. Pyrolitic graphite monochromator of diffracted beam was used to separate CuK_α ($\lambda = 0.15405$ nm) radiation. Scanning was carried out in a step scan mode with a step size of $\Delta 2\theta = 0.02°$ from 2° to 70° 2θ and a counting time of 10 sec/step. Equipment was calibrated by corundum Alfa Aesar α-Al_2O_3 (99.9 % purity) standard.

In order to obtain instrumental profile parameters of diffractometer DRON-6 the X-ray diffraction profile of the CeO_2 standard calcinated at 1300 °C temperature for 5 hours was collected by using the same experimental conditions. Both structural and microstructural parameters were subsequently refined in accordance with the theoretical model of the crystal structure of CeO_2 using program GSAS+EXPGUI [23, 24] and the Le Bail [25] as well as Rietveld profile fitting.

For purpose to evaluate the application limits of the Rietveld method to refine all parameters of the gyrolite crystal structure, the simulated X-ray diffraction pattern of gyrolite structure was generated with GSAS program, using the natural gyrolite crystal structure model with space group $P\bar{1}$ determined by Merlino S. (Table 1, Table 2 and Fig. 1) [1]. The crystal structure data of gyrolite were taken from the American Mineralogist Crystal Structure Database [26].

Table 1. Crystal lattice parameters of the natural mineral gyrolite [1, 26]

Parameter	*a*, nm	*b*, nm	*c*, nm	α, °	β, °	γ, °
Value	0.974	0.974	2.24	95.7	91.5	120

Table 2. Atomic positions, occupation parameters and temperature displacement parameters of the interlayer sheet of natural mineral gyrolite [1, 26]

Atom	*x*	*y*	*z*	Occupation	U_{iso}
Ca4	0.3302	0.6718	0.4983	1	0.05193
O1	0.2919	0.874	0.5464	1	0.11019
O2	0.0784	0.5475	0.4391	1	0.10132
O3	0.3931	0.4892	0.4478	1	0.15198
O4	0.5877	0.8303	0.5582	1	0.15958
Na5	0	0	0.5	1	0.17351
O5	0.7684	0.7748	0.4422	1	0.18998
O6	0.947	0.8255	0.5864	1	0.20644
O7	0.8687	0.1174	0.5489	1	0.19758

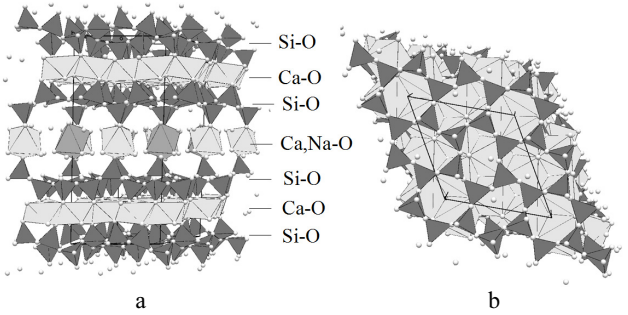

Fig. 1. Original crystal structure model of the natural gyrolite used for generating the simulated X-ray powder diffraction pattern: a – perspective view perpendicular to *c* parameter and b – projection along *c* parameter [1]

The refinements of simulated gyrolite crystal structure were performed with the program GSAS+EXPGUI using Le Bail and Rietveld methods too. The natural gyrolite crystal structure data determined by Merlino S. has been used as the initial structural model with space group – triclinic $P\bar{1}$, No. 2 (Table 1, Table 2 and Fig. 1) [1].

All polyhedral crystal structure drawings have been made by program DRAWxtl V5.3 [27].

3. RESULTS AND DISCUSSION

In order to generate the simulated X-ray diffraction pattern profile of gyrolite close to the real experimental profile, an experimental synthetic gyrolite profile function parameters that depend on the instrumental profile function as well as on the crystal structure of synthetic gyrolite must be evaluated. It was found that the diffractometer DRON-6 diffraction profile can be determined by a pseudo-Voigt function and Finger, Cox & Jephcoat [28] description of the reflection asymmetry, which describes the asymmetric profile distortion due to an axial divergence of the radiation.

Therefore, the simulated gyrolite diffraction pattern (Fig. 2, curve 1) was calculated using diffraction profile function parameters, determined by Le Bail and Rietveld methods from synthetic gyrolite diffraction pattern, recorded with a laboratory diffractometer.

