

Refinement

Refinement on F
 $R = 0.031$
 $wR = 0.041$
 $S = 1.227$
 1856 reflections
 85 parameters
 $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.851 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.581 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 isotropic (Zachariasen, 1963)
 Extinction coefficient:
 $8.9(1) \times 10^{-7}$
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

M^I-O1	1.998 (1)	$P1-O4$	1.589 (2)
M^I-O3^I	2.134 (1)	$P1-O5$	1.502 (2)
M^I-O5^{II}	2.103 (1)	$P1-O6^V$	1.588 (2)
$M^{II}-O2^{III}$	2.000 (1)	$P2-O1$	1.457 (2)
$M^{II}-O3^{IV}$	2.079 (1)	$P2-O3$	1.509 (1)
$M^{II}-O5^{IV}$	2.070 (1)	$P2-O4$	1.592 (2)
$P1-O2$	1.459 (1)	$P2-O6$	1.585 (2)
$O1-M^I-O3^{VI}$	176.40 (8)	$O3^{IV}-M^{II}-O3^{VI}$	180
$O1^{VII}-M^I-O3^I$	176.40 (7)	$O5^{IV}-M^{II}-O5^{VI}$	180
$O5^{II}-M^I-O5^{IV}$	166.37 (7)	$P1-O4-P2$	138.78 (8)
$O2^{III}-M^{II}-O2^{VIII}$	180	$P1^V-O6-P2$	134.57 (12)

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} - y, -z$; (ii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iii) $x, y - 1, z$; (iv) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $\frac{3}{2} - x, \frac{3}{2} - y, -z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $2 - x, y, \frac{1}{2} - z$; (viii) $2 - x, 1 - y, 1 - z$.

Refinements with distinct Zn and Ni sites gave worse results in terms of R values, residual electron density and S .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *BEGIN in SDP* (Frenz, 1985). Program(s) used to solve structure: Patterson and Fourier methods (*MolEN*; Fair, 1990). Program(s) used to refine structure: *LSFM in SDP*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF VAX in MolEN*.

We are grateful to a referee for helpful suggestions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1265). Services for accessing these data are described at the back of the journal.

References

- Averbuch-Pouchot, M. T. & Durif, A. (1983). *J. Solid State Chem.* **49**, 341–352.
 Beucher, M. & Grenier, J. C. (1968). *Mater. Res. Bull.* **3**, 643–648.
 Cruickshank, D. W. J. (1972). *J. Chem. Soc.* pp. 5486–5505.
 Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
 Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
 Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
 Genkina, E. A., Maksimov, B. A. & Mel'nikov, O. K. (1985). *Kristallografiya*, **30**, 885–889.
 Gunsser, W., Fruehauf, D., Rohwer, K., Zimmermann, A. & Wiedenmann, A. (1989). *J. Solid State Chem.* **82**, 43–51.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Läügi, M., Guitel, J. C., Tordjman, I. & Bassi, G. (1972). *Acta Cryst.* **B28**, 201–208.
 Nord, A. G. (1982). *Cryst. Struct. Commun.* **11**, 1467–1474.
 Nord, A. G. (1983). *Mater. Res. Bull.* **18**, 765–773.

- Nord, A. G., Ericson, T. & Werner, P. E. (1990). *Z. Kristallogr.* **192**, 83–90.
 Nord, A. G. & Lindberg, K. B. (1975a). *Acta Chem. Scand. Ser. A*, **29**, 1–6.
 Nord, A. G. & Lindberg, K. B. (1975b). *Acta Chem. Scand. Ser. A*, **37**, 539–543.
 Shchegrov, L. N., Antrapseva, N. M. & Ponomareva, I. G. (1989). *Izv. Akad. Nauk SSSR Neorg. Mater.* **25**, 308–312.
 Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1998). **C54**, 1211–1214

End Member of the Rhodium-Based Quaternary Borocarbides, $\text{ErRh}_2\text{B}_2\text{C}$

