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Single-Crystal Pulsed Neutron Diffraction of a Highly Hydrous Beryl

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Abstract

The crystal structure of a hydrous beryl with the highest water content on record and coupled with a very high sodium content $(Be_{3.0}(Al_{1.3}Fe_{0.3}Mg_{0.4})Si_{6.0}O_{18}[Na_{0.45}(H_2O)_{0.95}])$ has been refined from single-crystal diffraction data obtained at the ISIS pulsed neutron source in the time-of-flight Laue geometry. The results of the structure analysis allow unambiguous discrimination between the Na cations and the water molecules located in the channel Wyckoff positions 2(*b*) and 2(*a*), respectively, and contribute to the elucidation of the crystal chemical relations among the extra framework species and the cations in the framework sites. The water hydrogens are disordered over multiple sites, with the H—H vectors inclined *ca* 38° with respect to the sixfold symmetry axis, and one O—H vector directed along the axis. The resulting water geometry is different from the orientation of type I and type II water molecules, as reported in the literature from spectroscopic data. The results of the structure refinement based on the neutron diffraction data are compared with those from a refinement based on conventional single-crystal X-ray diffraction data collected on a fragment of the same beryl crystal, and with the results of a combined refinement carried out simultaneously on both data sets.

Introduction

The crystal structure of beryl contains stacks of six-membered rings of Si tetrahedra along [001], cross-linked by Be tetrahedra and Al octahedra. The framework structural channels running along the *c* axis are delimited by the six-membered rings, and often enclose minor amounts of water and alkali cations, the latter needed for charge balance in the Be→Li and Al→Fe,Mg framework substitutions. The crystal chemistry of the water molecules and cations has been extensively studied in the past by spectroscopic and diffraction methods (Wickersheim & Buchanan, 1959, 1965; Vorma, Sahama & Haapala, 1965; Wood & Nassau, 1967, 1968; Gibbs, Breck, & Meagher, 1968; Rehm, 1974; Hawthorne & Černý, 1977; Brown & Mills, 1986; Aurisicchio, Fioravanti, Grubessi & Zanazzi, 1988; Sherriff, Grundy, Hartman, Hawthorne & Černý, 1991). In spite of the effort spent on the

characterization of beryl, and its mineral varieties (aquamarine, morganite, emerald *etc.*), a remarkable ambiguity persists on the location of the guest atoms and molecules in the channels, and on the interpretation of the water molecule orientations with respect to the sixfold symmetry axis.

On the basis of a recent neutron single-crystal study on two beryl samples with different alkali contents (Artioli, Rinaldi, Ståhl & Zanazzi, 1993), a model was proposed with the Na cations occupying the smaller crystallographic 2(*b*) site (at 0,0,0) when a substantial amount of H_2O is present in the crystallographic site 2(*a*) (at 0,0,0.25), whereas they coexist with the water molecules in site 2(*a*) in nearly anhydrous or poorly hydrated beryls.

The present work is aimed at confirming the postulated cation distribution, by studying the most hydrous and sodium-rich beryl sample known to date: a blue sodic beryl from southeast Ireland (Sanders & Doff, 1991). The study was performed by means of pulsed neutron diffraction, the intense spallation source allowing the study of the small volume beryl crystals.

The results of the neutron diffraction experiment are compared with those obtained on a fragment of the same Irish beryl using conventional X-ray diffraction data. A combined refinement using both neutron and X-ray data sets was also carried out, in order to check the reliability of the structural model: by using both data sets, we are overdetermining the observed data, and the results are properly affected by the different scattering nature of the two diffraction techniques. As we are dealing with a silicate mineral, the use of data collected at different temperatures does not significantly affect the validity of the combined refinement, as discussed below.

