Burpalite, a new mineral from Burpalinskii massif, North Transbajkal, USSR : its crystal structure and OD character

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Abstract : Burpalite, a new mineral of the cuspidine-wöhlerite-låvenite family, was found in a fenitized sandstone in the western contact zone of the Burpalinskii alkaline massif, North Transbajkal, USSR. Burpalite, with idealized chemical formula $Na_2CaZrSi_2O_7F_2$ is monoclinic, space group $P2_1/a$, $Z = 4$, $a = 10.1173(8)$, $b = 10.4446(6)$, $c = 7.2555(3)$ Å, $\beta = 90.039(7)°$. It occurs as colourless platy crystals up to $1 \times 3 \times 5$ mm, with vitreous lustre. Mohs' hardness is 5-6 ; the density is 3.33(15) g/cm^3. Optically, burpalite is biaxial negative with $2V = 82(1)°$ and $n_\alpha = 1.627(2)$, $n_\beta = 1.634(2)$, $n_\gamma = 1.639(2)$. The strongest lines in the powder pattern (d in Å, intensity in parentheses) are : 2.962 (vs), 1.787 (s), 1.886 (ms), 1.556 (ms), 3.306 (m), 3.035 (m). The space group symmetry and cell parameters of burpalite pointed to one of the ten possible structure types derived by Merlino & Perchiazzi (1988) for the cuspidine-wöhlerite-låvenite family. This was confirmed by structure refinement to a final R of 0.067. The OD character of burpalite is described, and the relationships between burpalite and "orthorhombic låvenite" are discussed.

Key-words : burpalite, new mineral, crystal structure, cuspidine family, OD theory.

Introduction

The crystal structures of the minerals in the cuspidine-wöhlerite-låvenite group can be described in terms of two kinds of modules whose connection gives rise to the structures of the various phases : octahedral walls, four columns wide and extending along [001], and diorthosilicate groups. The octahedral walls are interconnected by corner-sharing to build a framework that is the common feature in all the structures of this family. Merlino & Perchiazzi (1988) have shown that, within reasonable metrical constraints (cell dimensions of ~10 × ~10 ×

~7.3 Å), there are ten different ways to distribute the Si_2O_7 units in the framework. Enumeration of the possible structure-types was not only useful to show the relationships among the different natural phases with known structure, but also to determine the unknown structures of other natural phases in the group : hiortdahlite I, hiortdalite II, baghdadite.

In the course of that work, a lot of minerals in the cuspidine-wöhlerite-låvenite family from various localities were examined. In particular, a specimen (labelled as hiortdahlite, from Burpalinskii massif, North Transbajkal, USSR) was examined with single-crystal X-ray

methods ; unit cell parameters and space group symmetry closely matched those of one of the ten possible structure-types, and indicated a new mineral in the group. The predicted crystal structure was subsequently confirmed through structure determination and refinement.

The present paper combines the crystallographic and structural data, obtained by the Italian authors, with the chemical and physical data, obtained by the Soviet authors (Khomyakhov *et al.*, 1988), to completely define the new mineral which was named burpalite, from the locality of occurrence. The new mineral and its name were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type material is deposited in the Fersman Mineralogical Museum, Moscow and in the Museo di Storia Naturale dell'Università di Pisa.

Optically, burpalite is biaxial negative with $2V_{meas} = 82(1)°$; optical orientation is $X = b$, $Y = c$, $Z = a$ with refractive indices (measured with $\lambda = 589$ nm), $n_\alpha = 1.627(2)$, $n_\beta = 1.634(2)$, $n_\gamma = 1.639(2)$. Dispersion is weak (r < v) and no pleochroism or absorption were observed.

