

# ‘Clinobarylite’ – barylite: order-disorder relationships and nomenclature

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## ABSTRACT

‘Clinobarylite’, BaBe<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, 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, *Pmn*2<sub>1</sub> 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<sub>1</sub> polytype, with unit-cell parameters  $a = 11.650$ ,  $b = 4.922$ ,  $c = 4.674$  Å, space group *Pmn*2<sub>1</sub>; barylite corresponds to the MDO<sub>2</sub> 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<sub>1</sub> 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-1*O* and barylite-2*O*, 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).

**KEYWORDS:** barylite, ‘clinobarylite’, OD theory, barylite-2*O*, barylite-1*O*.

## Introduction

‘CLINOBARYLITE’, BaBe<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, 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 *Pm*11, with  $a = 11.618$ ,  $b = 4.904$ ,  $c = 4.655$  Å,  $\alpha = 89.94^\circ$  and subsequently refined in the orthorhombic space group *Pmn*2<sub>1</sub> 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<sub>4</sub> tetrahedra and Si<sub>2</sub>O<sub>7</sub> groups

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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).

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

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  $Pmmm$  (more precisely  $P2_1/m2/n2_1/m$ ).  $L_2$  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,

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

$$Pmn2_1 \quad [0, \frac{1}{4}] \quad P2_1/m2/n2_1/m \quad (1)$$

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  $-x, \frac{1}{2}-y, \frac{1}{2}+z$  (II); this last unit is converted by the inversion centre in the  $L_1$  layer into the asymmetric unit  $x, \frac{1}{2}+y, \frac{1}{2}-z$  (III). Units (I) and (III) are related by a  $b$  glide normal to  $\mathbf{c}$  at  $z = \frac{1}{4}$ ; moreover, the mirror plane normal to  $\mathbf{a}$  is valid for the whole structure and the  $n$  glide normal to  $\mathbf{b}$  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

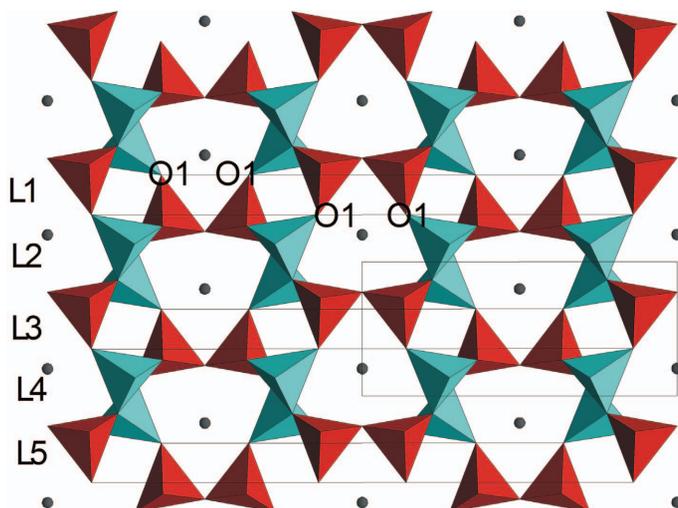


FIG. 1. The crystal structure of 'clinobarylite' (polytype  $MDO_1$  in the OD family of barylite) as seen down  $[001]$  ( $\mathbf{b}$  vertical), with indication of the unit cell. The sequence of OD layers is indicated.

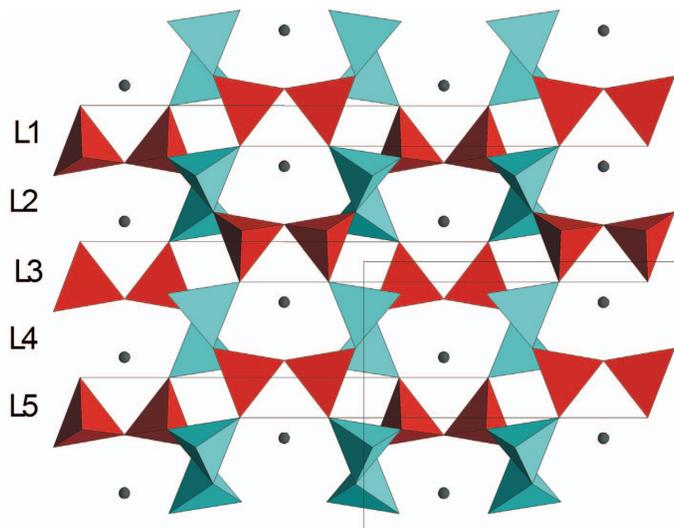


FIG. 2. Structure of polytype  $\text{MDO}_2$  in the OD family of barylite, as seen down  $[001]$  ( $b$  vertical), with indication of the unit cell. The sequence of OD layers is indicated.

coordinates given by Robinson and Fang (1977) for the  $\text{MDO}_2$  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  $\text{SiO}_4$  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 78°]. 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  $\text{MDO}_1$  structure, the atomic coordinates of ‘clinobarylite’ given by Krivovichev *et al.* (2004), and the atomic coordinates obtained on non-holotype material.

