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Single crystal refinement of the structure of baghdadite from Fuka (Okayama Prefecture, Japan)

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Abstract - The crystal structure of baghdadite, ideally $Ca_3Zr(Si_2O_7)O_2$, was refined using 1986 reflections to $R = 0.034$. Baghdadite is monoclinic, space group $P2_1/a$, with cell parameters a 10.432(3), b 10.163(2), c 7.356(2) Å, β 90.96(2)°. The refined crystal structure is in agreement with the structure of synthetic $Ca_3ZrSi_2O_9$. The structure is characterized by the presence of walls of cation polyhedra, four columns large, linked together by both direct connection as well as by disilicate groups. Baghdadite is the first phase in the cuspidine group in which the Pauling's fourth rule is violated.

Riassunto - La struttura cristallina della baghdadite, formula ideale $Ca_3Zr(Si_2O_7)O_2$, è stata raffinata fino ad un indice di accordo $R = 0.034$, utilizzando 1986 riflessi. La baghdadite è monoclina, gruppo spaziale $P2_1/a$, con parametri di cella a 10.432(3), b 10.163(2), c 7.356(2) Å, β 90.96(2)°. La struttura raffinata è sostanzialmente identica a quella del composto sintetico $Ca_3ZrSi_2O_9$. È caratterizzata dalla presenza di muri di poliedri, connessi tra loro sia per condivisione di vertici sia attraverso gruppi disilicato. La baghdadite è l'unica fase del gruppo della cuspidina in cui non è rispettata la quarta regola di Pauling.

Key words: *baghdadite; cuspidine group; crystal structure.*

Introduction

Baghdadite is a quite rare calcium zirconium disilicate belonging to the cuspidine group, a series of silicates with general formula $M_4(Si_2O_7)X_2$, where M denotes cations with various charges and ionic radii, characterized by an octahedral to roughly octahedral coordination. As described by Merlino and Perchiazzi (1985a), the crystal structure of the minerals in the cuspidine family is formed by two kinds of modules whose connection gives rise to the structures of the various phases: four columns wide 'octahedral' walls, extending along [001], and disilicate groups. The octahedral walls are interconnected by corner-sharing, forming the framework common to all the minerals in this family. The different ways in which the diorthosilicate groups may be connected to the octahedral walls give rise to the observed different unit cells and symmetries. Another difference is obviously related to their crystal chemistry, linked to the various possible cationic distributions within the polyhedra.

Baghdadite was found in melilite skarn in contact with banded diorite from the Dupezeh Mountains, Qala-Dizeh region, NE Iraq, and

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described by Al-Hermezi *et al.* (1986). Subsequently, it was described from garnet-vesuvianite skarns from Akagane mine, Iwate Prefecture, Japan (Matsubara and Miyawaki, 1999), from gehlenite-spurrite skarns from Fuka, Okayama Prefecture, Japan (Shiraga *et al.*, 2001), from melilite skarns from Flekkeren, Oslo Rift, Norway (Jamveit *et al.*, 1997), and from skarned carbonate xenoliths in the Yoko-Dovyren massif, Northern Baikal region, Russia (Galuskin *et al.*, 2007). Finally, Casillas *et al.* (2008) described the chemistry of Ca-Nb-Zr disilicates from metacarbonatites from the Basal Complex of Fuerteventura, Canary Islands, suggesting the existence of a wide solid solution between cuspidine, niocalite, and baghdadite. Baghdadite and its synthetic counterpart were also studied for their photoluminescence under UV excitation (Sidike *et al.*, 2006), with possible hints for the development of new phosphors.

Baghdadite has a cell of type III (according to Merlino and Perchiazzi, 1985a); the only other mineral with this kind of cell is burpalite, $Na_2CaZrSi_2O_7F_2$. The latter was found in a fenitized sandstone in the contact zone of the Burpalinskii alkaline massif (North Transbajkal, Russia). Its crystal structure was solved and refined (Merlino *et al.*, 1990), showing clearly that Zr cations are located in the outer columns of the octahedral walls, alternating along [001] with Ca cations.