Four chemical analyses were done with an electron microprobe, using the following standards : parakeldyshite (Si,Na,Zr), LiNbO₃ (Nb), Y₂SiO₅ (Y), MgF₂ (F), ilmenite (Ti,Fe), diopside (Ca) and spessartine (Mn). Water was determined by the Penfield method. K, Hf, Al, La, Ce, Sm, Gd and Er were sought but not detected. The mean analytical results and ranges are reported in Table 1. The empirical formula, recalculated on the basis of (O+F) = 9 is :
$(Na_{1.69}Mn^{2+}_{0.03}Fe^{2+}_{0.02}Y_{0.01})Ca_{0.98}(Zr_{0.96}Ti^{4+}_{0.05}Nb^{5+}_{0.01})$ $Si_{2.00}O_7[F_{1.61}(OH)_{0.26}]\cdot0.13H_2O$
which may be written in simplified form as $Na_2CaZrSi_2O_7(F,OH)_2$.

Occurrence

Burpalite occurs in a fenitized sandstone in the contact zone of the Burpalinskii alkaline massif, North Transbajkal, USSR. The Burpalinskii massif is located 120 km northeast of the northern extremity of Lake Bajkal, on the Maygunda river which is the left-hand tributary of the Mama river. The locality is the western contact of the massif, in the upper reaches of the Tryokhzyorny stream. Associated minerals are albite, nepheline, aegirine, alkali amphibole, biotite ; catapleiite, astrophyllite, fluorite and accessory loparite are also locally present.

Table 1. Chemical data for burpalite.

	wt%	range
Na₂O	13.86	(13.62-14.85)
CaO	14.52	(14.13-14.85)
MnO	0.60	(0.54-0.72)
FeO	0.43	(0.32-0.53)
SiO₂	31.82	(31.13-32.60)
TiO₂	1.06	(0.95-1.20)
ZrO₂	31.11	(30.30-32.65)
Nb₂O₅	0.22	(0.08-0.42)
Y₂O₃	0.32	(0.18-0.41)
H₂O	1.23	
F	8.1	
	103.27	
O=F	3.41	
	99.86	

Physical and chemical data

Crystals of burpalite are transparent to translucent, colourless or yellowish, with vitreous lustre, platy on (010) and elongated parallel to [001]. Crystal size ranges from $0.1 \times 0.3 \times 0.5$ to $1 \times 3 \times 5$ mm. Observed forms are {110}, {001}, {011}, {101} and {111}. Streak is white. Burpalite is brittle, with strong tenacity and Mohs' hardness 5-6. Fracture is conchoidal, and no parting or cleavage was observed. Density is 3.33(15) g/cm³, measured with micro-float method, and compares with a calculated value of 3.27 g/cm³. Burpalite is easily decomposed by 10 % hydrochloric acid at room temperature.

X-ray crystallography

Single-crystal rotation and Weissenberg photographs of burpalite show that it is monoclinic, space group $P2_1/a$. Various crystals were examined with single-crystal techniques, and some of them showed the presence of domains with låvenite-type structure. We defer discussion on this point after the description of the crystal structure of burpalite. Cell constants $a = 10.1173(8)$, $b = 10.4446(6)$, $c = 7.2555(3)$ Å, $\beta = 90.039(7)°$ were obtained by least-squares fitting of 36 high θ values obtained with an automatic four circle diffractometer.

The X-ray powder pattern of burpalite is reported in Table 2. Because of the paucity of

Table 2. X-ray powder pattern of burpalite.

I	d_{obs}(Å)	d_{calc}(Å)	hkl
w	7.3	7.267	110
mw	5.241	5.222	020
w	4.552	4.553	210
mw	4.153	4.148	201
w	3.862	3.857	$\bar{2}11$
		3.855	211
m	3.306	3.292	130
m	3.035	2.998	$\bar{1}31$
vs	2.962	2.949	$\bar{2}02$
mw	2.881	2.868	230
w	2.839	2.836	212
vw	2.531	2.529	400
vw	2.438	2.438	$\bar{1}32$
		2.438	132
vw	2.372	2.356	013
vw	2.291	2.294	113
mw	2.244	2.233	$\bar{3}22$
		2.232	322
w	2.052	2.046	150
mw	2.020	2.015	$\bar{3}32$
		2.014	332
vw	1.936	1.932	$\bar{3}13$
ms	1.886	1.887	520
vw	1.849	1.849	233
s	1.787	1.783	$\bar{4}32$
		1.782	432
vw	1.754	1.749	530
w	1.723	1.716	160
m	1.678	1.675	$\bar{2}43$
vw	1.602	1.595	$\bar{3}52$
		1.595	352
ms	1.556	1.547	360

