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The Rietveld Refinement of Beryls from Pegmatitic System at Piława Górna, Góry Sowie Block, SW Poland

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The studied beryl crystals came from the Julianna pegmatitic system exposed in the Dolnośląskie Surowce Skalne S.A. quarry at Piława Górna. This mineral occurs here in various forms and colours (green, yellow, white, pinkish and blue) in almost all pegmatite bodies. The paper describes the relationship between the structure and chemical composition of different coloured beryl crystals.

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1. Introduction

The beryl group consists of five mineral species:
beryl, $^{2a,2b}\square^{T2}\,Be_3^{O}Al_2(^{T1}Si_6O_{18})$;
bazzite, $^{2a,2b}\square^{T2}\,Be_3^{O}Sc_2(^{T1}Si_6O_{18})$;
stoppaniite, $^{2a,2b}\square^{T2}\,Be_3^{O}Fe_2^{3+}(^{T1}Si_6O_{18})$;
pezzottaite, $^{2a}Cs^{2b}\square^{T2}(LiBe_2)^{O}Al_2(^{T1}Si_6O_{18})$;
andindialite, $^{2a,2b}\square^{T2}(Al_2Si)^{O}Mg_2[^{T1}(Al_2Si_4)O_{18}]$,
where superscripts give occupied site symbols and $\square$ is a symbol of vacancy. Only beryl is widespread as a common accessory component of many rare-element pegmatites, sometimes found in the form of perfectly transparent and variously coloured crystals of gemstone quality.

Beryl, bazzite, stoppaniite, and indialite have hexagonal symmetry (space group $P6/mcc$), whereas pezzottaite is rhombohedral with space group $R3c$ [1, 2]. In the structure of all these minerals, flat Si_6O_{18} rings are spatially arranged one above another and linked by Be tetrahedra (T2) and Al octahedra (O), forming a lattice with open channels oriented along the crystallographic c-axis. The channels include 5.1 Ålarge cavities separated by smaller constrictions of approximately 2.8 Åin diameter. Alkali cations (Na^+, K^+, Rb^+ and Cs^+), and also traces of Ca^{2+} and water molecules can be located within the channels in two different positions: 2a and 2b with coordinates (0,0,1/4) and (0,0,0), respectively [3].

Recently, compositionally and colouristic differentiated beryl crystals have been found in a pegmatitic system at Piława Górna, the Góry Sowie Block, SW Poland [4]. Beryl is a common minor to accessory component of these pegmatites and occurs in the form of non-transparent, greenish to yellowish and bluish crystals, up to ≈30 cm in length, in NYF-affiliated (Nb–Y–F) bodies, and yellowish, white and pinkish crystals, up to ≈10–12 cm in length, in LCT-affiliated (Li–Cs–Ta) pockets.

2. Experimental details

Electron microprobe analyses of beryl were performed at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances at the University of Warsaw, using a Cameca SX 100 electron microprobe operating in wavelength-dispersive mode under the following conditions: accelerating voltage of 15 kV, beam current of 20 nA, beam diameter of 3 μm, peak count-time of 20 s, background time of 10 s. Standards, analytical lines, diffracting crystals and mean detection limits (in wt%) were as follows: albite — Na (K_α, TAP, 0.02), diopside — Si (K_α, TAP, 0.02), Mg (K_α, TAP, 0.01) and Ca (K_α, PET, 0.02), orthoclase — Al (K_α, TAP, 0.01) and K (K_α, PET, 0.02), rutile — Ti (K_α, LPET, 0.02), rhodonite – Mn (K_α, LIF, 0.06), hematite — Fe (K_α, LIF, 0.06), Cr_2O_3 — Cr (K_α, LPET, 0.06), V_2O_5 — (K_α, LIF, 0.06), pure Sc — Sc (K_α, LPET, 0.02), Rb-glass — Rb (L_α, TAP, 0.04) and Cs-glass — Cs (L_α, LPET, 0.07). The raw data were reduced with the PAP routine [5]. Compositional formulae were normalized to 18 O atoms per formula unit (apfu), with Li_2O and BeO iterated on the basis of the total sum of the analyzed tetrahedral and octahedral cations and calculated Li and Be equal to 11 apfu. It was assumed that substitutions in the T1, T2, and O sites are completely charge balanced by channel cations, i.e. $^{T1}Al+{}^{O}Mg+{}^{O}Fe+{}^{O}Mn-{}^{O}Ti-2{}^{T2}Si-{}^{T2}Al+{}^{T2}Li = Na+K+Rb+Cs+2Ca$, according to the procedure proposed by Aurisicchio et al. [6].