The crystal structures of the synthetic compound $Ca_3Zr(Si_2O_7)O_2$ and of the isostructural phase $Ca_3Hf(Si_2O_7)O_2$ were solved and refined by Plaisier *et al.* (1995) using neutron and X-ray powder diffraction data respectively. Surprisingly, ZrO_6 and HfO_6 octahedra were unusually edge-shared in both compounds, in contrast with the fourth rule of Pauling (Pauling, 1929), which stated that the high-valence cations tend not to share polyhedron elements with one another. In order to check if this unusual feature was presented also by natural baghdadite, a structural study was carried out. This paper deals with the solution and refinement of the crystal structure of a natural baghdadite through single crystal X-ray diffraction.

EXPERIMENTAL

Grayish-white crystals of baghdadite from Fuka, Okayama Prefecture (Japan) were used throughout this study. The studied sample corresponded to that identified with the label Bagh 2 in the paper by Sidike *et al.* (2006), and was kindly given us by the authors. The chemical composition of this specimen was reported as: $(Ca_{3.03}Na_{0.02})(Zr_{0.83}Ti_{0.10}Mg_{0.01}Mn_{0.01})(Si_{2.04}Al_{0.02}Fe_{0.01})O_9$ (Sidike *et al.*, 2006).

Preliminary X-ray investigations by single-crystal oscillation and Weissenberg photographs showed that the space group and cell parameters of baghdadite were consistent with the structure type 6 (cell type III) of Merlino and Perchiazzi (1985a). The studied crystal did not show the presence of domains of other phases of the cuspidine family, as far as we can see from long-exposed Weissenberg photographs.

A crystal fragment (~ 0.1 x 0.1 x 0.1 mm^3) was used for the determination of the unit cell and the intensity data collection. The refinement of 25 reflections measured on a Siemens P4 four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation led to the cell parameters: a 10.432(3), b 10.163(2), c 7.356(2) Å, β 90.96(2)°. A setting of the crystal axes in the space group $P2_1/a$ was preferred over the standard setting with space group $P2_1/c$, in order to get the same orientation of the unit cell of the other members of the cuspidine group, with $c \sim 7.3$ Å. Intensity data were collected with a θ-2θ scan, scan width 1°, scan speed 2°/min, from 3.5 to 60° in 2θ. A total of 2273 reflections were measured and corrected for Lorentz-polarization and absorption factors.

The crystal structure was solved by means of direct methods using the SHELXS-97 program (Sheldrick, 1997) in the space group $P2_1/a$;

during a first step, only the cations were located (Zr, Ca, Si). Through a successive Fourier synthesis calculation, the oxygen coordinates were found. The octahedral cation distributions were clarified by means of the observed thermal parameters and taking into accounts the known chemical data and the bond distances. Three out of the four independent octahedral sites were found fully occupied by calcium, namely Ca1, Ca2, and Ca3; the other site is occupied by Zr and Ti. In all sites, anisotropic displacement parameters were refined. The final reliability indices for 1986 reflections with $F_o > 4\sigma(F_o)$ were R_1 = 0.034 (0.041 for all the 2273 reflections), wR_2 = 0.086.

STRUCTURE DESCRIPTION

TABLE 1 reports site occupancies, atomic coordinates, and equivalent displacement parameters in baghdadite; the atomic coordinates are in good agreement with those of Plaisier *et al*. (1995), taking into account that the two sets of data are related by the transformation matrix 001/0-10/100. Selected bond distances and angles in baghdadite are given in TABLE 2.

The crystal structure of baghdadite is represented in Fig. 1 as seen along [001]. As in the other members of the cuspidine family, tilleyite ribbons are condensed to build up a tessellation of four-columns-wide polyhedral

TABLE 1
Site occupancies, final positions, equivalent isotropic displacement parameters atoms in baghdadite.

