

Stoppaniite, a new member of the beryl group: crystal structure and crystal-chemical implications

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Abstract: Stoppaniite, $(\text{Fe},\text{Al},\text{Mg})_4[\text{Be}_6\text{Si}_{12}\text{O}_{36}] \cdot (\text{H}_2\text{O})_2(\text{Na},\square)_2$, crystallizes in space group $P6/mcc$ with $a = 9.397(1)$, $c = 9.202(2)$ Å, $Z = 1$, $D_{\text{calc}} = 2.817$ g/cm³. An anisotropic least-squares refinement based on 367 independent reflections, collected by single crystal X-ray diffractometry (MoK α), converged to $R = 0.049$. In the [001] channels of the beryl-type structure the (0,0,1/4) and (0,0,0) positions are occupied by a water molecule and 50 % Na, respectively. About 0.5 excess Be p.f.u. substitutes mainly for Si and, in minor quantity, for octahedral cations. Bond length and valence analyses show that Fe is (mostly) bivalent and some OH substitutes for oxygen. A review of published chemical data for the relevant minerals shows that the beryl group can be defined with the general chemical formula $(\text{M}^{3+},\text{M}^{2+})_4[\text{Be}_6\text{Si}_{12}\text{O}_{36-z}(\text{OH})_z] \cdot (\text{H}_2\text{O})_y\text{A}_x$, where members with dominant $M = \text{Al}$ (beryl), Sc (bazzite) and Fe (stoppaniite) are known. Cation A (x presumably not larger than 1) is mainly Na, but also Cs; in the latter case the crystallographic positions of water ($y \leq 2$) and A are inverted. Limited substitutions for Be (mainly Li) and, to a minor extent, for Si (mainly Be) are reported.

Key-words: stoppaniite, new mineral, beryl group, crystal structure, crystal chemistry.

Introduction

In the last years several efforts have been done to decipher the complex crystal chemistry (*e.g.*, Deer *et al.*, 1986) of beryl on a structural basis (Artioli *et al.*, 1993 and 1995; Aurisicchio *et al.*, 1988; Hawthorne & Černý, 1977). This mineral has the ideal formula $\text{Al}_4[\text{Be}_6\text{Si}_{12}\text{O}_{36}]$ and a framework structure which is based on 6-fold rings of Si tetrahedra which are stacked along [001]. These rings are interconnected by Be tet-

rahedra and Al octahedra. The mentioned authors have shown that some large alkali cations (A) and water molecules are often present in the [001] channels formed by the rings. The same situation holds for bazzite, the Sc equivalent of beryl (Armbruster *et al.*, 1995).

The presence of extra-framework cations requires balancing substitutions in the octahedral (M) and/or tetrahedral sites (T' and T''). Major substitutions are Li^+ for Be^{2+} in T' and divalent metal ions for Al^{3+} in M . One (O2), out of two

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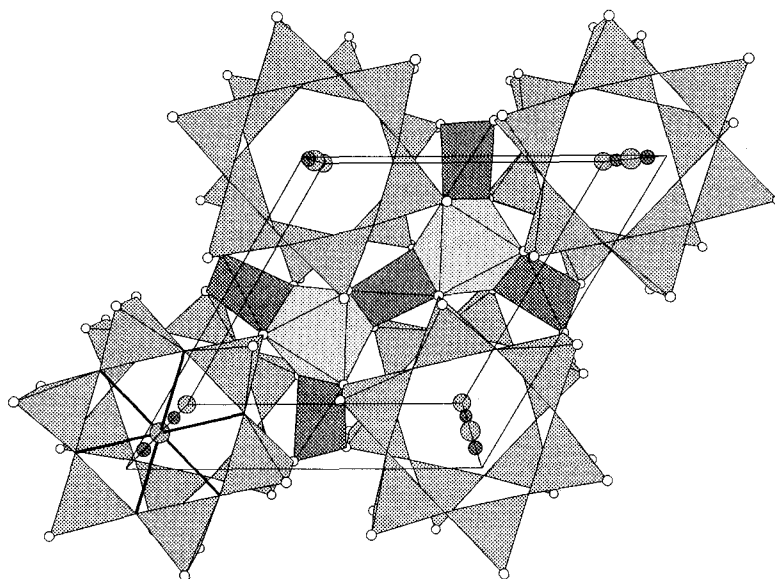