The X-ray powder pattern was recorded with a Gandolfi camera (114.6 mm diameter, FeK_α radiation). Indices were assigned taking account of the intensities measured in the single-crystal data collection. Intensities are indicated as follows: vs=very strong; ms= medium-strong; m=medium; mw=medium-weak; w=weak; vw=very weak.

the material and the possible presence of domains with låvenite-type structure in burpalite crystals, it was obtained with a Gandolfi camera using a crystal previously tested with the Weissenberg method to exclude the presence of låvenite-type domains. Indices were assigned taking into account the intensities measured in the single-crystal data collection. Similarities exist between the X-ray powder pattern of burpalite and those of the other minerals of this family, especially with that of baghdadite. An unambiguous distinction between burpalite and the other minerals of the group (apart from baghdadite, from which it differs in chemical composition) may be obtained by single-crystal X-ray crystallographic study.

Crystal structure determination and refinement

For the intensity data collection, we selected one crystal in which domains of låvenite-type

structure were almost completely absent. The intensity data were collected with a Philips PW-1100 single-crystal automatic four-circle diffractometer using $MoK\alpha$ radiation. A total of 2189 reflections was measured and corrected for Lorentz, polarization and absorption factors : this last correction was made according to the method of North et al. (1968). The space group and cell parameters of burpalite were consistent with structure type 6 (cell type III) of Merlino & Perchiazzi (1988) for the cuspidine group minerals ; this was used as starting model in the structure determination. We located one zirconium cation in the outer columns of the octahedral walls, within an octahedron not linked to diorthosilicate groups, as suggested by crystal-chemical considerations (Merlino & Perchiazzi, 1988), assuming that the other octahedral sites were occupied by calcium atoms. In three isotropic refinement cycles, the R index dropped to $R = \Sigma\|F_o\|-\|F_c\|/\Sigma\|F_o\| = 0.096$. The structure determination was completed by a series of least-squares cycles : the octahedral cation distribution and fluorine identification were made on the basis of the observed thermal parameters and peak heights in the Fourier synthesis, taking into account chemical data, bond distances and bond-valence calculations. Among the four independent octahedral positions, two were occupied by zirconium (Zr site) and calcium (Ca site), whereas the two remaining sites, Na1 and Na2, had mixed occupancies of sodium and calcium. As regards the anion sites, mixed occupancy was found at the F2 site. The site occupancies were refined in the last refinement cycles, in which anisotropic temperature factors were introduced for all atoms. Final occupancies were 0.8 Na + 0.2 Ca for Na1, 0.75 Na + 0.25 Ca for Na2, and 0.55 F + 0.45 O for F2, resulting in the crystal-chemical formula $(Na_{1.55}Ca_{0.45})Ca_1Zr_1Si_2O_7(F_{1.55}O_{0.45})$; this compares well with that obtained by the chemical analysis quoted in Table 1. The final R index for 1419 reflections with $F_o > 5\sigma(F_o)$ was $R = 0.067$. Scattering factors for neutral atoms and real and imaginary dispersions corrections were taken from the "International Tables for X-ray Crystallography" (1974). Final atomic positional and thermal parameters are reported in Table 3. All the calculations were done with the system SHELX 76 (Sheldrick, 1976). Observed and calculated structure factors are available from the authors (S.M. and N.P.) on request.

Table 3. Final atomic positional and thermal parameters for burpalite.

