'Clinobarylite'–barylite: order-disorder relationships and nomenclature

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ABSTRACT

'Clinobarylite', $BaBe_2Si_2O_7$, was defined as a monoclinic dimorph of orthorhombic barylite. Subsequently, its crystal structure was also proved to be orthorhombic, differing from barylite in terms of the space group symmetry, $Pmn2_1$ instead of $Pmnb$, and in unit-cell dimensions. Through the order-disorder (OD) theory, the polytypic relationships between 'clinobarylite' and barylite are described. 'Clinobarylite' corresponds to the MDO_1 polytype, with unit-cell parameters $a = 11.650$, $b = 4.922$, $c = 4.674$ Å, space group $Pmn2_1$; barylite corresponds to the MDO_2 polytype, with $a = 11.67$, $b = 9.82$, $c = 4.69$ Å, space group $Pmnb$. The re-examination of the holotype specimen of 'clinobarylite' confirmed its orthorhombic symmetry. Its crystal structure has been refined starting from the atomic coordinates calculated for the MDO_1 polytype and the refinement converged to $R_1 = 0.0144$ for 929 observed reflections [$F_o > 4\sigma F_o$]. Owing to their polytypic relationships, 'clinobarylite' and barylite should be conveniently indicated as barylite-$1O$ and barylite-$2O$, respectively; the name 'clinobarylite' should be discontinued. This new nomenclature of the barylite polytypes has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 13-E).

Introduction

'CLINOBARYLITE', $BaBe_2Si_2O_7$, was reported by Chukanov *et al.* (2003) as a new mineral from the Khibiny massif, Kola Peninsula, Russia. Its crystal structure was first described by Rastsvetaeva and Chukanov (2003) in the space group $Pm11$, with $a = 11.618$, $b = 4.904$, $c = 4.655$ Å, $\alpha = 89.94°$ and subsequently refined in the orthorhombic space group $Pmn2_1$ by Krivovichev *et al.* (2004), in a study carried out on a non-holotype specimen.

Both groups of authors maintained the close relationships between 'clinobarylite' and barylite, which have the same composition. "Relationships between the structures of barylite and clinobarylite can [...] be explained on the basis of sheets of BeO_4 tetrahedra and Si_2O_7 groups

parallel to (010) in clinobarylite and to (100) in barylite [...]. However, in barylite, two adjacent sheets have the opposite orientation, whereas, in clinobarylite, all sheets have the same orientation." (Krivovichev *et al.*, 2004, and figs 1a and b therein).

Whereas 'clinobarylite' is a mineral discovered recently, barylite has been known for >100 years. In fact, Blomstrand (1876) found it at Långban Mine, Sweden and regarded it as a Ba-Al-silicate. Its true chemical nature as a Ba-Be-silicate was proved by Aminoff (1923). Afterwards, barylite was found in several other localities, as listed by Petersen and Johnsen (1980). The first structural model was presented by Abrashev *et al.* (1965), who assumed the space group symmetry $Pn2_1a$, on the basis of the claimed strong piezoelectricity of the specimen they studied ["A very marked piezoelectric effect, greater than that for quartz" (Abrashev *et al.*, 1965)]. A subsequent study was performed by Cannillo *et al.* (1970), who solved the structure with the Patterson method and refined it to $R = 0.071$ in the centrosymmetric space group *Pnma*. They did not detect any piezoelectric effect but were using only a small amount of crystal fragments. However, they "made the same test on a comparable amount of quartz crystal fragments: the piezoelectric effect was in this case unequivocally detected'' (Cannillo *et al.*, 1970). Barylite was subsequently reexamined by Robinson and Fang (1977), who carried out a second harmonic test on "a rectangular cleavage fragment (largest dimension slightly over 1 mm)" which indicated that the crystal was definitely not centrosymmetric. However, they successfully refined the structure in the space group *Pnma* ($R = 0.06$) and an attempt to refine it in the space group $Pn2_1a$ "produced the same atomic coordinates as did the centrosymmetric refinement and the R value remained at 0.06" (Robinson and Fang, 1977).

The crystallographic data of the two minerals are compared in Table 1, where the unit-cell parameters obtained by Krivovichev *et al.* (2004) and by Robinson and Fang (1977) for 'clinobarylite' and barylite, respectively, are reported. For better comparison, the unit-cell data of barylite are referred to an axial setting with **a** and **b** exchanged with respect to the orientation assumed by Cannillo *et al.* (1970) and Robinson and Fang (1977). The space group corresponding to the new axial setting is *Pmnb*.

In order to clarify the actual symmetry of 'clinobarylite', its holotype specimen has been reexamined. In addition, the relationships between 'clinobarylite' and barylite have been discussed on the basis of order-disorder (OD) theory.

