

Beryl: Structural refinement of a sodium-rich natural crystal from Lassur mine (Ariège, France)

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SUMMARY

The crystal structure refinement of a blue beryl, abnormally rich in Na, collected in the mine of Lassur (Ariège, France) has been carried out. This Na-beryl is hexagonal, space group P6/mcc with $a=9.236(4)$, $c=9.201(5)$ Å; $D_{calc}=4.74$ g cm⁻³ for $Z=2$. From this refinement the following formula $Na_{0.3}Be_3Al_{2.1}Si_6O_{18} \cdot 0.9 H_2O$ was found. A substitution of Al atom by Fe atom in the octahedral site and an orientational disorder of the water molecules in the channels is proposed to explain the crystal structure of this beryl.

RESUMEN

Se ha realizado el refinamiento de la estructura de un berilo azul rico en sodio recogido en la mina de Lassur (Ariège, Francia). Este berilo cristaliza en el sistema hexagonal, grupo espacial P6/mcc, $a=9.236(4)$, $c=9.201(5)$ Å, $D_{calc}=4.74$ g cm⁻³, $Z=2$. El refinamiento de la estructura nos lleva a la fórmula $Na_{0.3}Be_3Al_{2.1}Si_6O_{18} \cdot 0.9 H_2O$. La difracción de rayos X nos muestra la existencia de una sustitución del átomo de Al por Fe y de un desorden orientacional que afecta a las moléculas de agua que ocupan los huecos existentes en esta estructura.

INTRODUCTION

The beryl structure type is one of the most complex silicate crystal structures. The dominant features in the structure are the hexagonal rings of six Si-O tetra-

hedra, these rings forming channels parallel to the *c* axis of the crystal (Bragg & West, 1926; Solov'eva & Bakakin, 1966; Strunz et al., 1971; Morosin, 1972). Although normally regarded as $Be_3Al_2Si_6O_{18}$, alkali beryls are known (Deer et al., 1962; Bakakin et al., 1969; Hawtorne & Cerny, 1977). Several authors (Sinkankas, 1964; Wyckoff, 1965; Vormann et al., 1965; Hawthorne & Cerny, 1977) suggest that these alkali ions and water molecules must evidently occupy some of the (2a) positions at $\pm (0,0,1/4)$ in the channels structure. Beryl was originally classified as a ring silicate (Deer et al., 1962; Sinkankas, 1964; Berry & Mason, 1966), but persuasive arguments have been advanced that beryl should be classified as a framework silicate (Zoltai, 1960; Gibbs et al., 1968; Hawtorne & Cerny, 1977; Lima-de-Faria, 1983).

The beryl reported here comes from a hematite mine of Lassur, Ariège (France). Close associated with a ferroan dolomite, this beryl occurs in fissures open in siderite, hematite, dolomite, pyrite and quartz lenticular layers included in the iron-bearing dolomitic rocks of Middle Devonian age from the northern zone of the Aston Massif (Fontan & Fransolet, 1982).

The present research was undertaken with the aim to detect any difference between pure and Na-beryl. At first, an analogy between this Na-Be cordierite (Povondra & Cech, 1978) was supposed thinking that Na-beryl is isotopic with pure beryl.

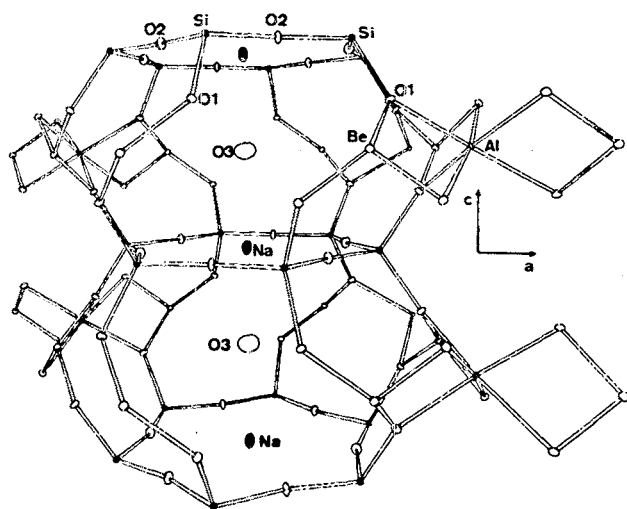


Figure 1. — Crystal structure of Na-beryl showing open channels parallel to the *c*-axis where Na ions and water molecules are placed projected on the (1010) plane.