Fig. 1. Perspective view of the crystal structure of stoppaniite along [001]. Tetrahedra T' (Be) and T'' (Si) are darkly and lightly shaded, respectively. Na and H_2O , along the axes of the tetrahedral (T'') rings, are shown as large and small filled circles respectively; Na - O1 bonds are given only for the bottom left [001] channel. Empty circles at two corners of the T'' tetrahedra represent O2 ions.

crystallographically independent anionic oxygens, is bound to all framework cations (M , T' and T''), while O1 is coordinated only by T'' and A. When the mentioned substitutions are present, O2 appears systematically underbonded (Aurisicchio *et al.*, 1988), a result which, in particular, could be derived from a poorly determined M^{3+}/M^{2+} ratio and/or an overlooked presence of OH groups substituting for O2. The lack of these data can also lead to an incorrect value of the cation contents, particularly if these are calculated from anhydrous chemical data on the basis of 36 O atoms p.f.u. (ignoring OH).

The crystal structure determination of stop-

paniite (Fig. 1), a new beryl-type mineral with Fe as dominating M cation approved by the IMA Commission on New Minerals and Mineral Names (96-008) [Rossi *et al.*, in prep. and this paper], provides further insight in the crystal chemistry of the beryl group.

Experimental

The same [001] prismatic crystal of stoppaniite [$0.2 \times 0.3 \times 0.2$ mm³; $D_{obs} = 2.79(3)$ g/cm³] from Vico (Latium - Italy), on which Rossi *et al.* (in

Table 1. Statistics of refinements; the refined variables are: a scale factor, x and y coordinates for T'' and O1 atoms, x , y and z coordinates for M and O2 atoms, occupancies of all the cations and anisotropic displacement parameters for all atoms.

$a=9.397(1)$, $c=9.202(2)$		Number of refined variables	36
Space Group	P6/mcc	R ($F > 4\sigma$)	0.041
		GooF ($F > 4\sigma$)	1.42
Refl. total	1560	R (calculated on F_o ; all refl.)	0.049
Refl. independent	367	GooF (all refl.)	1.31
Refl. $F > 4\sigma$	314		

Table 2. Fractional coordinates, occupancies in electrons and equivalent isotropic displacement parameters (U_{eq} in $\text{\AA}^2$); the standard uncertainty on the last digit of each number is shown in parenthesis.

Site	Coordinates			No. of electrons	U_{eq}
	<i>x</i>	<i>y</i>	<i>z</i>		
T' (Be)	1/2	0	1/4	4.1(1)	0.013(3)
T'' (Si)	0.3799(2)	0.1069(2)	0	14.0(2)	0.012(1)
M	1/3	2/3	1/4	20.2(2)	0.013(1)
A' (Na)	0	0	0	6.0(3)	0.038(3)
A'' (H ₂ O)	0	0	1/4	9.4(4)	0.057(4)
O1	0.3005(5)	0.2256(5)	0	8	0.018(1)
O2	0.4890(4)	0.1353(3)	0.1470(2)	8	0.022(1)

prep.) had performed chemical characterization, was used for measurements on a Siemens single-crystal X-ray diffractometer [$\lambda(\text{MoK}\alpha) = 0.71069 \text{ \AA}$, graphite monochromator]. The diffracted integrated intensities of 6 equivalent sets of reflections were collected up to $\sin\theta/\lambda = 0.7 \text{ \AA}^{-1}$, for a total of 1560 reflections, using the $\theta/2\theta$ scan mode and a θ speed ranging from 2 to $15^\circ/\text{min}$, with increasing intensity; 3 standard reflections were monitored every 100 reflections. Orientation matrix and cell parameters (Table 1) were determined by a least-squares procedure from the centring of 30 reflections with θ close to 20° .