The X-ray diffraction experiments were carried out on powdered samples in the range of 10–140° (2θ) using Empyrean PANalytical diffractometer (Co K_α radiation with $\lambda = 1.78901$ Å) equipped in PIX-cell^{3D} detector. The phase identification was carried out using the X'Rayan computer program and X-ray standard patterns in the form of ICDD files (card 09-0430). The unit-cell refinement (Table I) and Rietveld structure refinement were made using the FullProf Suite computer program package [7].

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3. Results and discussion

The averaged chemical composition for green and light green beryl crystals, coming from the NYF-affiliated bodies, can be defined as $(Na_{0.04-0.14}Rb_{0.00-0.01}Cs_{0.00-0.02})(Be_{2.18-3.00}Li_{0.00-0.56}Al_{0.00-0.02}Si_{0.00-0.25})(Al_{1.80-1.97}Mg_{0.00-0.08}Fe_{0.01-0.14})(Si_{5.99-6.00}Al_{0.00-0.01})O_{18}$ and $(Na_{0.04-0.12}Rb_{0.00-0.01}Cs_{0.00-0.02})(Be_{2.23-2.98}Li_{0.02-0.54}Si_{0.00-0.24})(Al_{1.90-1.98}Mg_{0.00-0.03}Fe_{0.01-0.08})(Si_{5.98-6.00}Al_{0.00-0.02})O_{18}$, respectively, while for a bluish crystal as $(Na_{0.08-0.26}K_{0.00-0.01}Rb_{0.00-0.01}Cs_{0.00-0.05}Ca_{0.00-0.01})(Be_{2.36-2.95}Li_{0.05-0.49}Si_{0.00-0.17})(Al_{1.95-1.98}Mg_{0.00-0.01}Fe_{0.02-0.05}Mn_{0.00-0.01})Si_{6.00}O_{18}$. Pinkish and light pinkish crystals originated from a nest of (Cs,Li)-bearing mineralization have the compositions $(Na_{0.06-0.32}K_{0.00-0.05}Rb_{0.00-0.02}Cs_{0.01-0.74}Ca_{0.00-0.03})(Be_{1.61-2.79}Li_{0.16-1.12}Si_{0.00-0.28})(Al_{1.97-2.00}Mg_{0.00-0.02}Fe_{0.00-0.02}Mn_{0.01})(Si_{5.99-6.00}Al_{0.00-0.01})O_{18}$, respectively, while a yellowish crystal $(Na_{0.02-0.34}K_{0.00-0.01}Rb_{0.00-0.01}Cs_{0.00-0.32}Ca_{0.00-0.01})(Be_{1.64-2.74}Li_{0.20-1.09}Si_{0.06-0.27})(Al_{1.92-2.00}Mg_{0.00-0.03}Fe_{0.00-0.07}Mn_{0.00-0.01})Si_{6.00}O_{18}$.

Figure 1 presents the diffraction patterns registered for all studied beryl samples. Figure 2 shows an exemplary unit-cell packing for light pink beryl. Structure refinement details for all studied beryl crystals were shown in Table I (at the end). In the samples of yellowish beryl and blue beryl the presence of additional phases (quartz and albite, respectively) was observed.

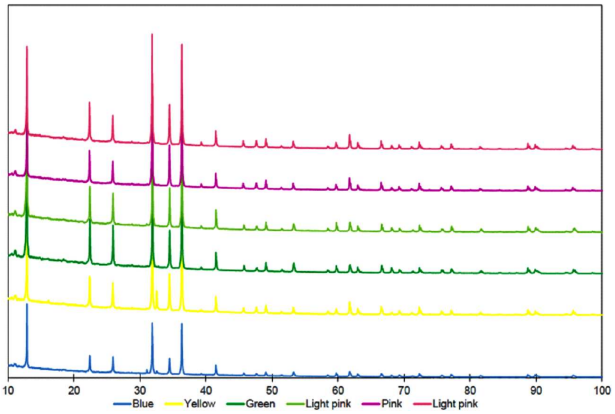

Fig. 1. Diffraction patterns for all beryl samples.