	x	y	z	B_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr	0.1070(1)	-0.1997(1)	0.6247(2)	1.21	148(5)	170(5)	141(5)	-2(4)	-7(3)	14(5)
Ca	0.1052(2)	-0.1999(3)	0.1260(3)	1.29	178(9)	155(10)	156(9)	1(9)	6(7)	-52(11)
Na1	0.3769(4)	-0.0743(4)	-0.1231(6)	1.57	161(20)	216(20)	219(19)	43(17)	-2(15)	-73(17)
Na2	0.3744(4)	-0.0708(4)	0.3759(5)	1.39	171(20)	204(19)	152(16)	-32(15)	1(13)	3(16)
Si1	0.1671(3)	0.1204(3)	-0.3479(4)	1.07	124(14)	106(14)	177(15)	1(12)	-8(11)	13(12)
Si2	0.1702(3)	0.1215(3)	0.0995(4)	1.04	93(13)	113(14)	189(15)	5(12)	-2(11)	-15(12)
O1	0.1681(12)	0.1468(12)	-0.1206(13)	3.23	639(75)	498(72)	91(40)	4(44)	38(43)	131(60)
O2	0.2658(8)	0.2316(8)	0.5830(14)	1.90	180(40)	158(44)	385(53)	-52(38)	86(35)	-56(33)
O3	0.2660(8)	0.2391(9)	0.1652(13)	2.24	204(41)	242(45)	405(54)	-117(38)	-10(35)	-35(34)
O4	0.0189(9)	0.1499(9)	0.5909(15)	2.25	175(42)	212(47)	469(61)	9(42)	25(39)	22(37)
O5	0.0171(9)	0.1469(11)	0.1584(15)	2.49	132(42)	363(59)	449(61)	-32(48)	11(38)	55(41)
O6	0.2148(8)	-0.0261(8)	0.6158(12)	1.43	188(40)	174(43)	183(40)	-40(33)	50(31)	37(33)
O7	0.2243(10)	-0.0173(8)	0.1381(14)	1.98	313(52)	90(41)	351(51)	17(36)	-71(40)	48(37)
F1	0.4894(8)	0.1110(8)	-0.1272(11)	2.08	304(42)	180(37)	306(40)	-21(33)	-5(32)	38(33)
F2	0.4837(8)	0.1203(8)	0.3745(12)	1.72	172(36)	132(36)	351(44)	3(34)	6(31)	61(30)

The anisotropic temperature factors ($\times 10^4$) are of the form : $\exp-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)$. The equivalent temperature factors B_{eq}, in Å^2, were calculated according to Hamilton (1959).

Structure description and discussion

The crystal structure of burpalite is represented in Fig. 1, with coordination polyhedra drawn as regular octahedra and tetrahedra. The connections between Si_2O_7 groups and octahedral walls are described by giving (in $c/8$ units) the heights of the octahedral cations and the bridging oxygens (in Si_2O_7 groups) with respect to a plane normal to the [001] direction and passing through the origin. As regards the octahedral walls, the outer columns have alternating Zr and Ca octahedra, whereas the inner columns have alternating Na1 and Na2 octahedra. This is shown also in Fig. 2, with the various polyhedra drawn with their actual shape.
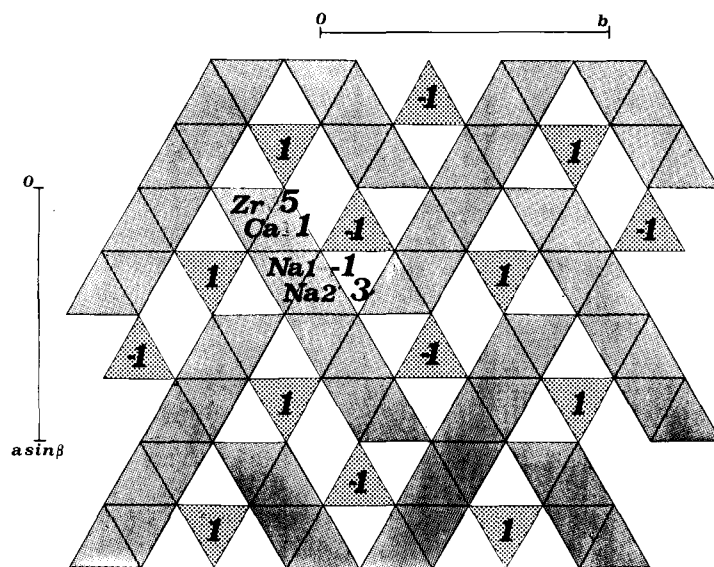
As in låvenite, the outer columns of the walls

