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Rietveld Structure Refinement of the Kyanite Crystal from Negovanu (Sebeş-Lotru Series) Using X-ray Powder Diffraction Data

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Abstract

Kyanite is one of the three Al2SiO5 polymorphs, the other two being andalusite and sillimanite. The three aluminum silicate polymorphs (kyanite, sillimanite, and andalusite) are of major importance in metamorphic and experimental petrology because of their abundance in metamorphosed lutitic rocks and relatively simple chemistry.

The crystal structure of kyanite sampled from crystalline schists of Sebeş-Lotru Series (Negovanu, Cibin Mountains, Romania) from Getic nappe of Southern Carpathians has been refined using X-Ray powder diffraction data and the Rietveld method. The Rietveld refinements were carried out using the computer program Diffrac^{plus} TOPAS 4.1 (Bruker AXS GmbH). Pseudo-Voigt (pV) profile function was used for the fit of the peaks. Rietveld refinement using X-Ray powder diffraction data of kyanite sample in space group P-1 (No.2), a=7.1491Å, b=7.8792Å, c=5.5912Å, α=89.75º, β=101.16º, γ=105.92º, Z=4, confirm the basic kyanite structure.

Key words: *crystal structure, kyanite, X-ray powder diffraction, Rietveld refinement*

Introduction

The Rietveld refinement technique using X-ray powder diffraction data provides a valuable approach for studying structures of minerals that do not form crystals suitable for single-crystal experiments. Basically, the Rietveld method uses analytical profile functions and least-squares algorithms to fit a theoretical to a measured pattern. Rietveld's work opened the path to extract detailed crystal structure information from powder diffraction using neutron and X-ray data. These days, the Rietveld method is not only used for structure analysis, but also for the quantification of multi-phase mixtures and the determination of the crystallite microstructure which covers size and strain. The method has been successfully used to refine structures for a variety of minerals and compounds [1, 2, 3, 4].

In the present study we used the Rietveld method to refine the crystal structure of the kyanite. The kyanite samples were collected from crystalline schists of Sebeş-Lotru Series from Negovanu (Cibin Mountains – Romania).

Crystalline schists of Sebeş-Lotru Series [5, 6] have widely developed in Sebeş Mountains, Cibin Mountains and Lotru Mountains, hence extending south and west until contact with Danubian autochthon. Crystalline schists of Sebeş-Lotru Series belong to the Upper pre-Proterozoic, and differ from other parts with a more advanced metamorphism. They are crossed

by alkaline rocks ultrabasics. In the central part of the Sebeş Mountains and western part of the Mountains Cibin are widespread micaschists with garnet, kyanite and staurolite [7, 8]. They also contain intercalations of amphibolites, paragneisses and schists with manganese silicates and gradually go down to quartzo-feldspathic gneisses complex, which is more widely spread in the southern part of the Sebeş Mountains.

Micaschistes represent most of the superior complex of Sebeş Mountains and of the western part of Cibin Mountains. These rocks occur in different varieties, among which there stand micaschistes with biotite, micaschistes with kyanite, micaschistes with staurolite. They have usually porphyroblastic texture, rendered by large crystalloblasts of kyanite, staurolite or almandine; large crystalloblasts of kyanite are grouped in lenses forming true kyanites. Micaschists usually consist of quartz, muscovite and biotite, as fundamental mass, wherein the abovementioned "index mineral" porphyroblasts develop. Accessory minerals represented by tourmaline, magnetite, ilmenite, and rarely hornblende [8].

Sebeş-Lotru series was metamorphosed into amphibolite facies conditions, and thus dependent on the degree of metamorphism the following areas of metamorphism can be identified: sillimanite area, kyanite and staurolite area and garnet area. The width of the first area is reduced; it is maintained along the Lotru valley and in Cibin basin valley [7, 9]. Kyanite and staurolite area overlaps most of Sebeş-Lotru series, therefore micaschistes from superior complex often present quartz-kyanite-staurolite-almandine-muscovite-biotite paragenesis. Crystalline schists in the northern area are metamorphosed under the conditions of the almandine zone.