Experimental

A gem-quality blue aquamarine crystal with a volume of *ca* 2.8 mm³ was mounted on the SXD time-of-flight Laue diffractometer at ISIS and checked for scattering power. The preliminary data collection test at room temperature showed satisfactory Bragg peak intensities and peak-to-background ratios, therefore, a full data set was collected at 100 K, using a closed-cycle liquid helium system. Each frame was accumulated for *ca* 2 h, and a total of 14 data frames were collected at a series of φ, χ settings. A total of 774 observed reflections with $I > 5\sigma(I)$ were integrated from the three-dimensional data array (internal agreement factor 0.064), corrected for absorption and merged to 254 symmetry-independent reflections which were used in the structure analysis.

A fragment of the blue beryl with a volume of *ca* 0.002 mm³ was used for the single-crystal X-ray diffraction experiment. The data were collected using Mo radiation on a Philips PW1100 four-circle diffractometer. The experimental procedure closely followed that described by Aurisicchio, Fioravanti, Grubessi &

Table 1. *Data collection and refinement parameters of beryl*

Pulsed neutron experiment

Wavelength range	1000–14 500 µs (0.48–7.05 Å)
Area detector (mm)	192 × 192 (64 × 64 pixels)
Crystal detector distance (mm)	125
Accelerator beam target	W
Source moderator	H_2O (310 K)
Maximum $(\sin\theta/\lambda)$ (Å^{-1})	1.6
Temperature (K)	100

X-ray experiment

Wavelength (Å)	Mo $K\alpha$ (0.71069)
Instrument	Philips PW1100
Maximum $(\sin\theta/\lambda)$ (Å^{-1})	0.8
Temperature (K)	293

Refinement parameters

	Neutron	X-ray	Combined
Total no. of observed reflections	774	1300	
Total no. of independent reflections	254	428	682
No. of variables	36	33	37
$R(F) = \Sigma\lvert F_o - F_c\rvert/\Sigma F_o$	0.059	0.025	0.030
$wR(F) = [\Sigma w(F_o - F_c)^2/\Sigma F_o^2]^{1/2}$	0.049	0.030	0.039

Zanazzi (1988) and previously used for a series of beryl structure refinements. Approximately 1300 reflections were measured by the ω–2θ scan mode in the θ range 2–35°, corrected for absorption by the semi-empirical method of North, Phillips & Mathews (1968), and they were merged to 428 symmetry-independent reflections used in the least-squares refinement (internal agreement factor 0.014).

Details of the neutron and X-ray data collection conditions are listed in Table 1.

Structure analysis and results

The structure refinement was performed with the *GSAS* computer package (Larson & Von Dreele, 1994), which allows the least-squares minimization of a structural model against multiple data sets. Crystal data: space group $P6/mcc$, refined lattice constants $a = 9.292\,(1)$, $c = 9.193\,(1)$ Å at 293 K from X-ray powder data (Sanders & Doff, 1991), and $a = 9.278\,(2)$, $c = 9.195\,(2)$ Å at 100 K from neutron single-crystal data. The starting coordinates for tetrahedral and octahedral atoms were from sample no. 1 of Artioli, Rinaldi, Ståhl & Zanazzi (1993). The chemical content of the (Al,Fe,Mg) octahedral site was fixed according to the results of the electron probe microanalysis performed on a fragment of the same crystal used for the diffraction data. The chemical composition indicates an octahedral cation proportion of Al:Fe:Mg = 0.63:0.16:0.21, and essentially perfect stoichiometry for Be and Si. The tetrahedral sites were therefore treated in all refinements as fully occupied.

Two well defined positive peaks in the difference Fourier synthesis of the neutron refinement, corresponding to sites 2(*a*) and 2(*b*), were assigned to water O and Na atoms, respectively. Assignment was based on relative peak intensities and on the presence of a negative

Table 2. *Final atomic coordinates, site occupancy factors and atomic displacement parameters for beryl*

The refinement code is N for the neutron data set, X for the X-ray data set, and XN for the combined refinement.