Fig. 1. Schematic drawing of the crystal structure of burpalite as seen along [001]. The connections between Si_2O_7 groups and octahedra are indicated by the heights of both the octahedral cations and the bridging oxygen in Si_2O_7 groups. The heights are given in $c/8$ units, with respect to the plane normal to the [001] direction and passing through the origin.
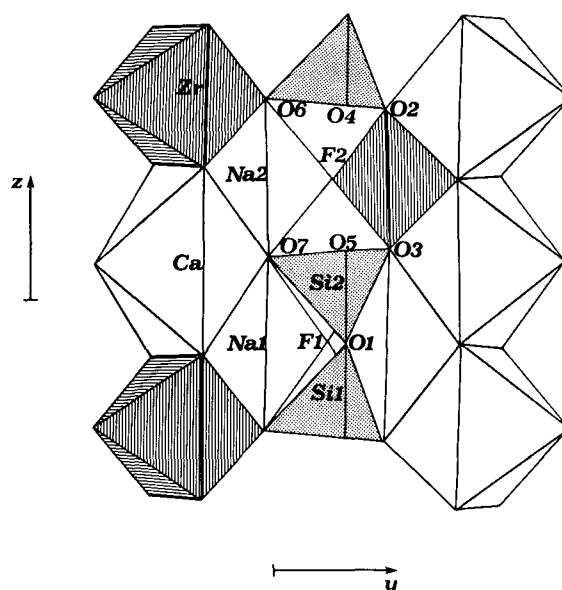
Fig. 2. Drawing of the crystal structure of burpalite, as seen along [100] : the structural slab between x ~ 0 and x ~ 1/2 is represented.

present alternation of large octahedra, with Si_2O_7 groups grasped on both sides, and small naked octahedra, but, in contrast to låvenite, the large octahedra in the outer columns are at different levels, approximately c/2 apart along [001]. The distribution of cations in the octahedral walls and the linking of disilicate groups to the walls are in keeping with the general rules discussed by Merlino & Perchiazzi (1988).

Diorthosilicate groups

The main geometrical features of the diorthosilicate groups are given in Table 4. The ⟨Si-O⟩ bond length is 1.621 Å, with extreme values 1.575 Å for Si2-O7, involving the only oxygen atom in the walls (O7) not linked to zirconium, and 1.672 Å for Si1-O1, involving the bridging oxygen atom (O1) in the disilicate

Table 4. Geometrical data for the diorthosilicate groups (Å, °) ; standard deviations are given in parentheses.

Si1 - 04^V	1.594(10)	01 - 02^V	2.528(15)	01 - Si1 - 02^V	100.7(6)
- 02^V	1.612(10)	01 - 04^V	2.580(17)	01 - Si1 - 04^V	104.4(6)
- 06^V	1.626(9)	01 - 06^V	2.673(14)	01 - Si1 - 06^V	108.3(5)
- 01	1.672(10)	02 - 04	2.641(13)	02^V - Si1 - 04^V	110.9(5)
		02 - 06	2.751(12)	02^V - Si1 - 06^V	116.4(5)
mean	1.626	04 - 06	2.709(13)	04^V - Si1 - 06^V	114.6(5)
Si2 - 07	1.575(10)	01 - 03	2.497(15)	01 - Si2 - 03	100.2(6)
- 05	1.629(10)	01 - 05	2.537(17)	01 - Si2 - 05	102.8(6)
- 01	1.619(10)	01 - 07	2.604(15)	01 - Si2 - 07	109.3(6)
- 03	1.638(10)	03 - 05	2.697(13)	03 - Si2 - 05	111.3(5)
		03 - 07	2.718(13)	03 - Si2 - 07	115.6(5)
mean	1.615	05 - 07	2.713(14)	05 - Si2 - 07	115.8(6)

The atoms of the different units are related to the symmetry equivalent atoms of the asymmetric unit as follows:

i	atom at	1-x,	-y,	1-z
ii	atom at	1-x,	-y,	-z
iii	atom at	-x,	-y,	1-z
iv	atom at	-x,	-y,	-z
v	atom at	x,	y,	-1+z
vi	atom at	1/2-x,	-1/2+y,	1-z
vii	atom at	1/2-x,	-1/2+y,	-z

group. The Si1-O1-Si2 angle is 161.1(9)°, in the range of values found for the other minerals of the group.