Absorption was empirically corrected by the Ψ -scan technique (North *et al.*, 1968); a further absorption correction was applied in the final stage of the refinement using the program DI-FABS (Walker & Stuart, 1983). A $|F_o|$ -based anisotropic refinement of the structure in space group $P6/mcc$ (No. 192) was carried out using the programs SHELXTL (Sheldrick, 1981) and UPALS (Lundgren, 1982) and a $1/\sigma(F_o)$ fixed weighting scheme. Scattering curves for neutral atoms were used with $\text{Fe}_{0.61}\text{Mg}_{0.18}\text{Al}_{0.21}$ and $\text{Si}_{0.96}\text{Be}_{0.04}$ mixed atoms, according to the chemical composition, for the *M* and the *T''* sites (Table 2), respectively. The highest residue in the final difference Fourier synthesis was $0.62 \text{ e/\AA}^3$ at (0.126, 0.040, 0) ($1.05 \text{ \AA}$ from Na).

Parameters for data collection and refinement are summarized in Table 1. Coordinates, occupancies (number of electrons) and equivalent isotropic displacement parameters are reported in Table 2; cation-oxygen distances are given in Table 3.¹

Table 3. Cation - oxygen distances in $\text{\AA}$; standard uncertainty, on the last digit, in parenthesis.

Bond	Distance	Bond	Distance
4 x Be-O2	1.632(3)	6 x M-O2	2.015(2)
Si-O1a	1.623(5)	6 x Na-O1	2.541(3)
Si-O1b	1.599(3)		
2 x Si-O2	1.631(3)	2 x Na-H ₂ O	2.300(1)
<Si-O>	1.621(4)		

Discussion

Crystal-chemical formula

The crystal of stoppaniite used in this work consists of a dominating Al-poor core (*S*) and an Al-rich rim (*B*). About one Na a.p.f.u. is present in both parts; water and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio could not be measured quantitatively because of the paucity of the material, but Raman spectra indicate fairly constant amount of water through the sample (Rossi *et al.*, in prep.). The presence, within the structural channels, of 9.4(3) and 6.0(3) electrons (Table 2) at (0,0,1/4) (2a) and (0,0,0) (2b), respectively, is consistent with a full occupancy of (2a) by water (plus Cs) and a 50 % statistical occupancy of (2b) by Na (plus K). These results agree with those obtained on beryl by neutron-diffraction (Artioli *et al.*, 1995).

The microprobe data of Rossi *et al.* (in prep.) and the presence of two H₂O molecules p.f.u. shown by the structural analysis lead to the following empirical formulae on the basis of 36 O

¹ A list of $|F_o|/|F_c|$ and anisotropic displacements can be obtained from authors, or through the E.J.M. Editorial Office - Paris.

atoms p.f.u. in the anhydrous part and, by analogy with beryl and bazzite, $\text{Fe}_{\text{tot}} = \text{Fe}^{3+}$:

$(\text{Fe}_{2.70}\text{Mg}_{0.64}\text{Al}_{0.42}\text{Mn}_{0.06}\text{Ti}_{0.02}\text{Sc}_{0.02})\Sigma_{3.86}[(\text{Be}_{6.88}\text{Si}_{11.60})\Sigma_{18.48}\text{O}_{36}] \cdot (\text{H}_2\text{O})_2(\text{Na}_{0.94}\text{K}_{0.02}\text{Cs}_{0.02})\Sigma_{0.98}$, $MW = 1207.68$ and $D_{\text{calc}} = 2.849 \text{ g/cm}^3$ for the core *S*; $(\text{Fe}_{1.24}\text{Mg}_{0.80}\text{Al}_{1.82}\text{Mn}_{0.02}\text{Ti}_{0.08})\Sigma_{3.96}[(\text{Be}_{6.12}\text{Si}_{11.92})\Sigma_{18.04}\text{O}_{36}] \cdot (\text{H}_2\text{O})_2(\text{Na}_{0.94}\text{Cs}_{0.02})\Sigma_{0.96}$, $MW = 1168.94$ and $D_{\text{calc}} = 2.758 \text{ g/cm}^3$ for the rim *B*. With particular reference to the core *S* and the ideal formula of beryl, the main features shown by the above formulae are (a.p.f.u.): (a) presence of about one Na; (b) $\text{Si} < 12$ and $\text{Be} > 6$; (c) $\text{Si} + \text{Be} > 18$; (d) sum of the octahedral (*M*) cations < 4 ; (e) total sum of the *M* and tetrahedral (*T*) cations larger than 22.