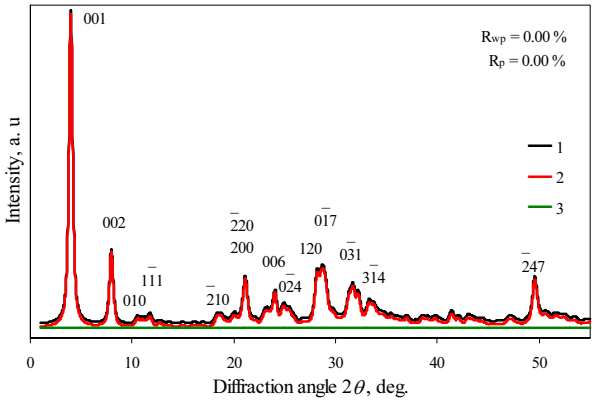

Fig. 2. X-ray powder diffraction patterns: 1 – the simulated using natural gyrolite structure model determined by S. Merlino (black), 2 – the calculated after the completion of Rietveld refinement (red), 3 – the difference between the simulated and the calculated diffraction profiles (green). The simulated and the calculated patterns are slightly shifted vertically for clarity (in color on-line)

Initially, the not biased crystal structure of Merlino S. model was refined. After several Rietveld refinement cycles of only the scale factor, the refined diffraction profile (Fig. 2, curve 2) fully coincides with the diffraction profile of the gyrolite structure theoretical model (Fig. 2, curve 1). The residual factors of the resulting difference profile are $R_{wp} = 0.00$ % and $R_p = 0.00$ % (Fig. 2, curve 3).

Testing and determination limits of the Rietveld method applicability for synthetic gyrolite crystal structure refinement was performed by changing in Merlino S. model the gyrolite crystal lattice parameters and the selected structural parameters such as: atomic coordinates, atomic occupation parameters and temperature displacement parameters. We have assumed that if the refined parameter will acquire the value statistically close to initial value after

completion Rietveld refinement, then it will be considered that the influence of this parameter on the change of diffraction profile is distinguishable by Rietveld method.

In the next step, the Merlino S. gyrolite crystal lattice parameters, all atomic coordinates, atomic occupation parameters in the interlayer sheet and all temperature displacement parameters were replaced by the false values of those parameters (Table 3, Table 4 and Fig. 3).

Table 3. Crystal lattice parameters of the starting biased gyrolite structure model

Parameter	a, nm	b, nm	c, nm	α, °	β, °	γ, °
Value	0.971	0.971	2.23	95.3	91.8	119

Table 4. Atomic positions, occupation parameters and temperature displacement parameters of the starting biased gyrolite structure model

Atom	x	y	z	Occupancy	U_{iso}
Ca4	0.33104	0.76263	0.49399	0	0
O1	0.40974	0.99503	0.5784	0	0
O2	0.25426	0.53789	0.4445	0	0
O3	0.4074	0.78957	0.48683	0	0
O4	0.79516	0.91383	0.58947	0	0
Na5	0	0	0.5	0	0
O5	0.83763	0.9044	0.44004	0	0
O6	0.75101	0.65744	0.51968	0	0
O7	0.87449	0.11872	0.52211	0	0

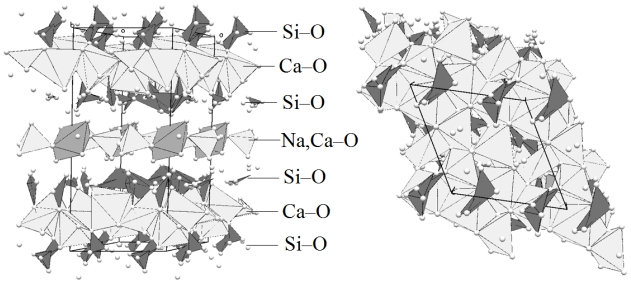

Fig. 3. The starting biased gyrolite structure model with wrong all atomic positions: a – perspective view perpendicular to c parameter and b – projection along c parameter

After one Rietveld cycle not refining any structural parameter the resultant diffraction curves are shown in Figure 4. The significant difference between the simulated (Fig. 4, curve 1) and the calculated (Fig. 4, curve 2) patterns shows that biased structural parameters values are far from those of initial structural model and the profile residual factors $R_{wp} = 44.1$ % and $R_p = 37.6$ % are very high.