Experimental Data

The sample was ground in an agate mortar with pestle to particle size smaller than about 20μm. X-ray powder diffraction data were measured at 24ºC using an automated Bruker D8 Advance θ-θ diffractometer, with CuKα radiation (λ = 1,54Å; 40kV; 40mA), a LynxEye solid-state Si detector and Bragg-Brentano geometry. Kβ radiation was eliminated by a Ni filter. Primary and secondary Soller slits were 2.5º. A fixed aperture and divergence slit of 0.6mm, a 0.6mm antidivergence slit and 0.1mm width detector slit were used. Data were obtained using 0.1º 2θ steps from 10º to 60º 2θ counting for 1 s per step. The powder was placed into a cavity mount in an attempt to minimize preferred orientation.

The Rietveld refinements were carried out using Diffrac^{plus} TOPAS 4.1 computer program (Bruker AXS GmbH). Pseudo-Voigt (pV) profile function was used for the fit of the peaks; the result of measurement shows that the peaks shape is Lorentzian. No effects due to surface roughness or preferred orientation were detected during refinements process.

During refinements, the positions of all atoms in the kyanite structure, along with individual isotropic temperature factors and the occupancies of the $^{[6]}$Al and $^{[4]}$Si sites were varied. Changes in site occupancies of the $^{[6]}$Al and $^{[4]}$Si sites were constrained to observe the measured composition.

Results and discussions

Rietveld refinement using X-Ray powder diffraction data of kyanite sample in space group *P*-1 (No.2), *a*=7.1491Å, *b*=7.8792Å, *c*=5.5912Å, α=89.75º, β=101.16º, γ=105.92º, confirm the basic kyanite structure. The goodness-of-fit, represented by *S* (Rwp/Rexp) was *S*=0.689. The parameters which represent the quality of the Rietveld refinement are in Table 1. Figure 1 shows a graphical representation of final Rietveld refinement (calculated data), the observed data and the difference between them.

Table 1. Rietveld quality parameters refinement.

Parameter	Value	Error
a (Å)	7.1491	0.003
b (Å)	7.8792	0.002
c (Å)	5.5912	0.002
α (º)	89.75	0.03
β (º)	101.16	0.02
γ (º)	105.92	0.05
Cry size L (nm)	99.95	9.65
LVol-IB (nm)	4464.16	5.73
LVol-FWHM (nm)	5400.52	8.98
Strain L	0.072	0.12
*e*0	0.019	0.02
Rexp (%)	18.43	-
Rwp (%)	26.72	-
Rp (%)	15.43	-
S (GOF)	1.45	-