	Wyckoff notation	Code	x	y	z	U_{eq} (Å²)	Site occupancy
Si	12(*l*)	N	0.3860 (5)	0.1123 (6)	0.0	0.0062	1.0
		X	0.38536 (7)	0.11225 (8)	0.0	0.0028	1.0
		XN	0.38536 (8)	0.11224 (8)	0.0	0.0032	1.0
Be	6(*f*)	N	1/2	0.0	1/4	0.0078	1.0
		X	1/2	0.0	1/4	0.0046	1.0
		XN	1/2	0.0	1/4	0.0054	1.0
Al	8(*h*)	N	0.6667	0.3333	1/4	0.0095	0.63
		X	0.6667	0.3333	1/4	0.0042	0.63
		XN	0.6667	0.3333	1/4	0.0048	0.63
Fe	8(*h*)	N	0.6667	0.3333	1/4	0.0095	0.16
		X	0.6667	0.3333	1/4	0.0042	0.16
		XN	0.6667	0.3333	1/4	0.0048	0.16
Mg	8(*h*)	N	0.6667	0.3333	1/4	0.0095	0.21
		X	0.6667	0.3333	1/4	0.0042	0.21
		XN	0.6667	0.3333	1/4	0.0048	0.21
O1	12(*l*)	N	0.3045 (4)	0.2300 (5)	0.0	0.0126	1.0
		X	0.3046 (2)	0.2298 (2)	0.0	0.0103	1.0
		XN	0.3047 (2)	0.2298 (2)	0.0	0.0106	1.0
O2	24(*m*)	N	0.4956 (3)	0.1421 (3)	0.1451 (2)	0.0087	1.0
		X	0.4945 (1)	0.1415 (1)	0.1450 (1)	0.0069	1.0
		XN	0.4947 (1)	0.1416 (1)	0.1451 (1)	0.0072	1.0
OW	2(*a*)	N	0.0	0.0	1/4	0.0236	1.01 (7)
		X	0.0	0.0	1/4	0.0532	1.10 (2)
		XN	0.0	0.0	1/4	0.0444	1.03 (2)
H	4(*e*)	N	0.0	0.0	0.146 (4)	0.0273	0.50 (3)
		XN	0.0	0.0	0.149 (3)	0.0264	0.52 (1)
Na	2(*b*)	N	0.0	0.0	0.0	0.0213	0.43 (8)
		X	0.0	0.0	0.0	0.0146	0.45 (1)
		XN	0.0	0.0	0.0	0.0143	0.44 (1)

region around site 2(*a*), which can be ascribed to the negative scattering of the water H atoms. The two most prominent negative peaks in the difference Fourier maps are located on the sixfold rotation axis, below and above the 2(*a*) oxygen site, and are symmetry-related by the mirror plane. As both hydrogen positions are within bonding distance from the oxygen, it is clear that the two positions are mutually exclusive, and their occupancy was constrained to half the site occupancy of the water oxygen during the final refinement. Unconstrained site occupancy refinement converged to 0.98 (8) for the water oxygen 2(*a*) site, and 0.61 (9) for the hydrogen position.

The difference-Fourier maps computed from the X-ray data clearly show two positive peaks on sites 2(*a*) and 2(*b*), although there is no indication of the H atoms on the symmetry axis. The refined occupancies of the two sites, assuming the allocation of O and Na atoms in the two positions, respectively, are in excellent agreement with the results of the neutron refinement.

The refinement of the structural model based on both neutron and X-ray data allows a better convergence during the least-squares cycles, and essentially no correlation is present between the site occupancy and the atomic displacement parameters. Although no additional information is offered by the combined refinement with respect to the separate refinements using neutron and X-ray data, this procedure was tested because it is of potential interest in structure analysis when partial data sets are available, obtained with different diffraction techniques and/or incident radiations. In the beryl case,

it should be noted that the structural parameters of most atoms are dominated by the X-ray data, although virtually all information on the H atoms is derived from the neutron scattering experiment, since the parameters obtained from the neutron data refinement are identical, within error, to those obtained in the combined refinement. The protons could not be identified, nor their position refined, in the refinement based on X-ray data alone. The combined refinement was performed in spite of the different temperatures in the two data collections, because the small temperature effect on the refined atomic displacement parameters is totally masked by the overestimation of the displacement parameters obtained from the neutron data set, as discussed below in detail.