Octahedral sites

Bond distances for the four independent cation sites are given in Table 5. In the outer columns of the walls, the zirconium coordination is a nearly regular octahedron, whereas the calcium coordination is a slightly distorted octahedron, with four long Ca-O distances to the oxygen atoms on the edges shared with zirconium polyhedra, and two shorter distances Ca-O7 and Ca-F1 to anions shared with Na1 and Na2. Two further very long bond distances

Table 5. Bond distance (Å) in the large cation polyhedra.

Zr -	O4^{iii}	2.082(12)	Ca -	F1^{vii}	2.194(8)
	O5^{iii}	2.088(12)		O7	2.258(9)
	O3^{vi}	2.088(12)		O4^{iii}	2.464(13)
	F2^{vi}	2.093(8)		O5^{iv}	2.468(13)
	O2^{vi}	2.108(11)		O3^{vii}	2.570(13)
	O6	2.117(9)		O2^{vi}	2.583(12)
mean		2.096	mean		2.423
			Ca -	O1^{vii}	2.797(12)
			Ca -	O1^{iv}	2.820(13)
Na1 -	F1	2.246(9)	Na2 -	F2	2.282(9)
	F1^{ii}	2.296(12)		F1^{ii}	2.310(12)
	F2^{ii}	2.356(12)		O7	2.364(13)
	O3^{vii}	2.447(11)		F2^{i}	2.367(12)
	O7	2.516(14)		O6	2.421(12)
	O6^{v}	2.555(13)		O2^{vi}	2.522(10)
mean		2.403	mean		2.378

involving the bridging oxygen atom in the disilicate group are listed in Table 5, and were taken into account in calculating bond-valence sums.

Bond valence balance

Table 6 reports the bond valence balance, calculated according to Brown & Wu (1976). The values associated with the fluorine atoms were calculated by adding 0.07 Å to the corresponding bond distances. The results given in Table 6 seem satisfactory : no significant deviations from the expected values were found ; the monovalent character of F1 is confirmed and the value found for F2, 1.239 v.u. compares with the expected one of 1.45 v.u.

Table 6. Bond valence balance.

	Zr	Ca	Na1	Na2	Si1	Si2	$\Sigma_c v$
O1		0.127 0.122			0.878	1.008	2.135
O2	0.627	0.195		0.162	1.027		2.011
O3	0.663	0.201	0.189			0.959	2.012
O4	0.675	0.252				1.078	2.005
O5	0.663	0.250				0.982	1.895
O6	0.611		0.155	0.196	0.989		1.951
O7		0.404	0.167	0.218		1.135	1.924
F1		0.398	0.244 0.221	0.212			1.075
F2	0.590		0.210	0.237 0.202			1.239

$\Sigma_c v$ gives the sum of bond valences reaching each anion.

OD relationships between the structure-types of burpalite and låvenite

Domains with låvenite-type structure are often present in burpalite crystals. This is due to the close structural relationships between the two minerals, relationships which can be conveniently discussed on the basis of OD-theory (Dornberger-Schiff, 1956, 1964, 1966). The burpalite-type and låvenite-type structures are two distinct ordered members in a family of OD-structures. Each structure in this family may be described in terms of equivalent layers of symmetry $P2_1am$ and translation periodicity $a = 11.12$, $c = 7.26$ Å (giving the values obtained for burpalite) ; the width of the layers is $b_o = b/2 = 5.22$ Å. Pairs of adjacent layers are geometrically equivalent in all the structures of the family. The symmetry characteristics common to the whole family are described by the OD groupoid symbol