Table 1. Crystal and refinement data

Schematical chemical formula	$\text{NaBe}_3\text{R}^{3+}\text{R}^{2+}\text{Si}_6\text{O}_{18}\cdot n\text{H}_2\text{O}$ $\text{R}^{3+} = \text{Fe, Al}; \text{R}^{2+} = \text{Mg}$
Colour	pâle blue
Space group	P6/mcc
<i>a</i> , Å	9.263(4)
<i>c</i> , Å	9.201(5)
<i>Z</i>	2
<i>c/a</i>	0.993
<i>D</i> _{meas} , g cm ⁻³	2.75(2) (Clerici's solution)* 2.78(1) (Berman balance)*
<i>D</i> _{calc} , g cm ⁻³	2.74
$\lambda(\text{MoK}\alpha)$, Å	0.7107
$\mu(\text{MoK}\alpha)$, cm ⁻¹	2.13
<i>F</i> (000)	532
Scan mode	0/20
Independent refl.	1799
Observed refl. (<i>I</i> > 3 σ)	751
Absorption correction	Gaussian integration
Transmission factor (max./min.)	1.025/1.020
Refinement method	full matrix
Weights	1/ σ^2
<i>R</i> final factor	0.042
GOF (Goodness-of-fit)	1.545

* After Fontan & Fransolet (1982).

EXPERIMENTAL

Na-beryl was separated by hand-picking fresh fragments of a sizeable beryl crystal being crushed to 0.1–0.3 mm. A blue pâle prism hexagonal crystal was used for the X-ray measurements. The lattice parameters obtained by least-squares refinement of the 2 θ values of 25 reflections are *a* = 9.201(4) and *c* = 9.201(5) Å. They are in agreement with those reported by Fontan & Fransolet (1982): *a* = 9.254(1) and *c* = 9.195(1) Å.

X-ray intensities were collected on a Syntex P2 diffractometer using the θ -2 θ scan technique up to ($\sin \theta/\lambda = 1.1827 \text{ \AA}^{-1}$ with MoK α filtered radiation). An absorption correction by Gaussian integration was applied to the intensities. From 1799 independent reflections measured, only 751 were considered as observed (*I* > 3 σ (*I*)), with σ (*I*) derived from counting statistics. Other experimental data are summarized in Table 1.

Microprobe analysis of single crystals gave an average composition of 62.569 wt% SiO₂, 13.740 wt% Al₂O₃, 2.733 wt% Fe₂O₃, 0.001 wt% MnO, 2.558 wt% MgO, 0.021 wt% CaO, 1.727 wt% Na₂O and 0.008 wt% K₂O.

REFINEMENTS

For the reduction of the intensities and refinement of the structure the X-ray system of crystallographic programs (Stewart et al., 1972) was used. Atomic scattering factors of Be, Al, Si, O, Mg, Na and Fe (Cromer & Mann, 1968) and anomalous dispersion terms for Si, Al and Fe were used for the structure factor calculations.

The atomic coordinates given by Bragg and West (1926) were used as starting values of structural parameters. The refinements were carried out in combination with three-dimensional Fourier synthesis and least-squares techniques using weights assigned according counting statistics ($w = 1/\sigma^2$) and including extra-framework cations and water molecules. The minimized function was $\sum w(\Delta F)^2$. All atoms were refined with anisotropic thermal parameters and at the end of the refinement, an extinction parameter was included. In the last cycle, the maximum shift to error ratio for the atomic parameters was 0.0006. Description of the different refinements were carried out and their residual values are summarized in Table 2.

Atomic positions, thermal parameters and popula-

TABLE 2. Results of the different refinements

Atom	Population parameter (PP)							
	1	1	1	1	1	1	1.036	1.051
Al	1	1	1	1	1	1	1.036	1.051
Na	0	0.378	0.378	0.378	0.378	0.378	0.312	0.374
O(3)(H ₂ O)	0	0	0.727	0.622	0.947	0.947	0.921	0.922
Fe	0	0	0	0	0	0	0.014	0
Mg	0	0	0	0	0	0	4	0
R	0.079	0.066	0.044	0.045	0.044	0.044	0.042	0.042
GOF	6.319	4.574	1.848	2.057	1.676	1.677	1.544	1.545
	Ideal composition	PP fixed	PP fixed	PP fixed	PP(Na) fixed	PP(Na)(O) refined	All PP refined	All PP refined

$$R = (\sum w|F_o - F_c|) / \sum |F_o|$$

$$\text{Goodness-of-fit} = (\sum w(F_o - F_c)^2) / (N_{\text{ref.}} - N_{\text{var.}})$$