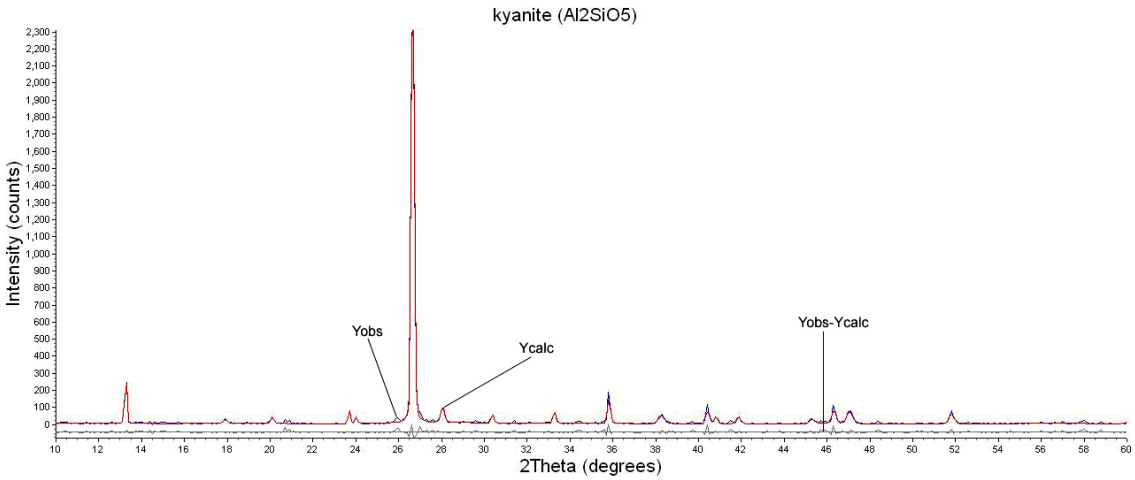

Fig. 1. Final Rietveld refinement showing the observed, calculated and difference pattern between both.

Compared to sillimanite and andalusite, kyanite is the high-pressure phase in the Al2SiO5 system. The crystal structure of kyanite was first deduced by Naray-Szabo et al. (1929) from the determination of staurolite structure and refined by Burnham (1963) from single-crystal X-ray diffraction data. It can be considered as distorted cubic closely-packed arrangement of O atoms, with 10% of the tetrahedral sites filled with Si and 40% of the octahedral sites filled with Al. The 12-14% higher density of kyanite compared to sillimanite and andalusite is partly influenced by this closely-packing feature. There are four crystallographically distinct Al sites (Al1, Al2, Al3, and Al4), and two Si sites (Si1 and Si2). The Al1 and Al2 sites are in the zigzag edge-sharing octahedral chains. The chains are cross-linked by alternating SiO4 tetrahedra and AlO6 octahedra with Si1 and Al4 on the one side and Si2 and Al3 on the other. The Al1 and Al3 octahedra share five edges with neighboring octahedral, whereas Al2 and Al4 share four edges with adjacent octahedral [10, 11, 12, 13]. Unit cell parameters and atomic coordinates are shown in table 2. Figure 2 shows the position of the atoms in refined structure of kyanite. Figure 3 shows 3D view of kyanite structure with AlO6 octahedra and SiO4 tetrahedra positions resulted from Rietveld refinement.

Table 2. Unit cell and atomic coordinates for kyanite derived from Rietveld refinement.

Space group *P*-1 (No.2), *Z*=4 *a*=7.1491Å, *b*=7.8792Å, *c*=5.5912Å, α=89.75º, β=101.16º, γ=105.92º							
Atom	Site	Np	x	y	z	Occ	Beq
Al1	s1	2	0.32573	0.70274	0.46405	1	1
Al2	s2	2	0.29819	0.69707	0.93633	1	1
Al3	s3	2	0.10024	0.38734	0.64014	1	1
Al4	s4	2	0.11131	0.91843	0.17239	1	1
Si1	s5	2	0.29761	0.06853	0.70768	1	1
Si2	s6	2	0.28774	0.32804	0.18198	1	1
O1	s7	2	0.10966	0.14666	0.12840	1	1
O2	s8	2	0.12564	0.68781	0.18140	1	1
O3	s9	2	0.27557	0.45100	0.96207	1	1
O4	s10	2	0.28094	0.93864	0.93424	1	1
O5	s11	2	0.10162	0.14712	0.66709	1	1
O6	s12	2	0.12279	0.62906	0.63903	1	1
O7	s13	2	0.28293	0.44545	0.42656	1	1
O8	s14	2	0.28852	0.94821	0.46184	1	1
O9	s15	2	0.50522	0.27666	0.26163	1	1
O10	s16	2	0.50102	0.23197	0.74819	1	1