After the simultaneous refinement of the crystal lattice parameters, all atomic positions, occupation parameters of the interlayer sheet and all temperature displacement parameters (overall 212 variables) the resultant fit of profiles (Fig. 5), the profile residual factors $R_{wp} = 0.24$ % and $R_p = 0.16$ % are very close to those in the initial stage (Fig. 2) and the refined lattice parameters (Table 5) differ little from the initial values (Table 1).

Although the diffraction profiles fits very well (Fig. 5, curves 1 and 2) and refined lattice parameters values (Table 5) suggest that the refinement has succeeded, however refined atomic coordinates are different from the Merlino S. model coordinates by values with standard deviations of the 0.1046, 0.1086 and 0.0432 in relative units, respectively in directions of x, y and z coordinates (Table 6).

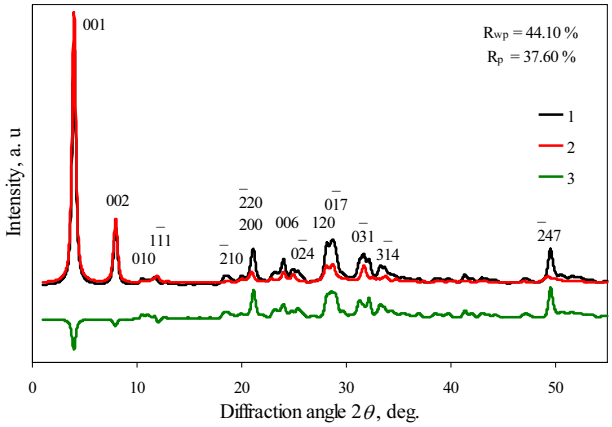

Fig. 4. X-ray powder diffraction patterns: 1 – the simulated of correct gyrolite structure model (black), 2 – the calculated of biased model after completion of one Rietveld cycle, when structural parameters were not refined, 3 – the difference between the simulated and the calculated patterns (in color on-line)

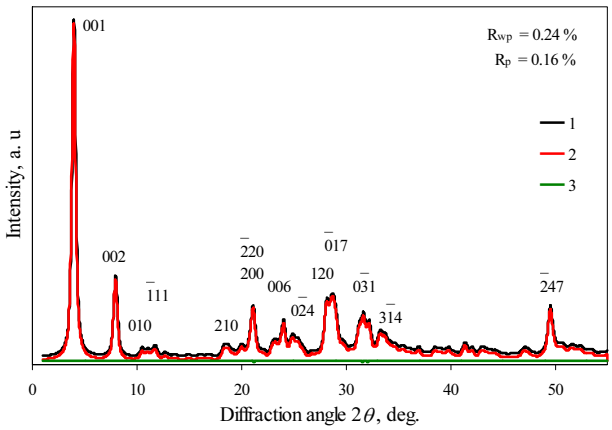

Fig. 5. X-ray diffraction patterns: 1 – the simulated of correct gyrolite structure model, 2 – the calculated pattern of biased gyrolite structure model after completion Rietveld refinement without using any structural restraints and constraints, 3 – the difference between simulated and refined patterns. The simulated and the calculated patterns are slightly shifted for clarity (in color on-line)

Table 5. Crystal lattice parameters of gyrolite crystal structure after completion Rietveld refinement free of restraints and constraints

Parameter	a, nm	b, nm	c, nm	α, °	β, °	γ, °
Value	0.9739	0.9741	2.2398	95.68	91.47	120

The obtained results show a statistically significant difference between the refined and actual values of the atomic positions. Also, atomic fractional occupancy parameters, especially of cationic Na atom, and temperature displacement parameters of interlayer sheet (Table 6) have highly different values from expected values indicating that

the refinement has failed. This conclusion is confirmed by final gyrolite structure perspective view shown in Figure 6 in which the Si-O tetrahedrons and Ca-O (Na-O) octahedrons are severely destroyed.

Table 6. Atomic positions, occupation parameters and isotropic temperature displacement parameters of the interlayer sheet of simulated gyrolite crystal structure after completion Rietveld refinement free of restraints and constraints

Atom	*x*	*y*	*z*	Occupancy	U_{iso}
Ca4	0.35735	0.74614	0.50739	0.99782	0.08488
O1	0.39405	1.09244	0.48264	0.89648	–0.03419
O2	0.17825	0.4591	0.45455	1.11519	0.04947
O3	0.21046	0.94813	0.59006	0.97543	–0.0079
O4	0.81508	1.02585	0.57837	1.25149	0.06016
Na5	0	0	0.5	–0.06812	0.19639
O5	0.71517	0.81908	0.4789	0.72282	0.012
O6	0.85724	0.65222	0.41392	0.96812	–0.02126
O7	1.0534	0.2641	0.51015	0.8879	0.03278