Site	*x*	*y*	*z*	U_{eq}
Zr ($Zr_{0.86}Ti_{0.14}$)	0.11369(3)	0.93630(4)	0.12244(5)	0.0069(1)
Ca1	0.59869(7)	0.19131(8)	0.62743(9)	0.0098(1)
Ca2	0.58822(7)	0.17104(8)	0.11794(9)	0.0095(1)
Ca3	0.61464(7)	0.57760(8)	0.63440(10)	0.0104(1)
Si1	0.81585(10)	0.37539(10)	0.83442(13)	0.0073(2)
Si2	0.80773(9)	0.36541(10)	0.40244(13)	0.0070(2)
O1	0.7747(3)	0.3929(3)	0.6177(4)	0.0156(6)
O2	0.7545(3)	0.0032(3)	0.0833(3)	0.0108(5)
O3	0.0324(3)	0.6169(3)	0.1402(4)	0.0156(6)
O4	0.7427(3)	0.7342(3)	0.1056(4)	0.0135(5)
O5	0.2237(3)	0.2650(3)	0.3565(4)	0.0112(5)
O6	0.7596(3)	0.4998(3)	0.3088(4)	0.0147(5)
O7	0.9573(3)	0.3344(3)	0.3779(4)	0.0130(5)
O8	0.5104(3)	0.3899(3)	0.0943(4)	0.0107(5)
O9	-0.0152(3)	0.1095(3)	0.6603(4)	0.0125(5)

TABLE 2
Selected bond distances (Å) and angles (°) in baghdadite.

Zr	- O9	1.970(3)	Ca1	- O3	2.333(3)	Si1	- O3	1.593(3)
	- O8	2.078(3)		- O7	2.350(3)		- O2	1.614(3)
	- O8	2.090(3)		- O9	2.362(3)		- O4	1.624(3)
	- O6	2.133(3)		- O5	2.441(3)		- O1	1.654(3)
	- O2	2.152(3)		- O6	2.483(3)		average	1.621
	- O4	2.199(3)		- O4	2.584(3)			
	average	2.104		- O1	2.753(3)			
				average	2.427			
Ca2	- O3	2.326(3)	Ca3	- O5	2.324(3)	Si2	- O7	1.605(3)
	- O5	2.327(3)		- O9	2.345(3)		- O6	1.607(3)
	- O7	2.369(3)		- O9	2.409(3)		- O5	1.622(3)
	- O8	2.373(3)		- O8	2.425(3)		- O1	1.650(3)
	- O2	2.449(3)		- O1	2.517(3)		average	1.621
	- O4	2.515(3)		- O2	2.579(3)			
	- O3	2.989(3)		- O7	2.717(3)		Si2-O1-Si1	148.4(2)
	average	2.478		- O6	2.962(3)			
				average	2.535			

walls, developing along [001]. Each wall is connected by corner sharing to other four walls and to six disilicate groups, whereas each Si_2O_7 groups links three walls. Four independent large cation polyhedra are present in the unit cell of baghdadite; three of them are occupied by calcium, whereas the Zr site is occupied by Zr^{4+} with minor Ti^{4+}; the refined occupancy of Zr site is $Zr_{0.86(1)}Ti_{0.14(1)}$. These occupancies are in good agreement with the chemical data (Sidike *et al.*, 2006), which indicate 3.03 Ca^{2+}, 0.83 Zr^{4+}, and 0.10 Ti^{4+}, in addition to minor constituents (Na, Mg, Mn, which sum up to 0.04 *apfu*).