$$P \; 2_1 \quad (a) \quad m$$
$$\{n_{2,\,1/2} \quad (2_2) \quad 2_{1/2}\}$$

in which the first line in the symbol gives the λ-POs, namely the partial operations which bring a layer into itself (Fig. 3), and the second line gives the σ-POs, namely the partial operations that bring a layer into coincidence with the next one (Fig. 4). The brackets around the second position of each line indicate that only a and c are translation vectors, corresponding to the translations of the structural layer. According to this symbol, two subsequent layers are related through a glide normal to a, with translational component $b_o + c/4$, and through distinct two-fold axes with translational
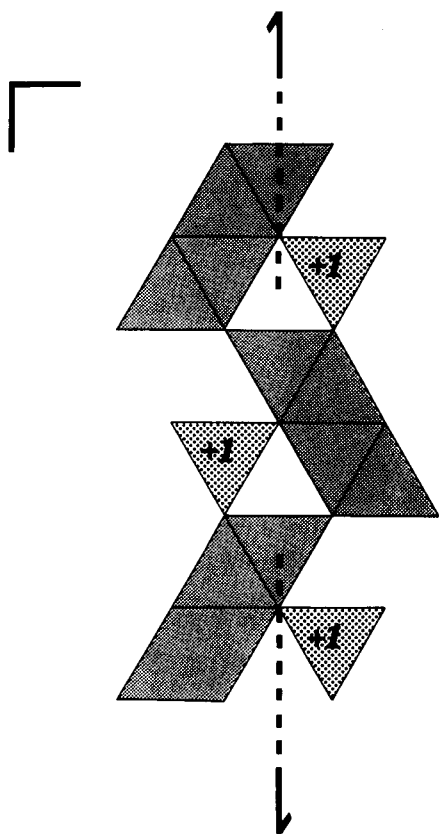
Fig. 3. Schematic drawing of the structural layer with symmetry $P2_1am$. The orientation of the λ-POs is indicated.

components b_0 and $c/4$. A pair of layers related by $n_{2,\,1/2}$, as well as by the other σ-POs represented in Fig. 4 at right, is geometrically equi-

valent to a pair of layers related by $n_{2,\,\bar{1}/2}$, as well as by the other σ-POs represented in Fig. 4 at left. Any sequence of operators $n_{2,\,1/2}$ and $n_{2,\,\bar{1}/2}$ defines a member of the family, and an infinite number of ordered polytypes (as well as disordered forms) are thus possible in this family. There are only two members with maximum degree of order, MDO structures according to the terminology of the theory : in these members, not only the pairs, but also the triples, quadruples, ...n-tuples of layers are geometrically equivalent. They correspond to the sequence $n_{2,\,\bar{1}/2}$-$n_{2,\,\bar{1}/2}$-$n_{2,\,\bar{1}/2}$,... (or $n_{2,\,1/2}$-$n_{2,\,1/2}$-$n_{2,\,1/2}$,...) which is realized in låvenite-type structure (MDO1), and to the sequence $n_{2,\,\bar{1}/2}$-$n_{2,\,1/2}$-$n_{2,\,\bar{1}/2}$-$n_{2,\,1/2}$,..., which is realized in burpalite-type structure (MDO2).

The space group symmetry of the two MDO structures may be derived by looking for those λ and σ-POs which become true symmetry operations of the whole structure. In MDO1, the λ-PO screw axis parallel to a is a total symmetry operation. Moreover, $n_{2,\,\bar{1}/2}$ is continued throughout the sequence of adjoining layers, and becomes a total symmetry operation corresponding to a b glide normal to a, with the assumption $b = 2b_0 - c/2$. The space group symbol for the låvenite-type structure is therefore $P2_1/b11$ ($P12_1/a1$ in the standard orientation). In MDO2, the λ-PO a glide normal to b is a total symmetry operation. Moreover, the σ-PO 2_2 parallel to b is continued throughout the sequence of adjoining layers and becomes a total symmetry operation, corresponding to a 2_1 screw axis, with the assumption $b = 2b_0$. The space group symbol for the burpalite-type structure is therefore $P12_1/a1$, the space group we have derived for burpalite.
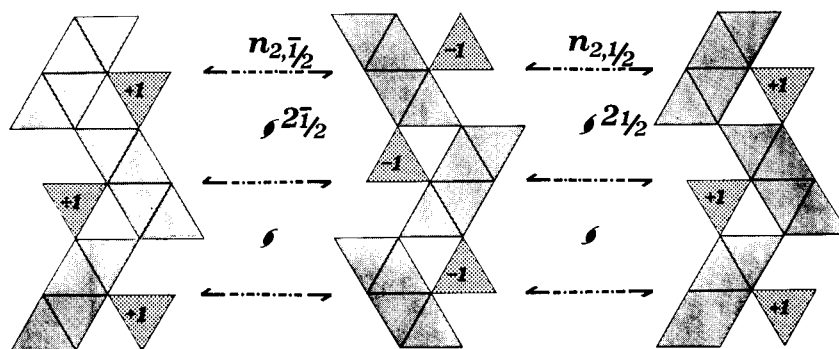