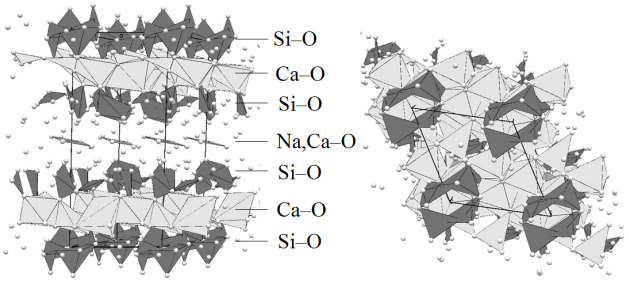

Fig. 6. The gyrolite structure after completion Rietveld refinement without using any structural restraints and constraints. a – perspective view perpendicular to *c* parameter and b – projection along *c* parameter

Therefore in the next step, the restraints (soft constraints) were applied for the bond lengths in the Si–O tetrahedrons and Ca–O octahedrons using the following bond lengths values: Si–O = 0.162 nm and O–O = 0.263 nm – in the silicate tetrahedrons; Ca–O = 0.24 nm, O–O = = 0.3394 nm and O–O = 0.48 nm – in the calcium octahedrons and Na–O = 0.24 nm – in the interlayer sheet. These bond lengths values have been calculated using global optimization method with program FOX [29]. Standard deviations for bond lengths were chosen 0.0015 nm – 0.002 nm as specified in literature [1]. Also the weights F for bond restraints were manually selected. After testing their influence on the geometry of the refined gyrolite crystal structure, the values of *F* during the refinement were gradually reduced from 1000 to 0.

After the simultaneous Rietveld refinement of gyrolite crystal lattice parameters, all atomic coordinates, atomic occupation parameters in the interlayer sheet and all temperature displacement parameters (overall 212 variables), the resulting diffraction profile acquired exactly the same shape as the simulated pattern and profile residual factors are identical to those gained in the simulated pattern profile refinement (Fig. 7), i. e. $R_{wp} = 0.00$ % and $R_p = 0.00$ %, whereas the difference between the atomic coordinates of gyrolite original model and of the refined biased model using soft constraints approaches to zero. Gyrolite crystal lattice atomic positions values (Table 7) were refined with standard deviations from Merlino S. model of 0.0010, 0.0010 and 0.0004 in relative units, respectively in directions of *x*, *y* and *z* coordinates. The obtained results show a statistically insignificant difference between the refined and the actual values of structural model atomic positions. This indicates that the crystal structure of gyrolite was refined correctly.

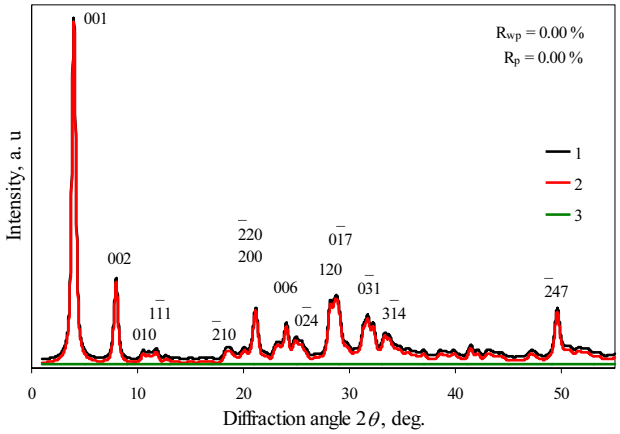

Fig. 7. X-ray diffraction patterns: 1 – the simulated of correct gyrolite structure model, 2 – the calculated of biased gyrolite structure model after completion Rietveld refinement using restraints on bond lengths, 3 – the difference between the simulated and refined patterns. The simulated and the calculated patterns are slightly shifted for clarity (in color on-line)

Table 7. Atomic positions, occupation parameters and isotropic temperature displacement parameters of the interlayer sheet of simulated gyrolite crystal structure after completion Rietveld refinement using restraints on bond lengths

Atom	*x*	*y*	*z*	Occupancy	U_{iso}
Ca4	0.32946	0.6713	0.49825	1.00875	0.05732
O1	0.29157	0.87329	0.54666	0.98884	0.10125
O2	0.07831	0.54817	0.43877	0.9936	0.09844
O3	0.39342	0.49074	0.44771	0.98229	0.14182
O4	0.58677	0.82991	0.55807	0.99377	0.15706
Na5	0	0	0.5	0.98368	0.16737
O5	0.76902	0.77268	0.44329	1.02151	0.20668
O6	0.94627	0.82473	0.58654	1.01297	0.21406
O7	0.86691	0.11543	0.54846	1.0069	0.20195

After completion Rietveld refinement using restraints on bond lengths the gyrolite crystal lattice perspective view (Fig. 8) is highly comparable to the Merlino S. model (Fig. 1) and also confirms successful refinement result.