Order-disorder (OD) relationships between 'clinobarylite' and barylite

A full understanding of the relationships between the two compounds may be obtained on the basis of OD theory (Dornberger-Schiff, 1964, 1966; Ferraris *et al.*, 2004). The crystal structure of 'clinobarylite' is represented in Fig. 1, as seen down [001]; it may be conveniently described as consisting of two kinds of layers, exemplified by L_1 and L_2 in Fig. 1. L_1 consists of the O1 atoms which are on the borders of a thin slab with layer symmetry *Pmnm* (more precisely $P2_1/m2/n\,2_1/m$). L_2 contains all the other atoms and presents layer symmetry $Pmn2_1$. Layers of L_1 and L_2 types regularly alternate in the **b** direction. The fact that the symmetry of the L_1 layer is higher than that of the L_2 layer suggests the possibility of polytypic relationships.

In 'clinobarylite' L_{2n} and L_{2n+2} are related through the 2_1 screw axes parallel to **c** [- - 2_1] and the n glide normal to **b** [- n -] which are symmetry elements of the L_{2n+1} layer lying between them. However, due to the symmetry of the L_{2n+1} layers, a different arrangement is possible. In it, the layers L_{2n} and L_{2n+2} are related through the inversion centres and the 2_1 axes parallel to **a** [2_1 - -] which are also symmetry elements of the L_{2n+1} layer between them.

In both, the described arrangements pairs of adjacent layers are geometrically equivalent (principle of OD structures) and the resulting structures have to be looked upon as belonging to one family of OD structures consisting of two different kinds of layers.

An infinite number of ordered polytypes, as well as of disordered structures, is possible,

TABLE 1. Unit-cell parameters of 'clinobarylite' and barylite.

Space group	'Clinobarylite' $Pmn2_1$	Barylite $Pmnb$
a (Å)	11.650	11.67
b (Å)	4.922	9.82
c (Å)	4.674	4.69

corresponding to the various possible sequences of operators ([- - 2_1] and [- n -], or inversion centres and [2_1 - -]) that may be active in L_{2n+1} layers. The symmetry relations common to all polytypes of this family are described by the OD groupoid family symbol

$$Pmn2_1 \quad {}_{[0,\,¼]} \quad P2_1/m2/n2_1/m \qquad (1)$$

The first line contains the layer-group symbols of the two constituting layers, the second indicates the positional relations between the adjacent layers (Grell and Dornberger-Schiff, 1982).

Among the various possible polytypes of the family, few polytypes exist which are called MDO (maximum degree of order) structures; they are those polytypes which contain the smallest possible number of different kinds of layer triples (principle of MDO structures). In the present case there is one way to attach L_{2n+1} layers to L_{2n} layers and two distinct ways to attach L_{2n} to L_{2n+1} layers; consequently one (L_{2n-1}; L_{2n}; L_{2n+1}) triple and two different (L_{2n}; L_{2n+1}; L_{2n+2}) triples are possible. Therefore the smallest number of different triples necessary to build a periodic polytype is two, and only two MDO polytypes are possible in this family.

The first MDO structure (MDO$_1$), which is obtained when [- - 2_1] and [- n -] operators are constantly active in the L_{2n+1} layers, corresponds to the structure of 'clinobarylite' represented in Fig. 1. On the basis of the symbol (1), it is easy to derive that its space group symmetry is just $Pmn2_1$.

The other MDO structure (MDO$_2$), which is drawn in Fig. 2, is obtained when inversion centres and [2_1 - -] axes are constantly active in the L_{2n+1} layers. In this MDO structure the asymmetric unit at x, y, z (I) is converted by the [- - 2_1] operator in the L_2 layer into the asymmetric unit $-x$, ½$-y$, ½$+z$ (II); this last unit is converted by the inversion centre in the L_1 layer into the asymmetric unit x, ½$+y$, ½$-z$ (III). Units (I) and (III) are related by a b glide normal to c at $z = ¼$; moreover, the mirror plane normal to a is valid for the whole structure and the n glide normal to b is a symmetry operator in both kinds of layer. Therefore, $Pmnb$ is the space group of this MDO polytype. The space group $Pmnb$ becomes $Pnma$ if we adopt the reference system assumed for barylite by Cannillo *et al.* (1970) and Robinson and Fang (1977).

Polytypic relationships between 'clinobarylite' and barylite

To check the actual polytypic relationships between 'clinobarylite' and barylite, the coordinates of the MDO$_1$ polytype ('clinobarylite') have been calculated on the basis of the set of
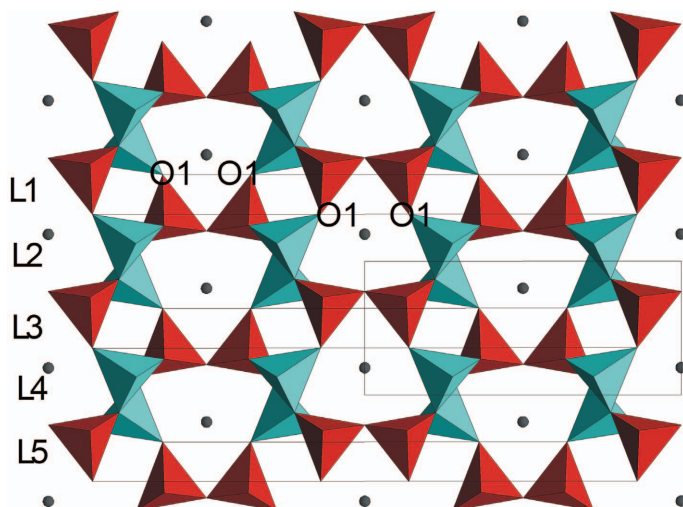

