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Single crystal X-ray investigation of norsethite, $BaMg(CO_3)_2$: one more mineral with an aplanar carbonate group

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Abstract. The crystal structure of norsethite, $BaMg(CO_3)_2$, [$a = 5.022(1)$ Å, $c = 16.77(1)$ Å, space group $R\bar{3}m$, $Z = 3$] was reinvestigated by single crystal X-ray methods working with both natural and synthetic material. The main features of an earlier structure determination using powder data were confirmed, but no significant deviation of the atomic arrangement from $R\bar{3}m$ was found. The carbonate group is aplanar; the most probable value for the distance of the carbon atom from the plane defined by the three oxygen atoms is estimated to be 0.044(7) Å.

Introduction

Norsethite, $BaMg(CO_3)_2$, was first described by Mrose et al. (1961) from the Green River formation at Westvaco trona mine in Wyoming, U.S.A. These authors recognized the close relationship of norsethite to both calcite and dolomite. From single crystal precession photographs they derived $R\bar{3}m$, $R3m$, and $R32$ as possible space groups, and because only the last one of the three is a subgroup of $R\bar{3}c$, the space group of calcite, they concluded that the space group of norsethite "must be $R32$" (l.c., p. 427).

The crystal structure of synthetic norsethite was determined by Lippmann (1968) from 30 X-ray powder lines. He noticed that $R\bar{3}m$ must not be excluded from the choice of the space groups, but he obtained in $R32$ a lower reliability index ($R = 0.035$) than in $R\bar{3}m$ ($R = 0.059$).

In connection with systematic studies of the aplanarity of the carbonate group in inorganic compounds it seemed interesting to reinvestigate the

Table 1. Summary of crystal data, X-ray measurements, and structure refinements for synthetic norsethite, $BaMg(CO_3)_2$

$a = 5.022(1)$ Å
$c = 16.77(1)$ Å
$c/a = 3.339$
$V = 366.3$ Å^3
$Z = 3$
$\mu(\mathrm{Mo}K\alpha) = 77$ cm^{-1}
$\varrho_{\mathrm{calc}} = 3.83$ g cm^{-3}

STOE four-circle diffractometer AED 2
program system STRUCSI (ECLIPSE S/140)
crystal dimensions: $0.06 \times 0.06 \times 0.19$ mm^3
graphite monochromatized Mo$K\alpha$ radiation
range of data collection: $7° \leq 2\,\theta \leq 100°$
scan speed: $2\,\theta:\omega = 1:1$
35 steps per reflection + (α_1, α_2) splitting
0.5 to 1.5 s per step; step width: 0.03°
total measured reflections: 3733
unique reflections: 526
used for refinement [$F_o \geq 3\,\sigma(F_o)$]: 524

	Model 1	Model 2	Model 3
Space group	$R\bar{3}m$	$R32$	$R\bar{3}m$
No. of variables	15	18	18
R	0.042	0.042	0.041
R_w	0.035	0.034	0.034

crystal structure of norsethite, because Lippmann (1968) had considered only models with exactly planar carbonate groups.

To find a grain of natural norsethite suitable for the collection of a reliable X-ray data set proved to be unexpectedly difficult. Finally, resort was taken to a crystal from the type locality (Smithonian Institution No. 137148), although its size and shape ($0.3 \times 0.6 \times 0.1$ mm^3) were rather unfavourable. The artifical norsethite used had been synthesized by Lippmann (1968).

Experimental

The new lattice parameters and the data concerning the intensity measurements are summarized in Table 1. The collected X-ray intensities were corrected for absorption (empirical ψ scans) as well as for the Lorentz and polarization effects. Complex scattering functions for neutral atoms from the *International Tables for X-ray Crystallography*, Vol. IV (1974) were employed. Secondary isotropic extinction was taken into account according to Zachariasen (1967). The F's obtained from the synthetic material are considered to be of superior quality because of the smaller absorption effects. Therefore, mainly the results derived from them will be discussed below. It is, however, to be mentioned that the structure parameters obtained from the natural crystal mostly agree with those obtained from the synthetic material within two e.s.d.'s.