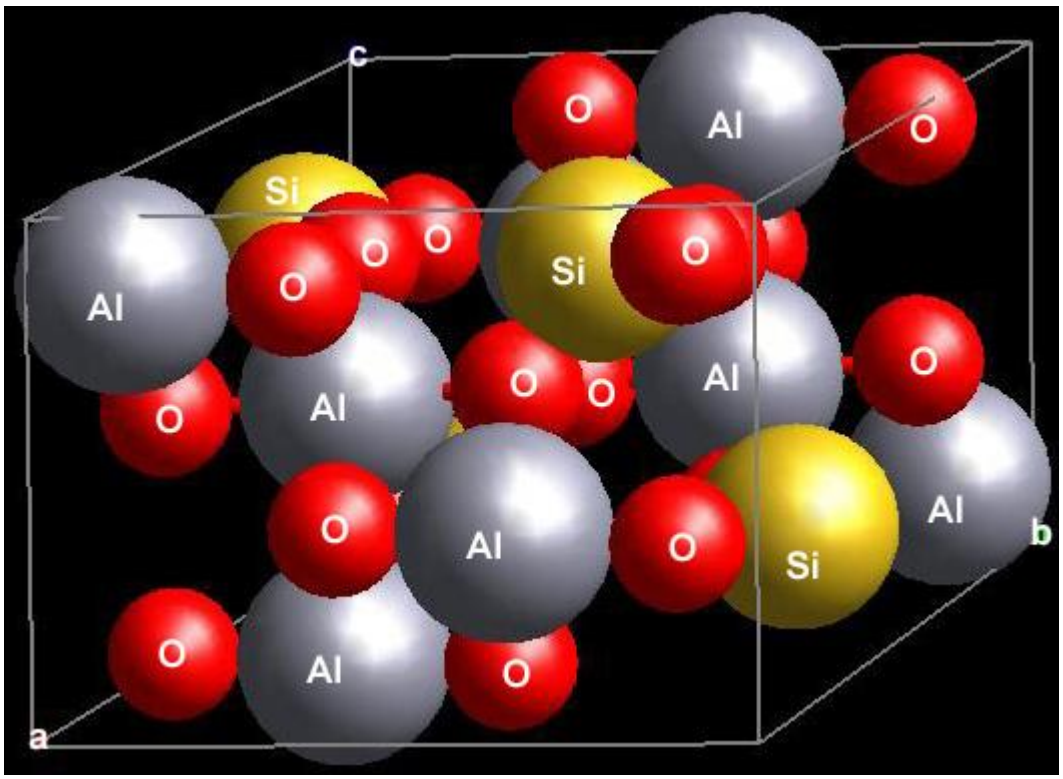

Fig. 2. The position of the atoms in refined structure of kyanite.