Site	MDO <sub>1</sub> polytype (calculated coordinates)			‘Clinobarylite’ (Krivovichev <i>et al.</i> , 2004)			‘Clinobarylite’ non-holotype material (this study)		
	$x$	$y$	$z$	$x$	$y$	$z$	$x$	$y$	$z$
Ba	$\frac{1}{2}$	0.1968	0.5417	$\frac{1}{2}$	0.2027	0.5079	$\frac{1}{2}$	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	$\frac{1}{2}$	0.7908	0.0905	$\frac{1}{2}$	0.7741	−0.0767	$\frac{1}{2}$	0.77669	0.09710
O4	0.6368	0.7144	0.6539	0.6330	0.7324	0.6450	0.63278	0.72972	0.64597

'CLINOBARYLITE'–BARYLITE: ORDER-DISORDER

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

<b>Crystal data</b>	
X-ray formula	BaBe <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>
Crystal size (mm)	0.21 × 0.21 × 0.10
Cell setting, space group	Orthorhombic, <i>Pmn</i> 2 <sub>1</sub>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.622(1), 4.9125(5), 4.6654(5)
<i>V</i> (Å <sup>3</sup> )	266.36(5)
<i>Z</i>	2
<b>Data collection and refinement</b>	
Radiation, wavelength (Å)	MoKα, λ = 0.71073
Temperature (K)	293
Maximum observed 2θ (°)	65.12
Measured reflections	2288
Unique reflections	937
Reflections <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )	929
<i>R</i> <sub>int</sub> after absorption correction	0.0185
<i>R</i> σ	0.0271
Range of <i>h</i> , <i>k</i> , <i>l</i>	−12 ≤ <i>h</i> ≤ 17, −7 ≤ <i>k</i> ≤ 7, −6 ≤ <i>l</i> ≤ 7
<i>R</i> [ <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )]	0.0144
<i>R</i> (all data)	0.0146
<i>wR</i> (on <i>F</i> <sub>o</sub> <sup>2</sup> )	0.0332
Gof	1.157
Number of least-square parameters	59
Maximum and minum residual peak (e/Å <sup>3</sup> )	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 MDO<sub>1</sub> 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 *Pmn*2<sub>1</sub>. The refinement

converged to a final *R*<sub>1</sub> = 0.0197 (*wR*<sub>2</sub> = 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).

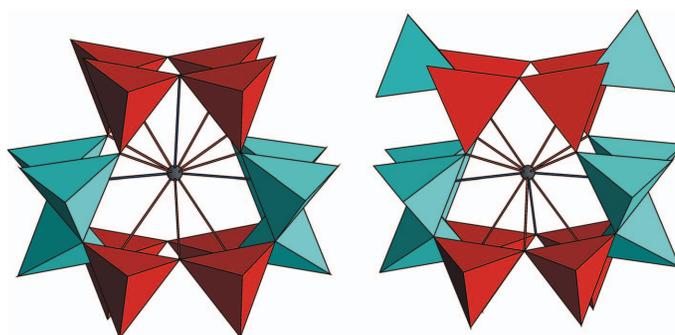


FIG. 3. Barium coordination in 'clinobarylite' (barylite-1O), left and in barylite (barylite-2O), right. It is clear that all the tetrahedra point in one direction in the first, whereas tetrahedra point in two opposite directions in the second one.

TABLE 4. Atomic coordinates and displacement parameters ( $\text{\AA}^2$ ) for ‘clinobarylite’.

Site	x	y	z	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$	$U_{\text{eq}}$
Ba	$\frac{1}{2}$	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)	0.001(2)	-0.002(2)	0.0001(7)	0.0077(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	$\frac{1}{2}$	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<sub>br</sub> (bridging O atom) distance (1.597 Å) was “significantly shorter than the Si–O<sub>nbr</sub> (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 ( $R_{\text{int}}$  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 MoK $\alpha$  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  $\omega$  and  $\varphi$  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<sup>3</sup>.