FIG. 1. The crystal structure of 'clinobarylite' (polytype MDO$_1$ in the OD family of barylite) as seen down [001] (**b** vertical), with indication of the unit cell. The sequence of OD layers is indicated.
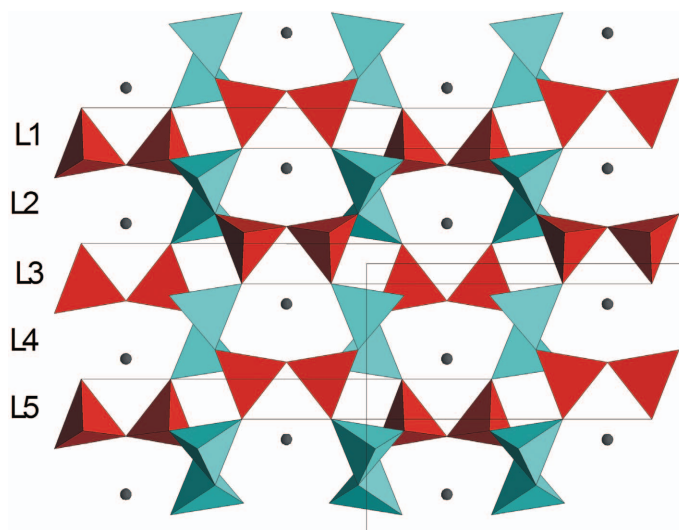
FIG. 2. Structure of polytype MDO$_2$ in the OD family of barylite, as seen down [001] (**b** vertical), with indication of the unit cell. The sequence of OD layers is indicated.

coordinates given by Robinson and Fang (1977) for the MDO$_2$ polytype (barylite).

The calculated coordinates are given in Table 2, compared with those found by Krivovichev *et al*. (2004) in their structure refinement. Small differences are observed in the *z* coordinates of Ba and O1 and correspond to shifts of 0.16 and 0.21 Å, respectively. However, a strong difference has been observed for the *z* coordinate of the O3 atom. Actually the *z*

coordinate found by Krivovichev *et al*. (2004) is unreliable, leading to highly deformed SiO$_4$ tetrahedra with 'impossible' bond angles [the O3−O4 distance is 2.033 Å, an unreliably short distance corresponding to an O3−Si−O4 angle of 78º]. It is appropriate to observe that the same mistake occurs in the paper by Rastsvetaeva and Chukanov (2003) for the *z* coordinates of the atoms O1 and O4, a pair of atoms corresponding to the O3 atom of Krivovichev *et al*. (2004).

TABLE 2. Comparison of the calculated atomic coordinates for MDO$_1$ structure, the atomic coordinates of 'clinobarylite' given by Krivovichev *et al*. (2004), and the atomic coordinates obtained on non-holotype material.

Site	MDO$_1$ polytype (calculated coordinates)			'Clinobarylite' (Krivovichev *et al*., 2004)			'Clinobarylite' non-holotype material (this study)		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Ba	½	0.1968	0.5417	½	0.2027	0.5079	½	0.20312	0.50779
Si	0.6279	0.6770	−0.0058	0.6282	0.6756	−0.0141	0.62824	0.67527	−0.01321
Be	0.7480	0.1780	−0.0023	0.7519	0.1671	−0.0147	0.75108	0.17066	−0.00007
O1	0.6346	0.3582	0.0122	0.6391	0.3521	0.0564	0.63887	0.35547	0.05418
O2	0.7712	0.1252	0.6505	0.7773	0.1340	0.6466	0.77691	0.13379	0.64766
O3	½	0.7908	0.0905	½	0.7741	−0.0767	½	0.77669	0.09710
O4	0.6368	0.7144	0.6539	0.6330	0.7324	0.6450	0.63278	0.72972	0.64597

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TABLE 3. Crystal and experimental data for the holotype specimen of 'clinobarylite'.