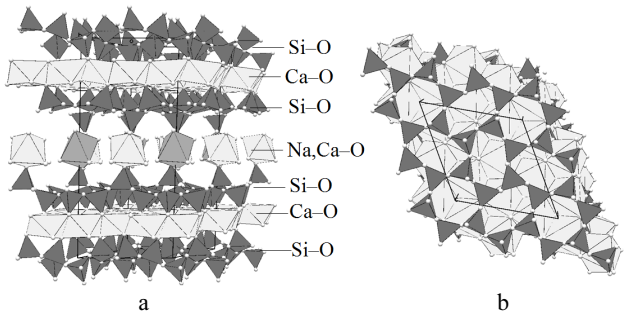

Fig. 8. The gyrolite structure after completion Rietveld refinement using structural restraints on bond lengths: a – perspective view perpendicular to *c* parameter and b – projection along *c* parameter

Refined crystal lattice parameters of gyrolite gained identical values (Table 8) as in the initial model (Table 1).

Table 8. Crystal lattice parameters of gyrolite crystal structure after completion Rietveld refinement using restraints on bond lengths

Parameter	*a*, nm	*b*, nm	*c*, nm	*α*, °	*β*, °	*γ*, °
Value	0.974	0.974	2.24	95.7	91.5	120

Other refinement result was achieved when statistical noise was added to the simulated X-ray diffraction profile of gyrolite crystal structure model (Fig. 9). The X-ray profile with standard deviation value of 6.8 % from ideal profile have been generated with program GSAS.

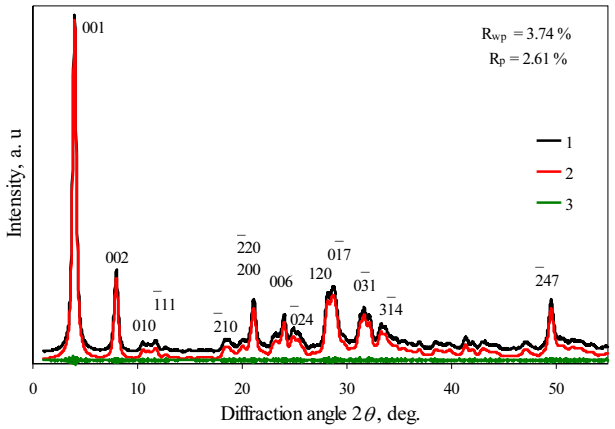

Fig. 9. X-ray diffraction patterns: 1 – the simulated of correct gyrolite structure model with added statistical noise, 2 – the calculated of biased gyrolite structure model after completion Rietveld refinement using restraints on bond lengths, 3 – the difference between the simulated and refined patterns. The simulated and the calculated patterns are slightly shifted for clarity (in color on-line)

In this case the final Rietveld refinement results are much higher (the received profile residuals R_p = 3.74 % and R_{wp} = 2.5 %) when compared to those obtained in the previous refinement, however the refined gyrolite crystal structure perspective view in Figure 10 is nearly identical to initial Merlino S. gyrolite structure model.

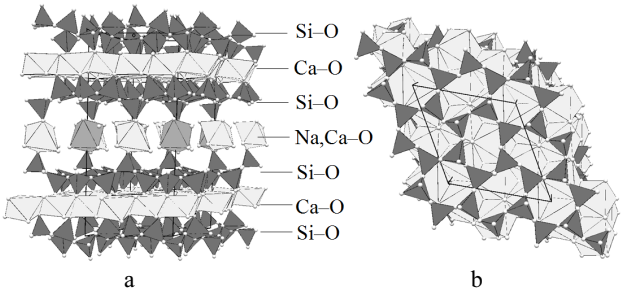

Fig. 10. The gyrolite structure after completion Rietveld refinement of simulated with noise diffraction pattern using structural restraints on bond lengths: a – perspective view perpendicular to *c* parameter and b – projection along *c* parameter

The atomic positions values (Table 9) and standard deviations values of 0.0048 and 0.0052 for *x* and *y* coordinates respectively and 0.0016 for *z* coordinate suggest that refinement have succeeded. This result have been obtained only using bond restraints weight *F* = 0.6.