On the hypothesis that some OH for O2 may be present (see below) and, therefore, $O < 36$ a.p.f.u. in the anhydrous part, the anomaly (e) can be avoided by calculating the formula on the basis of $(M + T) = 22$ a.p.f.u. Features (b), (c) and (d) can be explained by allowing some Be in the Si-deficient *T'* site and in *M*. On this basis, after normalizing the above empirical formulae of *S* and *B* to $(M + T) = 22$ a.p.f.u., the occupancy of 20.2(2) electrons of the site *M* (Table 2) is accounted for by taking $S/(S + B) = 0.75$. Finally, the following weighted crystal-chemical formula is obtained for the studied crystal of stoppaniite: $(\text{Fe}_{2.30}\text{Mg}_{0.67}\text{Al}_{0.77}\text{Be}_{0.16}\text{Mn}_{0.05}\text{Ti}_{0.03}\text{Sc}_{0.02})\Sigma_{4.00}[\text{Be}_6(\text{Si}_{11.55}\text{Be}_{0.45})\Sigma_{12.00}\text{O}_{36-z}(\text{OH})_z] \cdot (\text{H}_2\text{O})_2(\text{Na}_{0.93}\text{K}_{0.01}\text{Cs}_{0.02})\Sigma_{0.96}$, $MW = 1194.10$ and $D_{\text{calc}} = 2.817 \text{ g/cm}^3$ (for $z = 3.09$). A statistical analysis of 38 microprobe point analyses reported by Rossi *et al.* (in prep.) fully supports the crystal-chemical formula given above. In fact, a marked counter-variance is evident between the pairs Al/Fe and Si/Be (correlation coefficients - 0.99).

In order to balance the charges, the value of z shown in the crystal-chemical formula can range from 0.79 (for $\text{Fe}_{\text{tot}} = \text{Fe}^{3+}$) to 3.09 (for $\text{Fe}_{\text{tot}} = \text{Fe}^{2+}$). Even in the former case [$MW = 1191.8$ and $D_{\text{calc}} = 2.812 \text{ g/cm}^3$], the content of the framework cations cannot be calculated from the microprobe data on the basis of $O = 36$ a.p.f.u., because some OH must be present. The exact amount of OH substituting for O2 cannot be calculated since the ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ is not known. Actually (see below), Fe might be present in both states of oxidation as reported for Fe-bearing beryls (Deer *et al.*, 1986; Charoy *et al.*, 1996). The studied stoppaniite could be assigned a simplified formula $(\text{Fe}, \text{Al}, \text{Mg})_4[\text{Be}_6\text{Si}_{12}\text{O}_{36}] \cdot (\text{H}_2\text{O})_2(\text{Na}, \square)_2$ (with $\text{Na} \approx 1$) and the ideal end-member would be $(\text{Fe}^{3+})_3\text{Fe}^{2+}[\text{Be}_6\text{Si}_{12}\text{O}_{36}] \cdot (\text{H}_2\text{O})_2\text{Na}$.