Fig. 4. Schematic drawing indicating the orientation of the σ-POs relating subsequent layers, which are drawn as disconnected for clarity.

Table 7. A comparison between the unit cell parameters (Å, °) and the crystal-chemical formulae of burpalite, "orthorhombic låvenite", låvenite and baghdadite.

Burpalite[a]	"Orthorhombic[b] Låvenite"	Lavenite[c]	Baghdadite[d]
a 10.1173	b 10.05	b 9.98	a 10.42
	a 11.11	a 10.83	
b 10.4446	(asinβ 10.50)	(asinβ 10.29)	b 10.16
c 7.2555	c 7.23	c 7.23	c 7.36
β 90.039	β 109.0	β 108.1	β 91.1
Na₂CaZr(Si₂O₇)F₂	Na₂CaZr(Si₂O₇)F₂	· (Na,Ca)₂MZr(Si₂O₇)OF	Ca₃Zr(Si₂O₇)O₂

(a) Present work.
(b) Portnov et al.(1966); the parameters of the monoclinic cell are calculated
    from those given by Portnov et al.(1966) for the "orthorhombic" cell, through
    the transformations: $\underline{a} = (\underline{a}_{or} - \underline{c}_{or})/2$, $\underline{b} = \underline{b}_{or}$, $\underline{c} = \underline{c}_{or}$.
(c) Mellini(1981); M in the crystal-chemical formula represents (Mn, Fe, Ca, Ti).
(d) Al-Hermezi et al.(1986).

As single-crystal X-ray diffraction patterns indicate that domains with låvenite-type structure are present in some crystals of burpalite, electron diffraction and HRTEM (High Resolution Transmission Electron Microscopy) studies would be useful to characterize the domains and to reveal possible more complex polytypes. Similar studies should be done also on samples of låvenite from different occurrences, to examine possible stacking-disorder, micro-twinning and polytypic sequences.

The preceeding discussion seems germane to the status of the so-called "orthorhombic låvenite" (Portnov et al., 1966 ; Portnov & Sidorenko, 1975), reported from the same locality as burpalite. "Orthorhombic låvenite" has a chemical composition close to that of burpalite, with the same ideal crystal-chemical formula $Na_2CaZrSi_2O_7(F,OH)_2$; it presents a single-crystal diffraction pattern with orthorhombic symmetry and parameters $a = 21.01$, $b = 10.05$, $c = 7.23$ Å in a B-centered unit-cell ; it is polysynthetically twinned on (100). These features point to a monoclinic unit cell with $a = 11.11$, $b = 10.05$, $c = 7.23$ Å, $\beta = 108.99°$, twinned on (100), as was first suggested by Nickel (1966) and stated again by Nickel, as reported in Fleischer et al. (1977). "Orthorhombic låvenite" thus seems a polytype of burpalite, a twinned MDO1 structure with sequences of $n_2, \bar{1}/2^{-n_2}, \bar{1}/2^{-n_2}, \bar{1}/2 \cdots$ σ-POs alternating with sequences of $n_2, 1/2^{-n_2}, 1/2^{-n_2}, 1/2 \cdots$σ-POs. In Table 7, the corresponding parameters, and ideal crystal-chemical formulae of burpalite, "orthorhombic låvenite", låvenite and baghdadite are compared. As regards this last compound, the data given in Table 7 and the close resemblance of its powder pattern with that of

burpalite, strongly suggest an isostructural relationship with burpalite, the two phases being related via the coupled substitutions $Na^+ + F^- \rightleftarrows Ca^{2+} + O^{2-}$.

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