A least-squares refinement of the most probable structure according to Lippmann (1968) resulted in $R32$ in an atomic arrangement (model 2)

Table 2. Structure parameters with e.s.d.'s in parentheses for synthetic norsethite. $\mathrm{ATF} = \exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}\, a_i^*\, a_j^*\, h_i\, h_j]$

Atom	Position		Model 1 ($R\bar{3}m$)	Model 2 ($R32$)	Model 3 ($R\bar{3}m$)
Ba	3(a) 0,0,0 etc.	U_{11}	0.0113(1)	0.0113(1)	0.0113(1)
		U_{33}	0.0158(2)	0.0158(2)	0.0159(2)
Mg	3(b) 0,0,$\frac{1}{2}$ etc.	U_{11}	0.0096(5)	0.0095(5)	0.0095(5)
		U_{33}	0.013(1)	0.013(1)	0.014(1)
C	6(c) 0,0,z etc.	z	0.2391(3)	0.2392(3)	0.2392(3)
		U_{11}	0.0108(8)	0.0110(8)	0.0109(7)
		U_{33}	0.013(2)	0.012(2)	0.013(2)
O	[a]	x	0.1463(3)	0.164(5)	0.174(3)
		y	$\bar{x}$	−0.129(5)	−0.118(3)
		z	0.2420(2)	0.2416(2)	0.2416(2)
		U_{11}	0.043(1)	0.035(4)	0.025(4)
		U_{22}	U_{11}	0.042(6)	0.029(5)
		U_{33}	0.024(1)	0.025(2)	0.025(1)
		U_{12}	0.039(2)	0.033(4)	0.022(4)
		U_{13}	0.002(1)	−0.010(4)	−0.005(2)
		U_{23}	$-U_{13}$	−0.014(4)	−0.008(2)

[a] The oxygen atom occupies in model 1 the position 18(h) $x,\bar{x},z$ etc. of space group $R\bar{3}m$, in model 2 the position 18(f) x,y,z etc. of space group $R32$, and in model 3 the position 36(i) x,y,z etc. (occupancy: 0.5) of space group $R\bar{3}m$

Table 3. Interatomic distances (in Å) and bond angles (in °; given in brackets) with e.s.d.'s in parentheses for synthetic norsethite, $BaMg(CO_3)_2$. Only O−O distances < 3.5 Å are given. Model 3: O−O distances for polyhedra with symmetry 32

	Model 1	Model 2	Model 3
Ba−O	2.947(2) (12×)	2.88(2) (6×)	2.83(1) (6×)
		3.03(2) (6×)	3.07(1) (6×)
O−O	2.204(3) [43.9(1)] (6×)	2.21(5) (6×)	2.21(3) (6×)
	2.818(3) [57.1(1)] (6×)	2.82(5) (6×)	2.83(3) (6×)
	3.084(7) [63.1(1)] (6×)	3.10(1) (6×)	3.10(1) (6×)
Mg−O	2.060(2) (6×)	2.06(2) (6×)	2.06(1) (6×)
O−O	2.818(3) [86.3(1)] (6×)	2.82(5) (6×)	2.83(3) (6×)
		2.91(3) (3×)	2.87(2) (3×)
	3.005(6) [93.7(1)] (6×)	3.08(3) (3×)	3.13(2) (3×)
C−O	1.273(1) (3×)	1.28(3) (3×)	1.28(2) (3×)
O−O	2.204(3) [119.9(2)] (3×)	2.21(5) (3×)	2.21(3) (3×)