JINHUA YE,^a TOETSU SHISHIDO,^b TAKASHI KIMURA,^a TAKEHIKO MATSUMOTO^a AND TSUGUO FUKUDA^b

^aNational Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305, Japan, and ^bInstitute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980, Japan. E-mail: ye@nrim.go.jp

(Received 30 April 1997; accepted 18 February 1998)

Abstract

Erbium dirhodium diboron carbide, the end member of the rhodium-based quaternary borocarbides, was synthesized by the flux method. Structure analyses revealed that the compound crystallizes as a derivative structure of the ThCr_2Si_2 type, which can be viewed as a layered structure of tetrahedrally coordinated Rh_2B_2 thick layers and ErC NaCl -type layers. A comparison of the structural parameters of the $\text{RRh}_2\text{B}_2\text{C}$ (R is a rare earth metal) compounds showed that the atomic distance between transition metal atoms contracts significantly with decreasing rare earth size, resulting in increasing instability of compounds with smaller R .

Comment

A series of newly discovered quaternary borocarbides $\text{RT}_2\text{B}_2\text{C}$ (R is a rare earth and T is a transition metal) are reported to crystallize in a modified ThCr_2Si_2 -type structure (Ban & Sikirica, 1965) by an insertion of a C atom in the rare earth layer. The ThCr_2Si_2 -type structure seems to selectively accept rare earth atoms depending on the type of transition metals in the structure. For $T = \text{Ni}$, all lanthanides ranging from the large lanthanum down to the small lutetium ion are reported to form $\text{RNi}_2\text{B}_2\text{C}$ compounds (Siegrist, Cava *et al.*, 1994). For larger transition metals such as Rh, Ir, Pd and Pt, however, only larger lanthanides are found to form the stable $\text{RT}_2\text{B}_2\text{C}$ phase. No quaternary compound has

been obtained for the transition metals Co and Fe up to now.

Recently, we investigated the phase stability of the rhodium-based borocarbides by means of arc-melting synthesis (Ye *et al.*, 1997). We found that besides the reported LaRh₂B₂C compound (Siegrist, Cava *et al.*, 1994), smaller lanthanides can also form the RRh₂B₂C phase. For lanthanides ranging from La to Tb, the RRh₂B₂C phase forms in almost phase-pure form. For lanthanides smaller than Tb, however, an impurity phase of RRh₃B₂ co-exists with the RRh₂B₂C phase. The RRh₃B₂ phase increases its volume ratio to the RRh₂B₂C phase with decreasing lanthanide size, and becomes the only phase for the smallest lanthanide lutetium. The smallest lanthanide able to form the RRh₂B₂C compound was found to be erbium.

To obtain a better understanding of the rare earth size effects on the crystal chemistry of the quaternary borocarbides, we studied the structural parameters of GdRh₂B₂C, where rare earth Gd is a medium-sized lanthanide (Ye *et al.*, 1996). Recently, we succeeded in growing single crystals of ErRh₂B₂C, the end member of the rhodium-based quaternary borocarbides, using the flux method. We report here the results of the single-crystal structure analysis of the ErRh₂B₂C compound.

The structure of ErRh₂B₂C (Fig. 1) is basically the same as that of GdRh₂B₂C, a derivative structure of the ThCr₂Si₂ type. The structure can be viewed as a layered structure of ErC NaCl-type layers and Rh₂B₂ slabs. Within the ErC layer, the Er—C distance is 2.6055 (1) Å, showing less close packing compared with the atomic radius (Pearson, 1972) of metallic erbium (1.76 Å) and covalent carbon (0.77 Å). The Rh₂B₂ layers contain a square-planar Rh₂ array sandwiched between the boron planes. The Rh—Rhⁱⁱⁱ in-plane distance is 2.6055 (1) Å, which is shorter than found in metallic rhodium (2.70 Å), suggesting strong metal–metal bonding within the layer (see Table 2 for symmetry codes referred to in the text). Each Rh atom is coordinated by four B atoms to form an RhB₄ tetrahedron, with a B—Rh—Bⁱⁱ bond angle of 106.22 (6)° and a B—Rh—B^{vii} angle of 116.2 (1)°, deviating from the standard tetrahedral angle (109.5°). The RhB₄ tetrahedra share edges to form extended Rh₂B₂ slabs. The ErC and Rh₂B₂ layers are connected to each other by a B—C bond of 1.491 (3) Å, much shorter than the distance expected from the covalent boron (0.88 Å) and carbon radii.