Crystal data

X-ray formula	$BaBe_2Si_2O_7$
Crystal size (mm)	$0.21 \times 0.21 \times 0.10$
Cell setting, space group	Orthorhombic, $Pmn2_1$
a, b, c (Å)	11.622(1), 4.9125(5), 4.6654(5)
V (Å³)	266.36(5)
Z	2

Data collection and refinement

Radiation, wavelength (Å)	Mo$K\alpha$, $\lambda = 0.71073$
Temperature (K)	293
Maximum observed 2θ (º)	65.12
Measured reflections	2288
Unique reflections	937
Reflections $F_o > 4\sigma(F_o)$	929
R_{int} after absorption correction	0.0185
$R\sigma$	0.0271
Range of h, k, l	$-12 \leqslant h \leqslant 17, -7 \leqslant k \leqslant 7, -6 \leqslant l \leqslant 7$
R [$F_o > 4\sigma F_o$]	0.0144
R (all data)	0.0146
wR (on F_o^2)	0.0332
Gof	1.157
Number of least-square parameters	59
Maximum and minum residual peak (e/Å³)	0.72 (at 1.02 Å from Ba)
	-0.78 (at 1.03 Å from Ba)

Using a crystal of a non-holotype specimen from the same locality as the samples studied by Krivovichev *et al.* (2004) and Rastsvetaeva and Chukanov (2003), a structure refinement starting from the coordinates of the MDO₁ polytype obtained as written above was carried out. The unit-cell parameters are $a = 11.636$, $b = 4.914$, $c = 4.670$ Å, space group $Pmn2_1$. The refinement converged to a final $R_1 = 0.0197$ ($wR_2 = 0.0467$) for 981 unique reflections. The atomic coordinates are given in Table 2; the atoms are named as the corresponding atoms in the structure of barylite (Cannillo *et al.*, 1970; Robinson and Fang, 1977), apart from O3, corresponding to O4 in barylite, and O4, corresponding to O3 in barylite, to keep the same names used by Krivovichev *et al.* (2004).
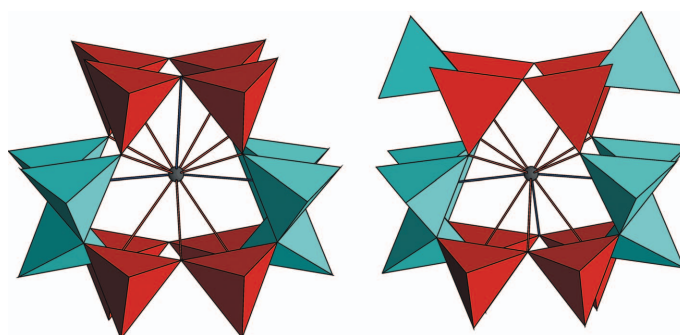

FIG. 3. Barium coordination in 'clinobarylite' (barylite-1*O*), left and in barylite (barylite-2*O*), right. It is clear that all the tetrahedra point in one direction in the first, whereas tetrahedra point in two opposite directions in the second one.

TABLE 4. Atomic coordinates and displacement parameters (Å^2) for 'clinobarylite'.

Site	x	y	z	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U_{eq}
Ba	½	0.20271(3)	0.50997(3)	0.0126(1)	0.0109(1)	0.0100(1)	0.0001(1)	0	0	0.0111(1)
Be	0.7511(2)	0.1697(5)	0.0026(13)	0.0075(10)	0.0070(8)	0.0086(10)	0.0011(2)	−0.002(2)	0.0001(7)	0.00777(4)
Si	0.62827(5)	0.67514(9)	0.9888(2)	0.0054(2)	0.0048(2)	0.0068(3)	0.003(2)	−0.0002(3)	−0.0004(2)	0.0057(1)
O1	0.63927(14)	0.3557(3)	0.0569(3)	0.0092(6)	0.0058(5)	0.0120(10)	0.0007(5)	0.0019(5)	0.0010(5)	0.0090(3)
O2	0.77737(13)	0.1338(3)	0.6511(3)	0.0082(7)	0.0048(5)	0.0074(6)	−0.0007(4)	0.0007(5)	−0.0010(5)	0.0068(2)
O3	½	0.7750(4)	0.1002(5)	0.0064(10)	0.0081(8)	0.0105(8)	−0.0034(6)	0	0	0.0084(4)
O4	0.6324(2)	0.7302(3)	0.6496(3)	0.0081(7)	0.0106(6)	0.0074(7)	0.0008(5)	0.0004(6)	−0.0016(5)	0.0087(3)

The mistake in the positioning of the z coordinate of atom O3 of Krivovichev *et al*. (2004) and atoms O1−O4 of Rastsvetaeva and Chukanov (2003) is due to the occurrence of a false minimum. In fact, we carried out several refinements starting with O3 placed at various values of the z coordinate and obtained the correct or erroneous values, as a function of the starting values.

Inconsistencies in the structural data presented by Krivovichev *et al*. (2004) were noted also by Di Domizio *et al*. (2012), who observed that the Si−O$_{br}$ (bridging O atom) distance (1.597 Å) was "significantly shorter than the Si−O$_{nbr}$ (non-bridging O atoms) distances (1.619−1.631 Å, in contrast with the previous observations specifically for disilicate compounds"; therefore they carried out a new structural study, which resulted in the expected correct parameters.

Single-crystal X-ray diffraction study of the holotype material

As the various studies pointing to orthorhombic symmetry were carried out on non-holotype specimens, we deemed it necessary to carry out a structural study with crystals from the holotype material to ascertain definitively the actual symmetry and metrics of 'clinobarylite'. Single crystal X-ray structural studies carried out on two distinct crystals of 'clinobarylite' from the holotype material confirmed that the symmetry is orthorhombic (R_{int} 0.0191 and 0.0185 for crystals 1 and 2, respectively), with no violation of systematic absences in both cases.