In the final cycles all atoms were treated as anisotropic and the atomic displacement parameters were refined together with the occupancy factors. Final R values are listed in Table 1; refined atomic coordinates, site occupancy factors and equivalent atomic displacement parameters are listed in Table 2.* The results of the three refinements generally agree quite well, in terms of the atomic coordinates as well as the atomic displacement and site occupancy parameters. The final equivalent displacement parameters for all atoms, apart from hydro-

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gen, obtained in the combined refinement are closer to those obtained from the X-ray data refinement, and this presumably reflects the larger number of X-ray reflections. Furthermore, the equivalent atomic displacement parameters resulting from the neutron refinement are systematically slightly overestimated with respect to the corresponding parameters obtained from the X-ray data, in spite of the fact that the neutron data were collected at a lower temperature. These systematic discrepancies have been known since earlier comparative studies (see for example: Hamilton, 1969; Coppens et al., 1984; Bats, Fuess & Elerman, 1986), although usually the temperature factors resulting from the neutron studies are smaller than those derived from the X-ray studies on the same compound. The differences are not directly related to the nature of the radiation employed, and they might rather be caused by the different volume of the crystals utilized in the two experiments and by the combination of absorption and extinction corrections. The effect has never been adequately explained, although there are claims that this reflects the inadequacy of the free-atom approximation for the X-ray scattering factors (Hamilton, 1969; Coppens, 1969; Coppens, Sabine, Delaplane & Ibers, 1969).

In the case of the present study, the small differences in the displacement parameters obtained by the two experiments have no influence on the refined occupancy factors and positional parameters, and will be neglected in the following discussion.

Discussion

The structure analysis leaves no ambiguities as to the identification of the atomic species located in the channel positions of the beryl structure. Furthermore, the refined occupancies of the $2(a)$ and $2(b)$ sites indicate an almost full occupancy for the water O, and the presence of approximately 0.43 Na atoms per formula unit. Both results are in excellent agreement with the chemical composition of the Irish hydrous beryl resulting from our electron-probe microanalysis, and from published results (Sanders & Doff, 1991).

The present data also help clarify the problems concerning the orientation of the water molecules in the channels. From spectroscopic data, two types of water molecules with different orientations of H—H vectors have been assumed: a type I water molecule, with the H—H vector parallel to the c axis (Wickersheim & Buchanan, 1959, 1965; Wood & Nassau, 1967, 1968), and a type II water molecule, having the H—H vector perpendicular to the sixfold symmetry axis (Wood & Nassau, 1967, 1968; Aines & Rossman, 1984). In their alkali-rich beryl sample no. 1, Artioli, Rinaldi, Ståhl & Zanazzi (1993) found a water geometry consistent with disordered molecules of type II, whereas the arrangement of the water molecule in the alkali-poor beryl sample no. 2 did not allow a straightforward interpretation.

The results of the present refinement indicate an orientation of the water molecule that is neither type I nor type II geometry.

The observed OW—H distance of 0.96 (4) Å is quite close to the mean internal O—H distance of the water molecule in crystalline hydrates (0.965 Å; Chiari & Ferraris, 1982). The water molecule is oriented with one O—H vector directed along the sixfold symmetry axis, and the H—H vector is inclined ca 38°. The second H atom is disordered around the water oxygen, as shown by the residual negative scattering density just above and below the mirror plane, forming a ring with radius ca 0.9 Å (Fig. 1). The fully occupied water oxygen site is therefore related to a statistically oriented water molecule, having one of the O—H vectors perpendicular to the mirror plane, and symmetrically disordered on either side of it.

The cation–hydrogen repulsion [Na—H distance 1.34 (4) Å] must also force the Na atoms to be located on the opposite side of the mirror plane with respect to the H atom on the symmetry axis. This is reflected in the occupancy of the Na site, which cannot be more than half occupied. Indeed, the occupancy of the Na site resulting from the refinement is slightly lower than 0.5. On the basis of the proposed ordered distribution of water molecules and sodium ions in the beryl channels, we may explain the observed Na occupancy as due to vacancies at the boundary between ordered domains with opposite orientations of hydroxyl O—H vectors.