Bond length and valence

Comparison of stoppaniite (Table 3) with beryl (Artioli *et al.*, 1993 and 1995; Aurisicchio *et al.*, 1988; Hawthorne & Černý, 1977) and bazzite (Armbruster *et al.*, 1995) shows that (i) in stoppaniite the M-O2 distance (2.015 Å) is between the corresponding distances occurring in beryl (≈ 1.9 Å) and in bazzite (2.080 Å); (ii) the Be-O2 distance (1.632 Å) is the shortest ever observed in these minerals; (iii) the average Si-O1 distance (1.611 Å) is among the longest so far reported in the beryl-group. Result (i) is explained on the basis of the ionic radii (*i.r.*) (Shannon, 1976) of the cations substituting for Al (*i.r.* = 0.535 Å) or Sc (*i.r.* = 0.745 Å). In this respect, Fe^{2+} (*i.r.* = 0.780 Å) more than Fe^{3+} (*i.r.* = 0.645 Å) can be expected in the octahedral site. The result (ii) tends to compensate the underbonding of O2 (bonded to *M*, *T'* and *T''*), which is caused by the $\text{M}^{2+} \rightarrow \text{Al}^{3+}$ substitution. Finally, the overbonding of O1 (bonded to *A* and *T''*), which arises from Na^+ ions in the (2b) site, is alleviated by the lengthening of the average Si-O1 bond. No hydrogen bonds can be established by H_2O as well as by the OH (possibly) substituting O2, since the shortest O...O contacts $[\text{H}_2\text{O} \cdots \text{O1} = 3.431 \text{ Å}$ and $\text{O2(OH)} \cdots \text{O1} = 3.297 \text{ Å}]$ are out of the range observed for O...O hydrogen bonds (Chiari & Ferraris, 1982).

Bond valence (Brown & Wu, 1976) and charge distribution (Hoppe *et al.* 1989; Ferraris & Nespolo, 1991) calculations (Table 4) show that better results in balancing the bonds are obtained by putting $z = 3.09$ in the weighted crystal-chemical formula given above. In principle, some substitution of Be^{2+} in *T'* with a higher-charged tetrahedral cation could contribute balancing O2; thus, a substitution like Li^+ for Be^{2+} in a M^{2+} -rich beryl-type compound should be ruled out. It clearly appears that the presence of a low-charge cation in *T''* (*e.g.*, Be^{2+}), even in small quantity, makes easier the balance of O1 in presence of increasing Na^+ in (2b). In principle, such a substitution in *T'* could balance even a full occupancy (2 a.p.f.u.) of site (2b): it is evident that this should be paralleled by further $\text{OH} \rightarrow \text{O2}$ substitution. However, considering that an increased occupancy of (2b) by Na^+ would require a stronger polarization of H_2O , which cannot establish hydrogen bonds, one Na p.f.u. appears to be the maximum quantity acceptable by the structure. This value, in fact, already requires 0.12 Pauling's bond strength for the Na- H_2O coordination bond.

Table 4. Charge (1) and bond valence (2) distribution and sums (Σ) for $z = 3.09$ in the weighted crystal-chemical formula of stoppaniite (see text) and [(3) and (4), same order] for an ideal formula $(\text{Fe}^{3+})_3\text{Fe}^{2+}[\text{Be}_6\text{Si}_{12}\text{O}_{36}](\text{H}_2\text{O})_2\text{Na}$.

Oxygen		T'	T''	M	Na	H(O2)	Σ
O1	(1)	—	2.06	—	0.05	—	2.11 e
	(2)	—	2.03	—	0.07	—	2.10 v.u.
	(3)	—	2.10	—	0.05	—	2.16 e
	(4)	—	2.07	—	0.07	—	2.14 v.u.
O2	(1)	0.50	0.93	0.37	—	0.13	1.93 e
	(2)	0.51	0.94	0.44	—	0.13	2.02 v.u.
	(3)	0.50	0.95	0.46	—	0	1.91 e
	(4)	0.51	0.96	0.50	—	0	1.97 v.u.
O(H ₂ O)	(1), (3)	—	—	—	0.18	—	2.18 e
	(2), (4)	—	—	—	0.11	—	2.11 v.u.

For the oxygen of the H₂O molecule, 2 v.u. or charges (e) are contributed by its two hydrogen atoms.