For the X-ray single-crystal studies, the intensity data were collected using a Bruker Smart Breeze diffractometer with an air-cooled CCD detector, with MoKα radiation. The detector-to-crystal distance was 50 mm. In the following discussion, only the data collection on crystal 2 will be described. 790 frames were collected in ω and φ scan modes, in 0.5° slices, with an exposure time of 10 s per frame. Data were corrected for Lorentz and polarization factors and absorption using the software package *APEX2* (Bruker AXS Inc., 2004). The statistical tests on the distribution of $|E|$ values ($|E^2−1| = 0.681$) and the systematic absences confirmed the space group $Pmn2_1$. The refined cell parameters are $a = 11.622(1)$, $b = 4.9125(5)$, $c = 4.6654(5)$ Å, $V = 266.36(5)$ Å^3.

The crystal structure of 'clinobarylite' was refined starting from the atomic coordinates of MDO$_1$ polytype using *SHELXL-97* (Sheldrick,

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TABLE 5. Selected bond distances for Si and Be sites (in Å) for 'clinobarylite'. For the sake of comparison, the Si−O and Be−O bond distances reported by Di Domizio *et al*. (2012) are given within square brackets.

Si−O1	1.606(2)	[1.607]	Be−O4	1.595(4)	[1.591]
−O4	1.606(2)	[1.616]	−O1	1.608(3)	[1.615]
−O2	1.630(2)	[1.632]	−O2	1.677(4)	[1.670]
−O3	1.653(1)	[1.657]	−O2	1.678(6)	[1.696]
Average	1.624	[1.628]	Average	1.640	[1.643]

2008). Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). Crystal data and details of intensity data collection and refinement are reported in Table 3. After several cycles of isotropic refinement, the R_1 converged to 0.020, confirming the validity of the structural model. Three cation sites occur in the crystal structure of 'clinobarylite', namely *Ba*, *Be* and *Si*. These sites were found fully occupied by barium, beryllium and silicon, respectively. The introduction of anisotropic displacement parameters lowered the R_1 value to 0.014 for 929 observed reflections [$F_o > 4\sigma F_o$] and 0.015 for all the 937 independent reflections. Atomic coordinates and displacement parameters are given in Table 4; selected bond distances are given in Table 5.

As indicated by the results reported in Table 5, the present crystal structure of 'clinobarylite' agrees with the structural model reported by Di Domizio *et al*. (2012). It consists of a framework of BeO_4 and SiO_4 tetrahedra; BeO_4 tetrahedra form chains parallel to the **c** axis through corner-sharing. These chains are linked together through disilicate groups parallel to the **a** axis. Ba^{2+} cations are hosted within structural cavities;

barium is twelve-fold coordinated, considering only the Ba−O distances shorter than 3.40 Å.

Whereas the coordination sphere of beryllium and silicon is similar in the two polytypes, a different bonding environment occurs for Ba^{2+} cations. In fact the coordination sphere of this cation placed in the L_{2n} layer spans a triple of layers L_{2n}, L_{2n+1}, L_{2n+2} or L_2, L_{2n-1}, L_{2n-2} and is, therefore, different in MDO_1 and MDO_2 polytypes (Table 6 and Fig. 3).

It is interesting to emphasize that this kind of structural topology is shown by a number of synthetic borates with composition MB_4O_7 (*M* divalent cation). Most present the MDO_1 structure type, whereas β-BaB_4O_7 displays the MDO_2 structure type (Table 7).

Redefinition of the 'clinobarylite'−barylite pair

The OD approach confirms the polytypic relationships between the two natural phases. As suggested by Krivovichev *et al*. (2004) and following the indications of the "Procedures involving the IMA Commission on New Minerals and Mineral Names and guidelines on mineral nomenclature" (Nickel and Mandarino,

TABLE 6. Ba^{2+} cation coordination (bond distances in Å) in 'clinobarylite' and barylite [data after Robinson and Fang, 1977]. O3 in 'clinobarylite' corresponds to O4 in barylite and *vice versa*.

	'Clinobarylite' (this study)		Barylite (Robinson and Fang, 1977)
Ba−O1	2.766(2) × 2	Ba−O1	2.822(7) × 2
−O3	2.841(2)	−O4	2.907(7)
−O4	2.860(2) × 2	−O3	2.905(7) × 2
−O4	3.084(2) × 2	−O3	3.042(7) × 2
−O1	3.114(2) × 2	−O1	3.043(7) × 2
−O2	3.307(2) × 2	−O2	3.312(7) × 2
−O3	3.400(2)	−O4	3.256(7)
Average	3.042	Average	3.034

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TABLE 7. Synthetic compounds with the structure-type of 'clinobarylite' and barylite, space group symmetry $Pmn2_1$ and $Pmnb$, respectively.