Aurisicchio et al. (1988), who studied beryl crystals by the single-crystal method, distinguished three compositional varieties of this mineral, dependently on structural site of the dominant substitution: *octahedral*, for which the substitution Me^{2+} for ^{O}Al is dominant, *tetrahedral* with Li substituted for ^{T2}Be, and *normal* with comparable sizes of both the replacements. They also presented effects of these substitutions on lattice parameters and c/a ratio of beryl.

Based on c/a ratio, we find that green, light green, and blue beryls with c/a values in the range 0.997–0.999

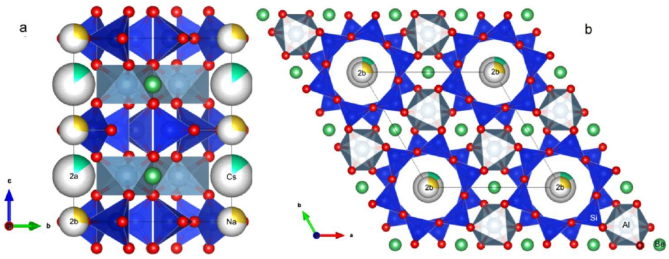

Fig. 2. Packing arrangement consistent with light pink beryl from Piława Górna. a) Projection along b, b) Projection along c.

match best to the *normal* beryl class in accord with their chemistry and NYF affiliation of the host pegmatite. On the other hand, the yellowish, pinkish and light pinkish beryls, with c/a values of 1.000–1.003, represent the *tetrahedral* variety, also in accord with the LCT affiliation of the host pegmatite. None of the studied beryls represent the octahedral variety. Generally, the substitution of Li for ^{T2}Be is manifested by an increase in the c unit-cell parameter, while substitution (Fe^{2+}/Mg) for ^{O}Al elevates the a unit-cell parameter.

4. Conclusions

The Rietveld structure refinement in cases of all the beryls allowed to corroborate their hexagonal structure corresponding to the space group $P6/mcc$. In spite of elevated Li amounts in the last group of the studied beryls, with the predominating replacement at the ^{T2}Be sites, none of the samples showed the rhombohedral symmetry typical of pezzottaite.

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TABLE I

Structure refinement details for beryl crystals from Piława Górna. Space group $P6/mcc$, R_p — profile factor, R_{wp} — weighted profile factor, R_{exp} — expected weighted profile factor, R_{B} — the Bragg factor, R_F — crystallographic factor

Crystal	Composition	Unit cell, $a = b/c$ [Å]	V [Å^3]	R_p	R_{wp}	R_{exp}	R_{B}	R_F
blue	$Cs_{0.08}Be_3Al_{1.66}Fe_{0.23}Si_6O_{18}$	9.2239(1)/9.2103(1)	678.627(1)	3.43	4.84	1.25	1.27	0.801
yellow	$Cs_{0.16}Be_3Al_{1.74}Fe_{0.19}Si_6O_{18}$	9.2212(1)/9.2240(1)	679.244(1)	3.96	5.45	1.10	1.31	0.918
green	$Cs_{0.06}Be_3Al_{0.88}Fe_{0.54}Si_6O_{18}$	9.2238(1)/9.2030(1)	678.077(6)	4.77	6.67	1.10	8.12	8.97
light green	$Na_{0.04}Cs_{0.08}Be_3Al_{1.80}Fe_{0.20}Si_6O_{18}$	9.2206(1)/9.2049(1)	677.746(1)	5.20	7.47	1.14	8.94	7.60
pink	$Na_{0.29}Cs_{0.17}Be_3Al_2Si_6O_{18}$	9.2210(1)/9.2302(1)	679.672(6)	4.23	5.91	1.20	6.81	6.29
light pink	$Na_{0.26}Cs_{0.16}Be_3Al_2Si_6O_{18}$	9.2212(1)/9.2284(1)	679.575(5)	3.83	5.23	1.16	3.81	3.42