The structure of ErRh₂B₂C is isomorphous with those of the recently discovered superconducting borocarbides RNi₂B₂C (Siegrist, Zandbergen *et al.*, 1994), where all the lanthanides are reported to form stable phases. However, for Rh, we found from arc-melting synthesis that only La–Er and Y could form an RRh₂B₂C compound, and an impurity phase appears with decreasing lanthanide size. By comparing distances between transition metals, we find that the Rh—Rh distance de-

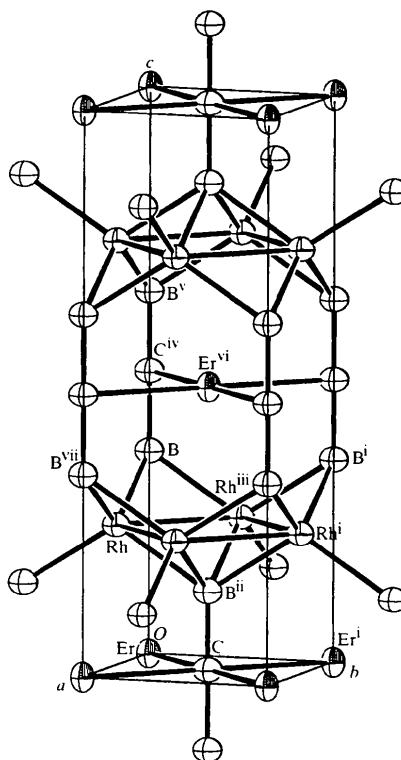


Fig. 1. ORTEP (Johnson, 1976) illustration of ErRh₂B₂C. Displacement ellipsoids are shown at the 95% probability level. The symmetry codes are the same as those in Table 2.

creases significantly from 2.7591 Å in LaRh₂B₂C to 2.6510 (2) Å in GdRh₂B₂C, and decreases further to 2.6055 (1) Å in ErRh₂B₂C. The Rh—Rh distances in GdRh₂B₂C and ErRh₂B₂C are both shorter than the atomic distance expected from the metallic Rh radius (2.70 Å), suggesting not only strong metal–metal bonding in the structure, but also the decreasing stability of RRh₂B₂C compounds with smaller R. On the other hand, for the transition metal Ni, the Ni—Ni distances are 2.6877 Å in LaNi₂B₂C and 2.5371 Å in GdNi₂B₂C, both longer than those calculated from the metallic Ni radius (2.50 Å). Even in the compound consisting of the smallest lanthanide lutetium, the Ni—Ni bonding distance is 2.4551 Å, which is about 1.8% shorter than expected from the metallic nickel radius. The T—T bond length in ErRh₂B₂C, where the rare earth erbium is the smallest lanthanide able to form RRh₂B₂C, contracts about 3.5% compared with the metallic Rh diameter, a larger contraction than in LuNi₂B₂C. From these crystallographic data, it is easy to understand that the ThCr₂Si₂-type structure could readily accept all lanthanides for nickel, while with the transition metal rhodium, lanthanides smaller than erbium have difficulty in forming the RRh₂B₂C phase. The slight deficiency in the Rh site, which was also revealed in GdRh₂B₂C, indicates the difficulty of accommodating the strain caused by the too large Rh atom.