	a (Å)	b (Å)	c (Å)	Ref.
'Clinobarylite' structure type (MDO$_1$)				
β-CaB$_4$O$_7$	10.590	4.372	4.195	1
SrB$_4$O$_7$	10.706	4.431	4.237	2*
SrB$_4$O$_7$	10.702	4.447	4.239	3*
SrB$_4$O$_7$	10.711	4.427	4.235	4
PbB$_4$O$_7$	10.840	4.457	4.244	2*
PbB$_4$O$_7$	10.860	4.463	4.251	5*
β-HgB$_4$O$_7$	10.656	4.381	4.187	6
EuB$_4$O$_7$	10.731	4.435	4.240	7**
'Barylite' structure type (MDO$_2$)				
β-BaB$_4$O$_7$	10.994	9.017	4.307	8

1: Huppertz (2003); 2: Perloff and Block (1966); 3: Pan *et al*. (2002); 4: Krogh-Moe (1964); 5: Corker and Glazer (1996); 6: Hemme *et al*. (2005); 7: Machida *et al*. (1980); 8: Knyrim *et al*. (2009).
* the authors adopt the space group symmetry $P2_1nm$ (**a** and **c** are inverted); ** the authors adopt the space group symmetry $Pnm2_1$ (**a** and **b** are inverted).

1987), the following nomenclature should be adopted:

barylite-1*O* for 'clinobarylite', which contains one layer of either type in the unit cell;
barylite-2*O* for barylite, which contains two layers of either type in the unit cell.

This new nomenclature of the barylite polytypes has been approved by the IMA-CNMNC (IMA 13-E, Williams *et al*., 2014). The name 'clinobarylite' should be discontinued.

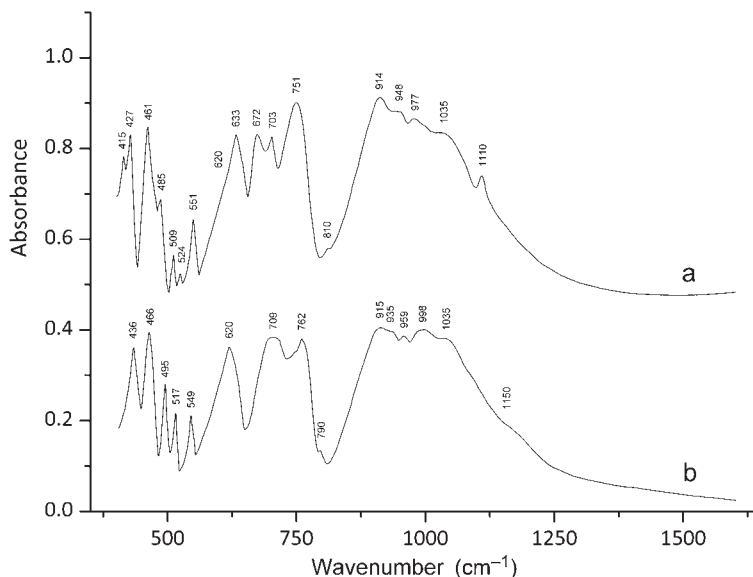As barylite-1*O* and barylite-2*O* are the only MDO structures in this family, it is likely that no

FIG. 4. Infrared spectra of barylite-2*O* from Långban, Sweden (*a*) and barylite-1*O* from Yukspor Mt., Khibiny, Russia (*b*).

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TABLE 8. Wavenumbers (cm^{-1}) of the IR absorption bands of barylite-1O and barylite-2O and their assignment.

Barylite-1O	Barylite-2O	Assignment
1150 sh	1110 s	
1035 s	1035 s	
998 s	977 s	
<u>959 s</u>	<u>948 s</u>	Si—O stretching vibrations
<u>935 sh</u>		
915 s	914 s	
790 w	810 w	
<u>762 s</u>	<u>751 s</u>	
709 s	703 s	
	672 s	Be—O stretching vibrations
	<u>633 s</u>	
620 s	620 sh	
549 m	551 m	
<u>517 m</u>	524 w	
<u>495 m</u>	<u>509 w</u>	
466 s	<u>485 m</u>	Bending vibrations of the framework
	461 s	
436 s	427 s	
	415 m	

s = strong band; m = band of medium strength; w = weak band; sh = shoulder.
Wavenumbers of diagnostic bands are underlined.

other natural stable polytype will be found. However, it is possible that small or large domains of one polytype are present in a matrix of the other polytype. The piezoelectric effect and the second harmonic generation observed in some crystals of barylite could be due to the presence of domains of the highly polar MDO$_1$ polytype.

Generally, in natural samples, a main polytype predominates over the other. The MDO$_1$ and MDO$_2$ polytypes of barylite can be distinguished by infrared (IR) spectroscopy. Several spectra of samples from different localities contain bands corresponding to only one polytype. The IR spectra of barylite-2O from Långban, Sweden and of barylite-1O from the Yukspor Mt., Khibiny, Russia, are shown in Fig. 4; wavenumbers and their assignment are given in Table 8.