Despite the obtained possibly good results, the crystal lattice parameters (Table 10) and especially occupation parameters and temperature displacement parameters of the interlayer sheet of simulated gyrolite crystal structure have acquired values (Table 9) noticeably different from those of initial structure model (Table 1).

Table 9. Atomic positions, occupation parameters and temperature displacement parameters of the interlayer sheet after completion Rietveld refinement of simulated with noise diffraction pattern using restraints on bond lengths

Atom	*x*	*y*	*z*	Occupancy	U_{iso}
Ca4	0.3308	0.6725	0.4986	1.133	0.109
O1	0.2939	0.8798	0.5494	0.784	0.061
O2	0.0809	0.5451	0.4384	1.044	0.15
O3	0.394	0.482	0.4517	0.603	–0.002
O4	0.5865	0.8283	0.5565	1.078	0.245
Na5	0	0	0.5	0.8	0.145
O5	0.7716	0.7685	0.4429	1.099	0.144
O6	0.9332	0.8193	0.5853	1.443	0.435
O7	0.8593	0.1121	0.5492	0.881	0.162

Table 10. Crystal lattice parameters of gyrolite crystal structure after completion Rietveld refinement of simulated with noise diffraction pattern using restraints on bond lengths

Parameter	*a*, nm	*b*, nm	*c*, nm	*α*, °	*β*, °	*γ*, °
Value	0.97384	0.97394	2.2402	95.72	91.51	119.98

For purpose to improve the refinement quality the values of atomic occupation parameters of the interlayer sheet were accepted equal to 1. Refining the lattice parameters, atomic positions and temperature displacement parameters (overall 203 variables) slightly decreased residuals to R_{wp} = 3.73 % and R_p = 2.55 %. In this case the standard deviations of atomic positions values decreased to 0.0038 and 0.0039 for *x* and *y* coordinates respectively and 0.0015 for *z* coordinate. These results have been obtained using bond restraints weight *F* = 0.3.

CONCLUSIONS

The refinement of gyrolite crystal structure theoretical model proved that the Rietveld method is suitable for determining not only the crystal lattice parameters of the lowest crystallographic symmetry compounds, but also the atomic coordinates of all atoms and the quantity of cationic atoms intercalated in the interlayer sheet of gyrolite crystal lattice.

The refinement of gyrolite structure all parameters could be achieved only using restraints (soft constraints) on bond lengths of Si–O = 0.162 nm and O–O = 0.263 nm in the tetrahedral sheets, Ca–O = 0.24 nm, O–O = 0.34 nm, O–O = 0.48 nm and Na–O = 0.24 nm in the octahedral and in the interlayer sheets. In this case the refinement of 212 variables have yielded the profile residual R_p = 0.00 % and the weighted profile residual R_{wp} = 0.00 %. Atomic positions were refined with standard deviations of 0.0010 and 0.0010 for *x* and *y* coordinates respectively and 0.0004 for *z* coordinate. The obtained refinement results indicate statistically insignificant differences from the true parameters values of the initial gyrolite structural model. The gyrolite structure was refined perfectly.

When the statistical noise was added to the simulated profile, the refinement yielded worse profile residuals R_p = 3.73 % and R_{wp} = 2.55 %. Even so the gyrolite crystal structure was refined correctly too. The atomic positions were refined with standard deviations of 0.0038 and 0.0039 for *x* and *y* coordinates respectively and 0.0015 for *z* coordinate. The latter refinement showed that for purpose to receive the proper results of refinement of compounds having lowest crystallographic symmetry the best possible quality of X-ray powder data from those specimens must be collected.

The Rietveld refinement of simulated X-ray diffraction pattern of gyrolite crystal structure, i. e. crystal lattice parameters, all atomic positions, all atomic displacement parameters, and fractional occupation parameters of interlayer atoms (overall 212 variables) without using restraints have yielded the profile residual R_{wp} = 0.24 % and the weighted profile residual R_p = 0.16 %. Atomic positions were refined with standard deviations of 0.1046 and 0.1086 for *x* and *y* coordinates respectively and 0.0432 for *z* coordinates. The gyrolite structure was not refined correctly despite the fact that the calculated profile was fitted quite well to the simulated pattern.

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