Experimental

Single crystals of $\text{ErRh}_2\text{B}_2\text{C}$ were grown from a copper flux (Shishido *et al.*, 1996). The crystals have a thin plate-like habit, with an average size of about $1.0 \times 1.0 \times 0.02$ mm. The chemical composition was analyzed by applying electron probe microanalysis (EPMA). The atomic ratio of Er:Rh:B:C was found to be close to 1:2:2:1, suggesting the composition of the new compound to be $\text{ErRh}_2\text{B}_2\text{C}$. A slight contamination from the copper solvent was also revealed. A small fragment cut from a bigger piece of crystal was used for intensity measurements.

Crystal data

$\text{ErRh}_2\text{B}_2\text{C}$
 $M_r = 406.70$
 Tetragonal
 $I4/mmm$
 $a = 3.6848$ (2) Å
 $c = 10.5520$ (5) Å
 $V = 143.272$ (7) Å³
 $Z = 2$
 $D_x = 9.427$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.7107$ Å
 Cell parameters from 25 reflections
 $\theta = 41.4$ – 47.4°
 $\mu = 39.99$ mm⁻¹
 $T = 292.0$ K
 Thin plate
 $0.10 \times 0.10 \times 0.02$ mm
 Gold

Data collection

Rigaku AFC-7R diffractometer
 ω - 2θ scans
 Absorption correction:
 by integration from crystal shape
 $T_{\min} = 0.158$, $T_{\max} = 0.719$
 4207 measured reflections
 363 independent reflections

363 reflections with $I > 0$
 $R_{\text{int}} = 0.04$
 $\theta_{\max} = 60^\circ$
 $h = -8 \rightarrow 8$
 $k = -9 \rightarrow 9$
 $l = -25 \rightarrow 25$
 3 standard reflections
 every 100 reflections
 intensity decay: 1.67%

Refinement

Refinement on F^2
 $R = 0.019$
 $wR = 0.020$
 $S = 1.70$
 358 reflections
 12 parameters
 Weighting scheme based
 on measured s.u.'s
 $(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 2.9$ e Å⁻³
 $\Delta\rho_{\min} = -3.6$ e Å⁻³
 Extinction correction:
 Zachariasen (1968) type
 2, Gaussian isotropic
 Extinction coefficient:
 102 (7)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{eq}
Er	0	0	0	0.00738 (2)
Rh†	1/2	0	1/4	0.00744 (2)
C	1/2	1/2	0	0.0053 (3)
B	0	0	0.3587 (3)	0.0085 (2)

† Site occupancy = 0.919 (4).

Table 2. Selected geometric parameters (Å, °)

Er—Er ⁱ	3.6848 (2)	Rh—B	2.170 (2)
Er—Rh	3.2177 (1)	Rh—C	3.2177 (1)
Er—B ⁱⁱ	3.002 (1)	B—C ^{iv}	1.491 (3)
Er—C	2.6055 (1)	B—B ^v	2.982 (6)
Rh—Rh ⁱⁱⁱ	2.6055 (1)		
Rh—Er ^{vi} —Rh ⁱⁱⁱ	47.7671 (9)	Er ^{vi} —Rh—B ⁱⁱ	86.97 (7)
Rh—Er ^{vi} —Rh ⁱ	69.862 (3)	Rh ⁱⁱⁱ —Rh—B	53.11 (3)
Rh—Er ^{vi} —C ^{iv}	66.1164 (7)	Rh ⁱⁱⁱ —Rh—B ⁱⁱ	126.89 (3)
B—Rh—B ⁱⁱ	106.22 (6)	Rh—B ⁱⁱ —Rh ⁱⁱⁱ	73.78 (6)
B—Rh—B ^{vii}	116.2 (1)	Rh—B ⁱⁱ —Rh ⁱ	116.2 (1)
Er ^{vi} —Rh—B	64.32 (5)	Rh—B ⁱⁱ —C	121.90 (7)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) y, x, z ; (iv) $x - \frac{1}{2}, y - \frac{1}{2}, \frac{1}{2} + z$; (v) $x, y, 1 - z$; (vi) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$; (vii) $1 + x, y, z$.