Redefinition of 'clinobarylite' as barylite-1O needs re-indexation of its powder X-ray diffraction diagram. A new powder X-ray diffraction pattern (PXRD) of barylite-1O from the holotype specimen of 'clinobarylite' was collected using the Gandolfi method on an Oxford Diffraction SuperNova diffractometer, with CuKα radiation.

The data are given in Table 9 in comparison with the data of barylite-2O from its type locality, Långban mine, Sweden, obtained using the Debye-Scherrer method in a camera with diameter 57.3 mm, with CuKα radiation. The PXRD of barylite-2O contains three intense reflections impossible for barylite-1O with halved b unit-cell parameter. This is a good diagnostic tool, along with the IR spectrum, for the distinction of the two barylite polytypes. Note that the reflection with d = 4.671 Å that was observed in the PXRD pattern of the mineral reported by Chukanov *et al*. (2003) and considered as an argument for the space group symmetry Pm is absent in this pattern. Its nature remains unclear; in particular, the calculated PXRD pattern of barylite-2O does not contain this reflection either.

Acknowledgements

TABLE 9. Powder XRD data for the holotype barylite-1O from Khibiny, Kola, Russia and barylite-2O from Långban, Sweden.

		Barylite-1O				Barylite-2O	
I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	$h\ k\ l$	I_{obs}	d_{obs}	$h\ k\ l$
79	5.80	51	5.811	200			
13	4.87	1	4.913	010	60	4.88	020
37	4.514	27	4.525	110	30	4.50	**120**
46	4.326	28	4.330	101			
					10	3.74	220
					10***	3.42***	211***
80	3.381	85	3.383	011	100	3.37	021
28	3.248	28	3.248	111	50	3.24	121
78	3.043	78	3.042	310	80	3.04	320
95	2.981	91	2.980	301			
100	2.923	100	2.924	211	40	2.94	221
					80***	2.68***	031***
					35***	2.61***	131***
23	2.502	22	2.501	410	10	2.51	420
25	2.457	34	2.456	020	10	2.42	040
7	2.403	9	2.403	120			
29	2.333	37	2.333	002	50	2.33	002
9	2.262	14	2.262	220			
39	2.205	46	2.204	411	40	2.25	421
21	2.170	9, 17	2.173, 2.165	021, 202			
6	2.136	13	2.136	121			
54	2.075	17, 19, 4, 19	2.101, 2.081, 2.074, 2.073	510, 501, 320, 112	40	2.09	520, 501, 122
8	2.033	8	2.036	221	25	2.00	241
5	1.937	8	1.937	600	30	1.91	600
14	1.897	19	1.896	321	20	1.88	341
17	1.851	22	1.851	312	15	1.85	322
2	1.816	3	1.819	402			
13	1.741	10	1.740	421	70	1.74	441
3	1.709	7	1.706	412			
53	1.682	11, 15, 7	1.691, 1.681, 1.674	022, 611, 122	60	1.69	042, 621
					5	1.66	142
13	1.624	9	1.624	222	10	1.62	242
28	1.591	9	1.588	521	20	1.590	541
29	1.563	2, 15	1.564, 1.561	701, 512	15	1.555	522
38	1.532	13	1.532	131	10	1.530	161
35	1.491	6, 4, 6, 7	1.493, 1.490, 1.490, 1.483	231, 711, 602, 013	40	1.503	261
					5	1.483	023
50	1.440	4, 10, 11, 1	1.446, 1.443, 1.437, 1.435	621, 303, 213, 331	10	1.451	641
30	1.426	13	1.427	430	40	1.424	460
3	1.376	3	1.376	720	40	1.375	740
5	1.364	1, 3	1.368, 1.364	522, 431			
16	1.336	2, 9, 2	1.339, 1.335, 1.331	530, 811, 132	30	1.342	560
4	1.321	2, 2	1.321, 1.319	413, 721			
6	1.307	4, 2, 3	1.306, 1.306, 1.304	232, 123, 712			
12	1.293	7	1.293	503	50	1.289	503
3	1.274	4	1.274	622			
13	1.248	5, 1, 7	1.250, 1.244, 1.244	820, 901, 323	50	1.245	840, 343
3	1.234	7	1.233	802			
17	1.220	3, 10	1.221, 1.217	140, 432	30	1.215	180, 462
7	1.178	1, 5	1.182, 1.177	141, 613			
7	1.163	1, 4, 2	1.166, 1.164, 1.161	004, 241, 532			
4	1.145	5, 2	1.144, 1.144	523, 204			

* Only reflections with intensities $\geqslant 1$ are given. ** Calculated from single-crystal data. *** Reflections possible only for barylite-2O, the polytype with doubled b unit-cell parameter.

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References

Abrashev, K.K., Ilyukhin, V.V. and Belov, N.V. (1965) Crystal structure of barylite, $BaBe_2Si_2O_7$. *Soviet Physics − Crystallography*, **9**, 691−699.

Aminoff, G. (1923) Om en association med barili och hedyphan vid Långban. *Geologiska Föreningens i Stockholm Förhandlingar*, **45**, 124−143.