Figure 2 shows one of the walls, in which the coordination number of the various polyhedra ranges from six to eight. Ca1 and Ca2 sites regularly alternate in the outer columns of the octahedral walls. Ca1 site is seven-fold coordinated, with six bond distances ranging from 2.333 to 2.584 Å, and an additional longer bond (2.753 Å) with O1. Like Ca1, also Ca2 site is seven-fold coordinated, with six bond

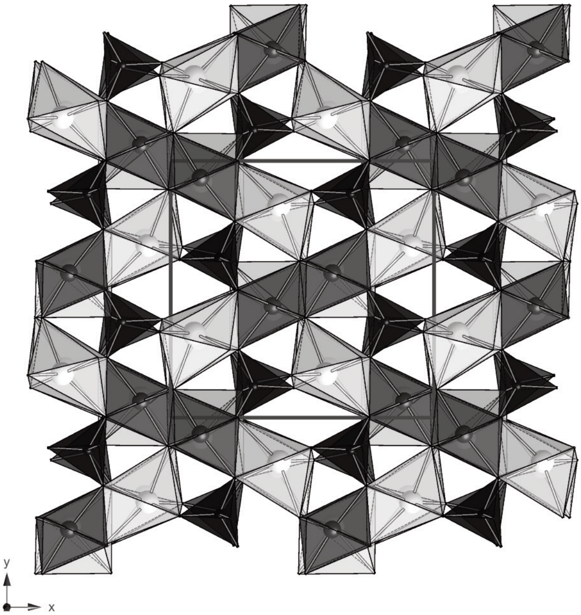

Fig. 1 - Crystal structure of baghdadite as seen down [001]. The Ca-centred polyhedra are light gray, the Zr-centred octahedra are dark gray, whereas the disilicate groups are black.

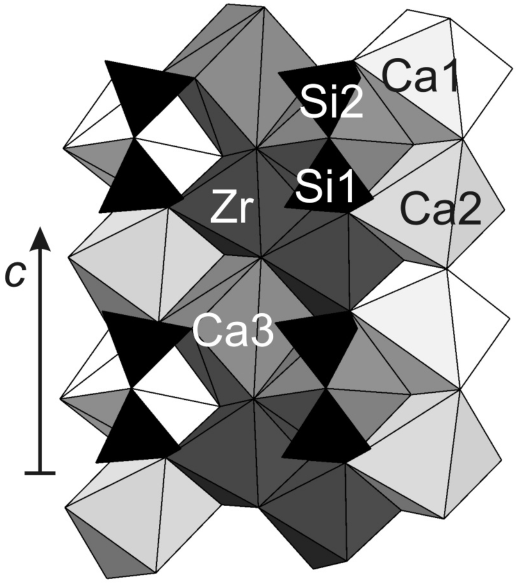

Fig. 2 - View of linkages of the disilicate groups to the polyhedral wall, as seen down [1-10], with **c** vertical.

distances in the range between 2.326 and 2.515 Å, and an additional bond (2.989 Å) with O3. In the inner part of the octahedral walls, Zr and Ca3 alternate along [001]. Ca3 is an eight-fold coordinated site, with six bond lengths between 2.324 and 2.579 Å, and two additional long bonds (2.717 and 2.962 Å). Finally, Zr is octahedrally coordinated, with bond distances ranging from 1.970 to 2.199 Å. The Zr octahedral site shows a distortion δ, defined as the difference between the longest and shortest distances in the polyhedron, of 0.229 Å. This value can be compared with the values found at other Zr sites in minerals of the cuspidine family. In låvenite, the Zr site (with minor substitutions of Nb; Mellini, 1981) has δ = 0.214 Å; in hiortdahlite I (Merlino and Perchiazzi, 1985b) it has δ = 0.176 Å; in wöhlerite from Los archipelago, Guinea (unpublished data), and in wöhlerite from Brevig, Norway (Mellini and Merlino, 1979), δ = 0.124 and 0.115, respectively; in hiortdahlite II (Merlino and Perchiazzi, 1987) δ = 0.092 Å; and in burpalite (Merlino *et al*., 1990) δ = 0.035 Å. The quite large distortion of the Zr polyhedron in baghdadite may be due to the partial substitution of Zr^{4+} by Ti^{4+}; this situation has been observed also in låvenite from Los archipelago (unpublished data), in which the refined occupancy of Zr site is $(Zr_{0.79}Ti_{0.21})$ and the δ value is 0.247 Å. In fact, small cations with high charge, like titanium and niobium, give rise to the off-centre displacement (Megaw, 1968).