The crystal structure of ‘clinobarylite’ was refined starting from the atomic coordinates of MDO<sub>1</sub> polytype using *SHELXL-97* (Sheldrick,

‘CLINOBARYLITE’–BARYLITE: ORDER-DISORDER

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  $\text{BeO}_4$  and  $\text{SiO}_4$  tetrahedra;  $\text{BeO}_4$  tetrahedra form chains parallel to the *c* axis through corner-sharing. These chains are linked together through disilicate groups parallel to the *a* axis.  $\text{Ba}^{2+}$  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  $\text{Ba}^{2+}$  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<sub>1</sub> and MDO<sub>2</sub> 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  $\text{MB}_4\text{O}_7$  (*M* divalent cation). Most present the MDO<sub>1</sub> structure type, whereas  $\beta\text{-BaB}_4\text{O}_7$  displays the MDO<sub>2</sub> 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.  $\text{Ba}^{2+}$  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

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 <sub>1</sub> )				
$\beta$ -CaB <sub>4</sub> O <sub>7</sub>	10.590	4.372	4.195	1
SrB <sub>4</sub> O <sub>7</sub>	10.706	4.431	4.237	2*
SrB <sub>4</sub> O <sub>7</sub>	10.702	4.447	4.239	3*
SrB <sub>4</sub> O <sub>7</sub>	10.711	4.427	4.235	4
PbB <sub>4</sub> O <sub>7</sub>	10.840	4.457	4.244	2*
PbB <sub>4</sub> O <sub>7</sub>	10.860	4.463	4.251	5*
$\beta$ -HgB <sub>4</sub> O <sub>7</sub>	10.656	4.381	4.187	6
EuB <sub>4</sub> O <sub>7</sub>	10.731	4.435	4.240	7**
‘Barylite’ structure type (MDO <sub>2</sub> )				
$\beta$ -BaB <sub>4</sub> O <sub>7</sub>	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  $P2_1nm$  ( $\mathbf{a}$  and  $\mathbf{c}$  are inverted); \*\* the authors adopt the space group symmetry  $Pmn2_1$  ( $\mathbf{a}$  and  $\mathbf{b}$  are inverted).

1987), the following nomenclature should be adopted:

barylite-1O for ‘clinobarylite’, which contains one layer of either type in the unit cell;  
barylite-2O 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-1O and barylite-2O are the only MDO structures in this family, it is likely that no

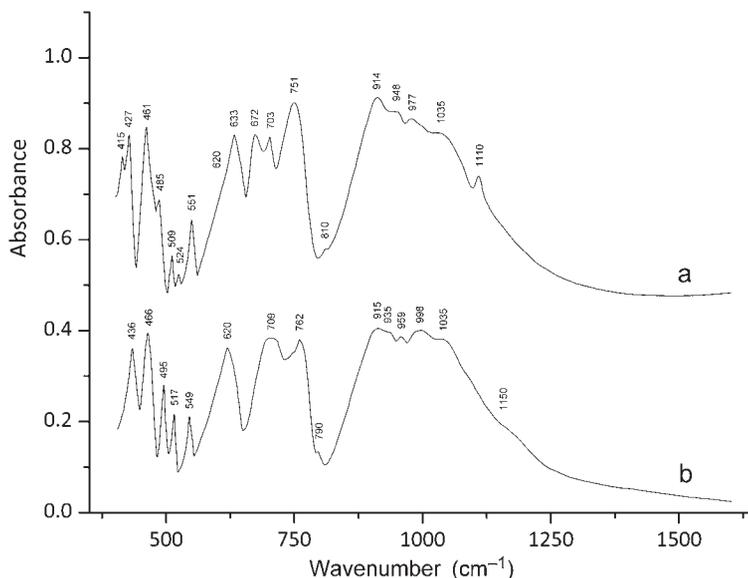


TABLE 8. Wavenumbers ( $\text{cm}^{-1}$ ) of the IR absorption bands of barylite-1*O* and barylite-2*O* and their assignment.

Barylite-1 <i>O</i>	Barylite-2 <i>O</i>	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	
	<u>672 s</u>	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<sub>1</sub> polytype.

Generally, in natural samples, a main polytype predominates over the other. The MDO<sub>1</sub> and MDO<sub>2</sub> 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-2*O* from Långban, Sweden and of barylite-1*O* 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-1*O* needs re-indexation of its powder X-ray diffraction diagram. A new powder X-ray diffraction pattern (PXRD) of barylite-1*O* from the holotype specimen of 'clinobarylite' was collected using the Gandolfi method on an Oxford Diffraction SuperNova diffractometer, with CuK $\alpha$  radiation.

The data are given in Table 9 in comparison with the data of barylite-2*O* from its type locality, Långban mine, Sweden, obtained using the Debye-Scherrer method in a camera with diameter 57.3 mm, with CuK $\alpha$  radiation. The PXRD of barylite-2*O* contains three intense reflections impossible for barylite-1*O* 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-2*O* does not contain this reflection either.

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

Barylite-1O					Barylite-2O		
$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$	$h k l$	$I_{\text{obs}}$	$d_{\text{obs}}$	$h k l$
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	<b>120</b>
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
13	1.624	9	1.624	222	5	1.66	142
28	1.591	9	1.588	521	10	1.62	242
29	1.563	2, 15	1.564, 1.561	701, 512	20	1.590	541
38	1.532	13	1.532	131	15	1.555	522
					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  $\geq 1$  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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