Blomstrand, C.W. (1876) Bidrag till kännedomen af Långbans-grufvans mineralier. *Geologiska Föreningens i Stockholm Förhandlingar*, **3**, 123−133.

Bruker AXS Inc. (2004) *APEX 2. Bruker Advanced X-ray Solutions*. Madison, Wisconsin, USA.

Cannillo, E., Dal Negro, A. and Rossi, G. (1970) On the crystal structure of barylite. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, **26**, 53−62.

Chukanov, N.V., Pekov, I.G., Rastsvetaeva, R.K., Shilov, G.V. and Zadov, A.E. (2003) Clinobarylite, $BaBe_2Si_2O_7$, a new mineral from Khibiny massif, Kola Peninsula. *Zapiski Vserrosijskogo Mineralogicheskogo Obshchestva*, **132**, 29−37 [in Russian].

Corker, D.L. and Glazer, A.M. (1996) The crystal structure and optical non linearity of $PbO·2B_2O_3$. *Acta Crystallographica*, **B52**, 260−265.

Di Domizio, A.J., Downs, R.T. and Yang, H. (2012) Redetermination of clinobarylite, $BaBe_2Si_2O_7$. *Acta Crystallographica*, **E68**, 178−179.

Dornberger-Schiff, K. (1964) *Grundzüge einer Theorie der OD Strukturen aus Schichten*. Abhandlungen der Deutschen Akademie der Wissenschaften zu Berlin, Klasse für Chemie, Geologie und Biologie, **3**. Akademie Verlag, Berlin, pp. 106.

Dornberger-Schiff, K. (1966) *Lehrgang über OD Strukturen*. Akademie Verlag, Berlin, pp. 64.

Ferraris, G., Makovicky, E. and Merlino, S. (2004) *Crystallography of Modular Materials*. Oxford University Press, Oxford, UK.

Grell, H. and Dornberger-Schiff, K. (1982) Symbols of OD groupoid families referring to OD structures (polytypes) consisting of more than one kind of layer. *Acta Crystallographica*, **A38**, 49−54.

Hemme, H., Weil, M. and Huppertz, H. (2005) High-pressure synthesis and crystal structure of the new orthorhombic polymorph β-HgB_4O_7. *Zeitschrift für Naturforschung*, **60b**, 815−820.

Huppertz, H. (2003) β-CaB_4O_7: a new polymorph synthesized under high pressure/high temperature conditions. *Zeitschrift für Naturforschung*, **58b**, 257−265.

Knyrim, J.S., Römer, S.R., Schnick, W. and Huppertz, H. (2009) High-pressure synthesis and characterization of the alkaline earth borate β-BaB_4O_7. *Solid State Sciences*, **11**, 336−342.

Krivovichev, S.V., Yakovenchuk, V.N., Armbruster, T., Mikhailova, Y. and Pakhomovsky, A. (2004) Clinobarylite, $BaBe_2Si_2O_7$: structure refinement, and revision of symmetry and physical properties. *Neues Jahrbuch für Mineralogie, Monatshefte*, **2004**, 373−384.

Krogh-Moe, J. (1964) The crystal structure of strontium diborate, $SrO·2B_2O_3$. *Acta Chemica Scandinavica*, **18**, 2055−2060.

Machida, K.I., Adachi, G.Y. and Shiokawa, J. (1980) Structure of europium (II) tetraborate. *Acta Crystallographica*, **B36**, 2008−2011.

Nickel, E.H. and Mandarino, J.A. (1987) Procedures involving the IMA Commission on New Minerals and Mineral Names, and guidelines on mineral nomenclature. *The Canadian Mineralogist*, **25**, 353−377.

Pan, F., Shen, G., Wang, R., Wang, X. and Shen, D. (2002) Growth, characterization and nonlinear optical properties of SrB_4O_7 crystals. *Journal of Crystal Growth*, **241**, 108−114.

Perloff, A. and Block, S. (1966) The crystal structure of the strontium and lead tetraborates $SrO·2B_2O_3$ and $PbO·2B_2O_3$. *Acta Crystallographica*, **20**, 274−279.

Petersen, O.V. and Johnsen, O. (1980) First occurrence of the rare mineral barylite in Greenland. *Tschermak's Mineralogische und Petrographische Mitteilungen*, **27**, 35−39.

Rastsvetaeva, R.K. and Chukanov, N.V. (2003) Crystal structure and microtwinning of the new mineral clinobarylite, $BaBe_2Si_2O_7$. *Doklady Chemistry*, **388**, 23−25.

Robinson, P.D. and Fang, J.H. (1977) Barylite, $BaBe_2Si_2O_7$: its space group and crystal structure. *American Mineralogist*, **62**, 167−169.

Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112−122.

Williams, P.A., Hatert, F., Pasero, M. and Mills, S.J. (2014) New minerals and nomenclature modifications approved in 2014. *Mineralogical Magazine*, **78**, 558.

Wilson, A.J.C. (1992) *International Tables for Crystallography*. Volume C. Kluwer, Dordrecht, Netherlands.