The different bonding properties of Ca and Zr give rise to the different patterns of bond distances within the coordination polyhedra. In fact, the value of the average bond distances in Ca sites ranges from 2.427 to 2.535 Å whereas the average bond distance in the Zr site is distinctly smaller (2.104 Å). Average bond distances are in good agreement with the values found by Plaisier *et al.* (1995); Zr site in natural baghdadite is smaller than in the synthetic phase (2.104 Å in contrast to 2.120 Å), due to the partial substitution of Zr^{4+} by Ti^{4+}.

The diorthosilicate groups are formed by two independent Si sites, Si1 and Si2. The average bond length is 1.621 Å, with values ranging from 1.593 to 1.654 Å; in both Si tetrahedra, the

Table 3
Bond valence balance (v.u.) of baghdadite.

	O1	O2	O3	O4	O5	O6	O7	O8	O9	$\Sigma_{cations}$
Zr		0.54		0.47		0.57		0.66 0.64	0.88	3.76
Ca1	0.12		0.37	0.19	0.28	0.25	0.36		0.34	1.91
Ca2		0.27	0.38 0.06	0.23	0.38		0.34	0.33		1.99
Ca3	0.23	0.19			0.38	0.07	0.13	0.29	0.36 0.30	1.95
Si1	0.92	1.03	1.09	1.00						4.04
Si2	0.93				1.01	1.05	1.05			4.04
Σ_{anions}	2.20	2.03	1.90	1.89	2.04	1.93	1.88	1.92	1.89	

longest bond distance is that between Si and the bridging oxygen O1. These relatively long distances correspond to weaker bond strengths, with the possibility of the bridging oxygen to make additional bonds with Ca1 (2.753 Å) and Ca3 (2.517 Å). The Si1 - O1 - Si2 angle is 148.4°, which is the smallest value so far found in cuspidine minerals. In fact, the Si - O_{br} - Si angles vary from 149.5° in one of the two independent disilicate groups of wöhlerite (Mellini and Merlino, 1979) to 176.7° in hiortdahlite II (Merlino and Perchiazzi, 1987). In the only other phase with a cell of type III, burpalite, the corresponding value is 161.1°.

TABLE 3 reports the bond valence balance calculated according to Brese and O'Keeffe (1991), assuming the cationic distribution obtained through the structural refinement. No significant deviations from the expected values were found. All anionic sites are occupied by oxygen atoms, as suggested by the chemical analyses. The over-saturation of the bridging oxygen O1 is characteristic of all the minerals belonging to the cuspidine family; this over-saturation could be an effect due to the use of an inadequate relation between bond length and bond strength, that does not take into account other parameters, such as the bond angle and the shielding effects of the other oxygen atoms of the disilicate groups with respect to the bonds between cations and bridging oxygen atoms (Mellini, 1981).

DISCUSSION

The results of the structural determination and refinement of baghdadite from single-crystal intensity data are in good agreement with those of the structural study of Plaisier *et al.* (1995) on the synthetic analogue. The unusual edge-sharing between the Zr-centered octahedra is confirmed.