The single crystallinity of the samples was initially checked and the space group of the samples was investigated using a precession camera. After careful observation of various diffraction patterns, only hkl reflections with $h + k + l = 2n + 1$ were recognized to be systematically absent, indicating that the crystal should belong to one of the following space groups: $I\bar{4}2m$, $I\bar{4}m2$, $I422$, $I4mm$ and $I4/mmm$. The space group was finally determined to be $I4/mmm$ through structure analysis based on all these space groups, which will be described hereafter. Neither long-range superstructure reflections nor streaking were observed. The full-matrix least-squares refinement was carried out by adopting the ThCr_2Si_2 -type structure (Ban & Sikirica, 1965) as the initial structure model. The Er, Rh and B atoms were assigned at the crystallographic positions of the Th, Cr and Si atoms, *i.e.* the $2a$, $4d$, and $4e$ sites of the space group $I4/mmm$, respectively, while the C atoms were assigned at the $2b$ site, the center of the Er plane. By varying the scale factor, the isotropic extinction and the atomic positional and anisotropic displacement parameters, the least-squares refinement converged to unweighted and weighted agreement factors, R and wR , of 0.0362 and 0.0418, respectively. Furthermore, the occupancy parameter of the Rh atom was refined, revealing a slight deviation from full occupation at the $4d$ sites to 0.919 (4), and leading to further convergence of R to 0.0242 and wR to 0.0209. The slight deficiency in the Rh occupancy might suggest a partial substitution of the site by Cu atoms, whose existence has been revealed by the EPMA composition analysis. Refinement of the occupancy of other sites did not indicate obvious deficiency, and R and wR were no longer improved. Five strong reflections in the low angle region of $2\theta < 30^\circ$, which might be strongly affected by absorption and extinction effects, were excluded in the final stage of the structure refinement. This refinement resulted in a final R and wR of 0.0189 and 0.0195, producing an F_o versus F_c list in very good agreement. The final difference electron-density map had maxima and minima of 2.9 and -3.6 e Å⁻³, respectively, in the vicinity of the Er atoms. A possible deviation from a centrosymmetric structure was examined by means of full-matrix least-squares refinement in all the non-centrosymmetric space groups $I\bar{4}2m$, $I\bar{4}m2$, $I422$ and $I4mm$. No shift in structural parameters larger than the errors was observed and no significant improvements in the results of the structure analyses were obtained. Therefore, we determined the space group of $\text{ErRh}_2\text{B}_2\text{C}$ to be $I4/mmm$, the one of highest symmetry among the possible space groups.

Data collection: *MSCI/AF C Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/AF C Diffractometer Control Software*. Data reduction:

TEXSAN PROCESS (Molecular Structure Corporation, 1992). Program(s) used to refine structure: TEXSAN LS. Software used to prepare material for publication: TEXSAN FINISH.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1189). Services for accessing these data are described at the back of the journal.

References

- Ban, Z. & Sikirica, M. (1965). *Acta Cryst.* **18**, 594–599.
 Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Pearson, W. B. (1972). In *The Crystal Chemistry and Physics of Metals and Alloys*. New York: John Wiley.
 Shishido, T., Ye, J., Sasaki, T., Matsumoto, T. & Fukuda, T. (1996). *J. Ceram. Soc. Jpn.* **104**, 1117–1120.
 Siegrist, T., Cava, R. J., Krajewski, J. J. & Peck, W. F. Jr (1994). *J. Alloys Compd.* **216**, 135–139.
 Siegrist, T., Zandbergen, H. W., Cava, R. J., Krajewski, J. J. & Peck, W. F. Jr (1994). *Nature*, **367**, 254–256.
 Ye, J., Shishido, T., Kimura, T., Matsumoto, T. & Fukuda, T. (1996). *Acta Cryst.* **C52**, 2652–2655.
 Ye, J., Shishido, T., Sasaki, T., Takahashi, T., Obara, K., Note, R., Matsumoto, T. & Fukuda, T. (1997). *J. Solid State Chem.* **133**, 77–81.
 Zachariassen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Acta Cryst. (1998). **C54**, 1214–1217