The unusual orientation of the water molecule in the blue Irish beryl is due to the balance of the electrostatic
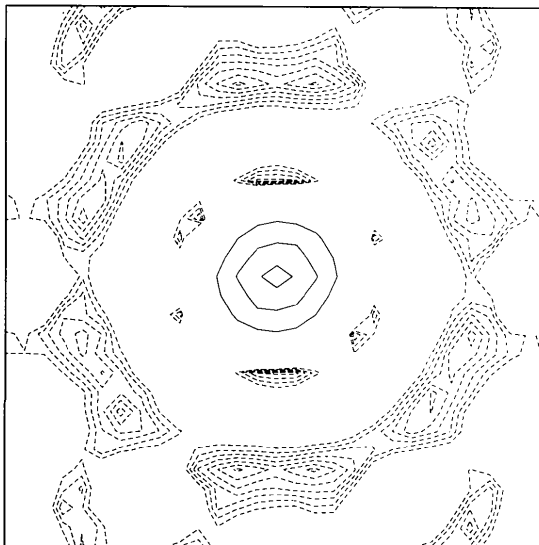

Fig. 1. Fourier synthesis map of neutron diffraction data showing the negative region near the $2(a)$ water oxygen site. The (001) plane of projection for a slice comprised between $z = 0.224$ and $z = 0.276$ has its horizontal axis parallel to the [010] direction, centre-to-edge is 1.4 Å. Contours at fixed arbitrary intervals; solid and dashed lines mark positive and negative regions, respectively.

forces acting on it: repulsion between one of the water H atoms and the Na cations, and hydrogen bonding of the other H atom to the O1 framework oxygens surrounding the structural channel. These rather weak bonding contacts allow a large freedom of motion of the water molecules about their equilibrium position (Boutin, Prask & Safford, 1965) so that the water has a clear zeolitic character, although a strict alternation of water molecules and Na cations along the channel makes hydration and dehydration processes in beryl rather difficult even under hydrothermal conditions (Wood & Nassau, 1968), since the alkali cations are effectively limiting the diffusion of the water molecules.

The observed geometry of the water molecules in site 2(a) may be interpreted as an ensemble of positions having a common direction of one O—H vector, and can partially explain why in alkali-rich beryls both type I and type II water molecules have been reported from spectroscopic measurements.

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Site Preference of Cations and Structural Variation in $Y_3Fe_{5-x}Ga_xO_{12}$ ($0 \leq x \leq 5$) Solid Solutions with Garnet Structure

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Abstract

The crystal structures of $Y_3Fe_{5-x}Ga_xO_{12}$ ($0 \leq x \leq 5$) solid solutions ($x = 0.0$, 1.0, 1.6, 2.0, 2.5, 3.0, 3.6, 3.8, 4.6 and 5.0) with garnet structure were refined by single-crystal X-ray diffraction analyses. Site preferences of cations in the crystal structure were examined in detail. The smaller Ga^{3+} ion occupies only the four-coordinated site in the composition range $x = 0.0$–1.6 (region I), whereas the larger Fe^{3+} ion occupies only the six-coordinated site from $x = 5.0$ to 3.8 (region III). Both cations occupy these two sites from $x = 1.6$ to 3.8 (region II). The tendency for site preference of cations changes near $x = 1.6$ and 3.8. When Ga^{3+} and Fe^{3+} occupy only the four- (region I) and six-coordinated sites (region III), respectively, the enhancement of the cation–cation interaction can be considered as a result of the geometric restriction due to the variation of cation size. The change in tendency for cation site preference is most probably caused by the increased cation–cation interaction. Crystal data: cubic, $Ia3d$, $Z = 8$, $Mo K\alpha$, $\lambda = 0.71069 \text{ Å}$; at $x = 0.0$: $a_0 = 12.375(1) \text{ Å}$,

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