Baghdadite is the only species of the cuspidine family in which both F^- and OH^- are absent. In this regard, it is interesting to note that baghdadite seems to be formed only in F-free parageneses. In the type locality, it is associated with perovskite, calcite, wollastonite, melilite, baddeleyite, and schorlomite (Al-Hermezi *et al.*, 1986); at Fuka, baghdadite appears in association with gehlenite, spurrite, tilleyite, perovskite, grandite garnet, and vesuvianite (Shiraga *et al.*, 2001). In the Ioko-Dovyren massif, baghdadite is associated with dovyrenite, foshagite, Zr-bearing hydrogarnets, brucite, and calcium hydrosilicates (Galuskin *et al.*, 2007); it is noteworthy that dovyrenite is the F-free Zr-analogue of roumaite, found in the miarolitic cavities of nepheline syenite from the Los archipelago, in association with a series of F-bearing minerals, among which fluorite and villiaumite are reported (Biagioni *et al.*, 2010). In contrast with all the above listed F-free paragenesis, baghdadite is reported in association with F-rich cuspidine at Flekkeren, Oslo Rift, Norway (Jamveit *et al.*, 1997), where both phases were recognized on the basis of only microprobe analyses. However, the absence of X-ray diffraction data for both the associated phases prevents any hypothesis about their coexistence, and additional studies seem necessary.

In the minerals of the cuspidine group, fluorine anions are usually located in the positions corresponding to the O8 and O9 sites in the present description (TABLE 1). In such four-fold coordinated anionic sites (Fig. 3), no hydroxyl group can be located, neither in baghdadite nor in other phases of the cuspidine group. In fact, hydroxyl groups would require an open three-fold coordination, in order to avoid the electrostatic repulsion between the proton and the surrounding cations. These crystal-chemical considerations are in agreement with experimental results obtained by Van Valkenburg & Rynders (1958). They tried to hydrothermally synthesize OH-bearing cuspidine from batches in which the fluorine content was progressively reduced. It

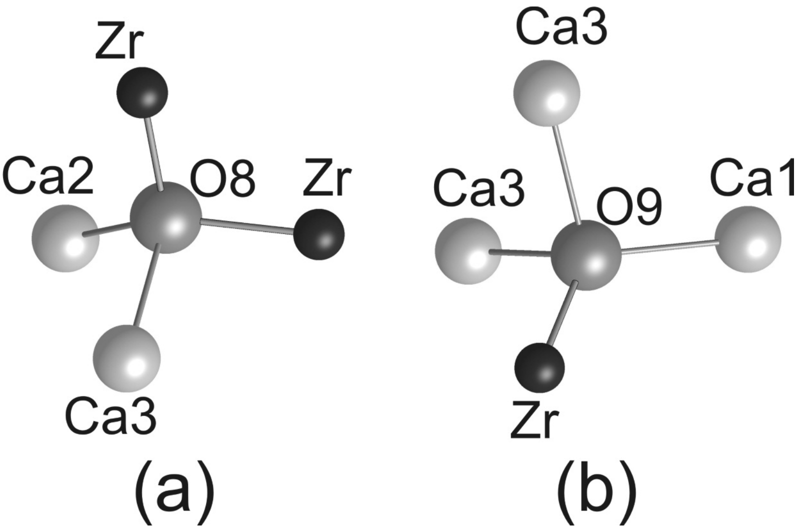

Fig. 3 - Four-fold coordination of the O8 and O9 oxygen atoms in baghdadite. These sites correspond to F site in cuspidine.

was observed that, as the F^- content of the batches decreased, there was a reduction in the amount of formed cuspidine and a corresponding increase in the production of the $6CaO{\cdot}3SiO_2{\cdot}2H_2O$. Finally, when fluorine was completely absent, cuspidine did not crystallize at all. On the other hand, in all the runs where cuspidine crystallized, the powder diffraction patterns and the indices of refraction of this phase were identical to those of stoichiometric synthetic cuspidine $Ca_4(Si_2O_7)F_2$.

Therefore, the absence of univalent anions in baghdadite requires the presence of high-charge cations in the Zr site, in order to achieve the correct bond-valence balance (~ 2 *v.u*) in the O8 and O9 sites. That is probably the reason for the stabilization of the unusual cationic distribution in the octahedral walls of baghdadite, with the consequent violation of the fourth Pauling rule.

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