A Cementitious Compound with Composition 3CaO·Al₂O₃·CaCO₃·11H₂O

MICHEL FRANCOIS, GUILLAUME RENAUDIN AND OMER EVRARD

Laboratoire de Chimie Minérale, URA CNRS 158, Université Henri Poincaré, Nancy I, Faculté des Sciences, BP 239, 54506 Vandoeuvre lés Nancy CEDEX, France. E-mail: francois@lcm.u-nancy.fr

(Received 8 July 1997; accepted 18 March 1998)

Abstract

The tetracalcium dialuminium hydroxide carbonate pentahydrate Ca₄Al₂(OH)₁₂CO₃·5H₂O is a layered compound constituted by positively charged [Ca₄Al₂(OH)₁₂]²⁺ main layers and negatively charged [CO₃·5H₂O]²⁻ interlayers. The Al³⁺ and Ca²⁺ ions are six- and sevenfold coordinated by O atoms, respectively. A water molecule occupies the seventh coordination site of

each of three Ca²⁺ ions among the four contained in the main layer. Thus, among the five water molecules contained in the interlayer, two of them can be considered as only slightly bonded. One O atom of the carbonate group occupies the seventh coordination site of the remaining Ca²⁺ ion. Moreover, every O atom of the carbonate groups contributes to the formation of relatively strong hydrogen bonds with water molecules, providing cohesion of the interlayer. The planar CO₃²⁻ groups are tilted by 21.8 (9)° from the planes formed by the layers.

Comment

The compound 3CaO·Al₂O₃·CaCO₃·11H₂O and several of the many related basic salts called AFm phases are important because they are formed on hydration of cements. They form positively charged brucite-like [Ca₂(Al,Fe)(OH)₆]⁺ layers and negatively charged [X_z·nH₂O]⁻ interlayers to attain electroneutrality, where X is a monovalent anion (OH⁻, Cl⁻, NO₃⁻, AlO₂⁻) with z = 1, or a bivalent anion (CO₃²⁻, SO₄²⁻) with z = ½, and where n can vary depending on the humidity and on the nature of the inserted anions. To date, structures based on single-crystal data have been determined for the monosulfate 3CaO·Al₂O₃·CaSO₄·12H₂O (Allmann, 1977) and the chloride 3CaO·Al₂O₃·CaCl₂·11H₂O (Tersis *et al.*, 1987) only. A structural model for the carbonate equivalent has been proposed but not refined (Ahmed & Taylor, 1967). In fact, many uncertainties persist concerning the symmetry and the composition, such as the number of water molecules, of the carbonate compound. Triclinic lattice parameters based on single-crystal measurements have been published by Fischer & Kuzel (1982).

The title compound crystallizes in the non-centrosymmetric space group P1. It contains 27 crystallographic

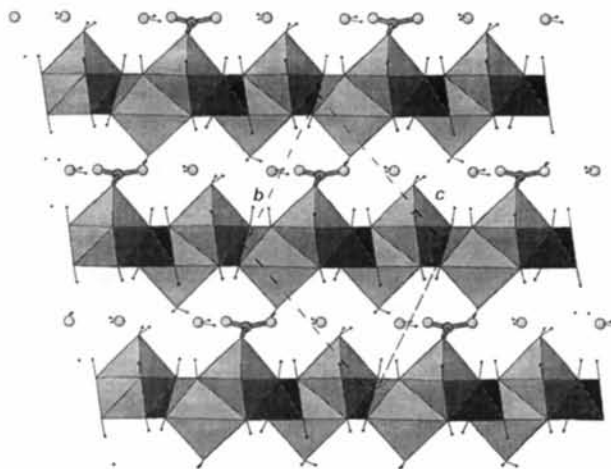


Fig. 1. Projection of the layer structure of 3CaO·Al₂O₃·CaCO₃·11H₂O along [100].