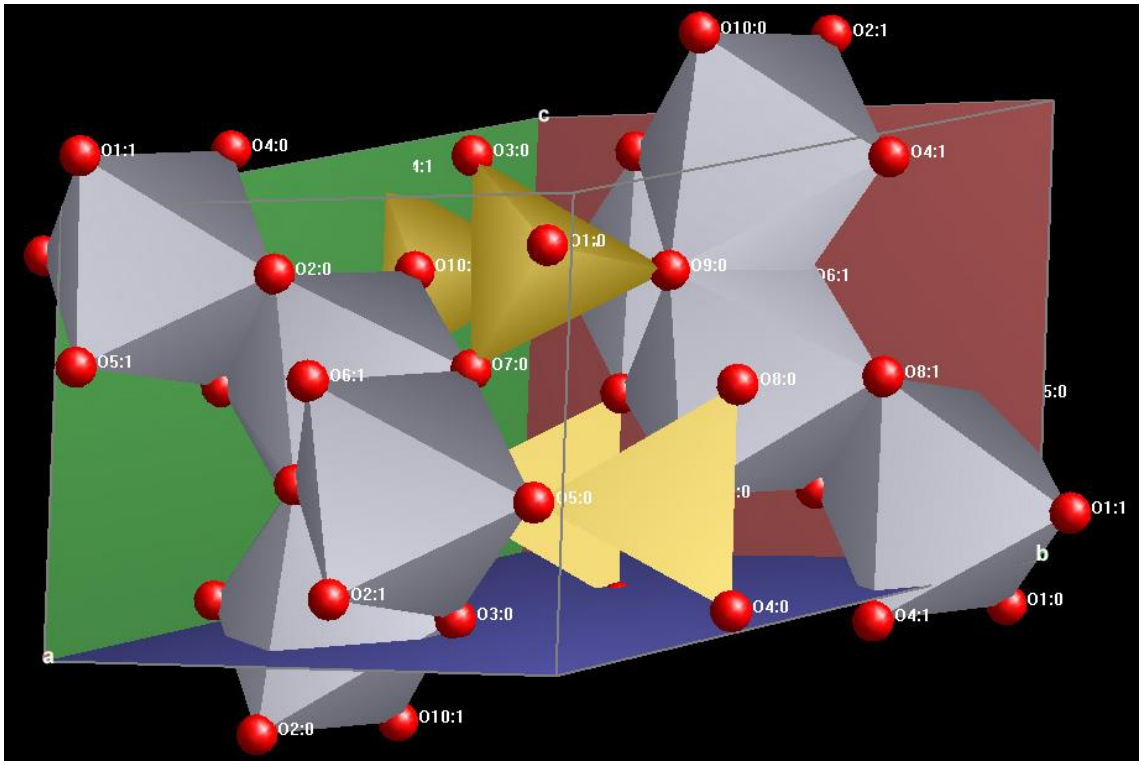

Fig. 3. 3D view of kyanite structure resulted from Rietveld refinement
(Al atoms in center of octahedra and Si atoms in center of tetrahedra).

Conclusions

Kyanite is one of the three aluminum silicate polymorphs, the other two being andalusite and sillimanite. Formed in metamorphosed aluminous rocks at moderate temperatures and moderate to high pressures, kyanite may be associated with garnet, corundum and staurolite, the latter having a crystal structure that is very closely related to the structure of kyanite. In the kyanite structure, aluminums are coordinated by six oxygens, while silicons are coordinated by four oxygens. The oxygen atoms are arranged in a closely-packed way.

The crystal structure of kyanite from Sebeş-Lotru Series (Negovanu, Cibin Mountains, Romania) was refined by means of the Rietveld method using X-ray powder diffraction data. These kyanite crystals may have a negative effect on the final results due to the contamination of the sample with muscovite and quartz (considering the fact that the kyanite crystals were sampled from a micaschist made up of quartz, muscovite and kyanite).

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Rafinarea Rietveld a structurii cristaline a distenului de la Negovanu (seria de Sebeş-Lotru) utilizând date de difracţia razelor X pe puberi

Rezumat

Distenul este una din cele trei faze polimorfe ale silicatului de aluminiu Al2SiO5, celelalte două fiind andaluzitul şi sillimanitul. Cele trei faze polimorfe ale silicatului de aluminiu Al2SiO5 prezintă o importanţă majoră în petrologia metamorfică şi experimentală datorită abundenţei lor în rocile lutitice metamorfozate şi a chimiei relativ simple.

Structura cristalină a unor cristale de disten prelevate din şisturile cristaline ale Seriei de Sebeş-Lotru (Negovanu, Munţii Cibinului) din Pânza Getică a Carpaţilor Meridionali a fost rafinată folosind difracţia de raze X pe pulberi şi metoda Rietveld. Rafinarea Rietveld a fost realizată cu ajutorul programului de calculator Diffrac^{plus} TOPAS 4.1 (Bruker AXS GmbH). Pentru potrivirea peakurilor a fost folosită funcţia pseudo-Voigt (pV). Rafinarea Rietveld utilizând date de difracţie de raze X pe pulberi a eşantionului de disten în grupul spaţial P-1 (No.2), a=7.1491Å, b=7.8792Å, c=5.5912Å, α=89.75º, β=101.16º, γ=105.92º, Z=4, a confirmat structura de bază a distenului.