Table 3. List of atomic parameters corresponding to the last refinement (R = 0.042)

Atom	x	y	z	U11	U22	U33	U12	U13	U23	PP
Be	0.5	0	0.25	0.0072(8)	0.0076	0.006(1)	0.0038(6)	0	0	
Al	0.5555	0.3333	0.25	0.0035	0.0035	0.0043(3)	0.0017(1)	0	0	1.051(4)
Si	0.38610(6)	0.11331(6)	0.5	0.0041(2)	0.0036(2)	0.0045(2)	0.0021(2)	0	0	
O(1)	0.4960(1)	0.1428(1)	0.35485(9)	0.0092(3)	0.0094(4)	0.0061(3)	0.0057(3)	0.0024(3)	0.0006(3)	
O(2)	0.3057(2)	0.2318(2)	0.5	0.0123(6)	0.0091(6)	0.0165(6)	0.0088(5)	0	0	
Na	0	0	0	0.0111	0.0111	0.029(3)	0.0056(9)	0	0	0.374(8)
O(3)(H ₂ O)	0	0	0.25	0.0692	0.0692	0.039(4)	0.035(2)	0	0	0.92(2)

Table 4. Comparison of the interatomic distances in refined beryl structures

References	1	2	3	4	5	6
Al-O x6	1.94	2.10	1.917(8)	1.907(8)	1.906(3)	1.938(1)
Be-O x4	1.73	1.62	1.656(12)	1.672(12)	1.677(3)	1.652(1)
Si-O1			1.594(12)	1.618(12)	1.608(4)	1.618(1)
Si-O1			1.598(12)	1.599(12)	1.601(4)	1.603(1)
Si-O2 x2			1.614(12)	1.617(12)	1.612(3)	1.612(7)
Mean	1.58	1.62	1.605	1.613	1.608	1.611

References: 1: Bragg & West (1926); 2: Vorma et al. (1965); 3: Solov'eva & Bakakin (1966); 4: Bakakin et al. (1969); 5: Hawthorne & Cerny (1977); 6: This work.

tion factors of the best refinement (R=0.042) are given in Table 3. Lists of the structure factors may be obtained from the authors. A projection of the structure on (10 $\bar{1}$ 0) is shown in Figure 1. Interatomic distances are reported in Table 4 and compared with the data of other published papers on the beryl structure.

DISCUSSION OF THE RESULTS

As is shown in Table 2, a considerable decrease in the residual R value is obtained when non-framework atoms are included in the structure.

A difference Fourier synthesis of the model corresponding to the ideal formula (R=0.079) shows strong peaks of 18. and 9. elec./Å³ at (0,0,0) and (0,0,1/2) positions respectively. These peaks were interpreted to be Na and water molecules as is known that they occupy positions in the SiO₄ channels. Refinement of the occupancy factors of these non-framework atoms gave values of PP(Na)=0.378(8) and PP(H₂O)=0.95(2) and a R value of 0.044. As Na and O atoms occupy (2b) and (2a) positions, the above values for PP correspond to the proportions in which Na atoms and H₂O molecules enter in the formula. A feature of this refinement is the large values of the thermal

parameter for the O(3) atom of the water molecules, as compared with the framework oxygens. Water molecules can adopt several orientations in the open channel, which can be defined as an orientational disorder. Although the O-atom is placed on a 6-fold axis, hydrogen atoms are disordered between six of twelve possible atomic sites. This could explain the high values of the thermal parameters of the O(3) atom. As a final remark for this refinement, it can be mentioned that an attempt to interchange the positions of Na and O(3) produce un reasonable values in its thermal parameters.

With the aim of solving the problem of the possible substitution of some Al by Fe atoms, an attempt was made to refine a model in which Fe replace a small proportion of Al atoms. Refined value for the population factor of the Fe atoms was kept quite small and the same results for the R values are obtained when the population factor for the Al atoms is refined alone (see Table 2).

In our opinion this result and the small values of the thermal parameters of the Al atom, indicates a deficit of electrons at the Al site, which could be explained by a substitution of Al by Fe atoms. Because the almost identical X-ray scattering powers of Na and Al, population parameters refinement for these elements were unsuccessful.

According to this refinement, the formula $\text{Na}_{0.3}\text{Be}_3\text{Al}_{2.1}\text{Si}_6\text{O}_{18} \cdot 0.9 \text{H}_2\text{O}$ is proposed for this no common natural beryl.

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