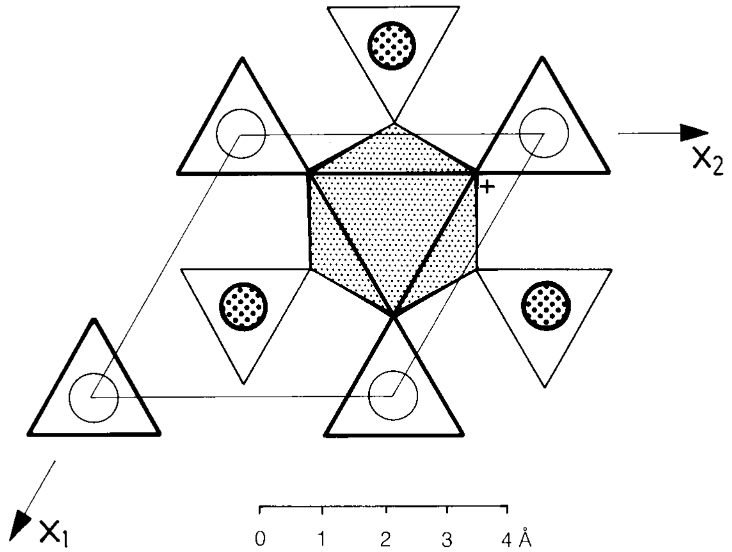

Fig. 1. Crystal structure of nosethite (model 1). Projection of a slab with $0 \leq z \leq 1/3$ parallel to [001]. Circles: Ba atoms (weak: $z = 0$, bold: $z = 1/3$). MgO_6 octahedron dotted ($z = 1/6$). Triangles: carbonate groups (weak: $z \sim 0.10$, bold: $z \sim 0.24$). Cross: position of the O atom according to Lippmann (1968)

which is considerably closer to symmetry $R\bar{3}m$ than his model. In the model favoured by Lippmann the angle α of the bond direction C–O with the x-axis measures 17.6°, while we obtain in space group $R32$ $\alpha = 26.1(1.0)°$; an ordered structure in space group $R\bar{3}m$ requires $\alpha = 30.0°$. Therefore, the structure was also refined in space group $R\bar{3}m$, with the oxygen atoms on the position 18(h) $x, \bar{x}, z$ etc. (model 1). The reliability index obtained was practically the same as in $R32$ although the number of variables was lower by three; the parameters for the anisotropic thermal motion changed for all the atoms, including the oxygen atom, only slightly. A least-squares refinement again in $R\bar{3}m$, but with a splitted oxygen atom gave practically the same R value, but now a somewhat smaller angle α was obtained, i.e. $\alpha = 23.7(0.7)°$ (model 3). Refinements with a data set up to $\sin\theta/\lambda = 0.60$ Å^{-1} yielded R's ~ 0.01 and structure parameters rather similar to those obtained from the large set for all three models. The structure parameters obtained for synthetic norsethite are compiled in Table 2. The data set collected from the natural norsethite yielded again very similar sets of parameters, but the R values were always higher by ~ 0.01.

The single crystal intensity distribution showed no significant deviation from Laue symmetry $\bar{3}2/m$, and after mixing the intensities according to Laue symmetry $\bar{3}$ only, the refinement in $R\bar{3}$ resulted in an atomic arrangement which did not deviate significantly from that obtained in space group $R\bar{3}m$ (model 1).

Discussion

From the preceding chapter follows that according to our single crystal X-ray work the atomic arrangement of norsethite is most appropriately described in space group $R\bar{3}m$ (model 1). Models 2 and 3 seem both to be unnecessary complicated descriptions of the structural information which can be derived from our measured intensities. Table 3 presents important interatomic distances and bond angles for the three models, as obtained from the intensities collected from the synthetic crystal.

The difficulties in elucidating the true space group arise (a) from the fact that in both $R\bar{3}m$ and $R32$ the same lattice complexes are available for the atoms Ba, Mg and C, and (b) from the possibility to describe the lattice complex of the oxygen atom in $R\bar{3}m$ – 18(h) in Wyckoff notation – also as a non-characteristic orbit in $R32$, namely of position 18(f) with the specification $y = \bar{x}$ (Engel et al., 1984).

The carbonate group in norsethite is clearly aplanar. As in dolomite, the apex of the very flat pyramid points towards the "Mg-sheet" (Zemann, 1981, Effenberger et al., 1981, 1983). For our model 1 the distance d of the C atom from the plane defined by the three O atoms is 0.049(6) Å. If one considers also the aplanarities obtained for the other two models, and further also those obtained for natural norsethite, $d = 0.044(7)$ Å seems to be the most probable value for the aplanarity of the carbonate group in norsethite. As expected this aplanarity is considerably larger than in dolomite, where $d = 0.018(1)$ Å was found by Effenberger et al. (1981, 1983).

A further refinement of the crystal structure of norsethite would be possible by single crystal neutron work, but crystals of appropriate size are not available at present.

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