From beryl to stoppaniite

Taking into account chemical data, structural results and correlations between cations, the following major substitutional mechanisms lead from beryl to stoppaniite [$\square$ stands for vacancies in the sites (2a) and (2b); $\text{M}^{2+} = \text{Mg}, \text{Fe}^{2+}, \text{Be}$]: (1) $(\text{Na}^+ + \text{M}^{2+})$ for $\square + \text{Al}^{3+}$; (2) H₂O for $\square$ higher than in beryl; (3) Fe^{3+} for Al^{3+} and/or (3') $(\text{Fe}^{2+} + \text{H}^+)$ for Al^{3+} ; (4) $(\text{Be}^{2+} + 2\text{Al}^{3+})$ for $(\text{Si}^{4+} + 2\text{M}^{2+})$ and/or (4') $(\text{Be}^{2+} + 2\text{H}^+)$ for Si^{4+} . Because of the crystallographic multiplicity of the involved sites, substitutions (1) and (2) can reach a maximum value of 2 a.p.f.u. both for Na and H₂O. This maximum value for H₂O is reached in the studied sample where the total of alkalis is 1 a.p.f.u. for reasons discussed above. Presumably the Fe^{3+} content shown in the ideal formula given above represents the maximum value for (3). In beryl, mechanism (1) may be (partially) replaced by $(\text{Na}^+ + \text{Li}^+)$ for $(\square + \text{IVBe}^{2+})$.

It has to be noted that the substitution $\text{OH} \rightarrow \text{O2}$ can be related at least to two mechanisms of cation substitutions involving both octahedral (3') and tetrahedral (4') sites. Even if with a variety of interpretations, the presence of additional H has been previously suspected by several authors on the basis of IR and Raman spectra (Armbruster *et al.*, 1995; Aurisicchio *et al.*, 1994; Hagemann *et al.*, 1990; Winkler, 1996; plus references therein quoted). In the present case the substitution $\text{OH} \rightarrow \text{O2}$ has been proved by crystal-chemical considerations. By the way, the usual

interpretation of IR and Raman data on the basis of two types of H₂O in the channel should be critically revised. In fact, the neutron-diffraction data of Artioli *et al.* (1995) have shown that, at least in their Na-rich beryl, only one type of water occurs which has one O-H vector parallel to the six-fold axis and the other one rotationally disordered around the same axis.

The beryl group

On the basis of the previous discussion on the substitution mechanisms in beryl (*cf.* Deer *et al.*, 1986), the discovery of stoppaniite, and recent structural data [*e.g.*, the neutron-diffraction work of Artioli *et al.* (1995) and the refinement of bazite by Armbruster *et al.* (1995)] it is clear that the current formula given for beryl, $\text{Be}_6\text{Al}_4[\text{Si}_{12}\text{O}_{36}]$, is inadequate since it ignores major contents of water and alkalis which usually occupy the structural channel. A more suitable formula $(\text{M}^{3+}, \text{M}^{2+})_4[(\text{T}')_6(\text{T}'')_{12}\text{O}_{36-x}(\text{OH})_x](\text{H}_2\text{O})_y\text{A}_x$ is proposed for the beryl group, where: M = octahedral cations; $\text{T}' = \text{Be}$ (mainly), $\text{Li}, \dots$; $\text{T}'' = \text{Si}$ (mainly), $\text{Be}, \dots$; $\text{A} = \text{Na}$ (mainly), Cs, K . For the reasons discussed above, x is expected not to be higher than 1. If $\text{A} = \text{Cs}$ this cation moves to (0,0,1/4) substituting (part of) H₂O, as shown by Artioli *et al.* (1993) and by the electron content in stoppaniite (Table 2). The shift of the alkali cation from the smaller (2b) to the larger (2a) site (Table 3) is related to the size of the Cs ion.

The exchange $\text{Cs} \rightarrow \text{H}_2\text{O}$ is known since long time in pollucite, $\text{CsAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ (Náray-Szabó, 1938), with respect to analcime, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ (Ferraris *et al.*, 1972; Taylor, 1930). This analogy and the absence of hydrogen bonds established by H_2O indicate a zeolite-like nature of the channel contents of stoppaniite and, in general, of the beryl group minerals.

Members with Al (beryl), Sc (bazzite) and Fe (stoppaniite) as dominant *M* cation have been reported. On the basis of chemical data showing as high as about 0.8 Mg atoms p.f.u. (Aurischio *et al.*, 1988; Deer *et al.*, 1986), the existence of a member having Mg as the dominant *M* cation is likely. Particularly interesting is the Al-poor bluish beryl from Mohave County (Arizona) described by Schaller *et al.* (1962), where the dominant *A* cation should be Cs; however, a structural refinement of (apparently) the same sample by Aurischio *et al.* (1988) did not confirm the Cs content.

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