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# Crystal structure of synthetic $K_2Mg(CO_3)_2$

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$K_2Mg(CO_3)_2$ / *Crystal structure*

**Abstract.** The structure of synthetic $K_2Mg(CO_3)_2$ is trigonal with space group $R\bar{3}m$, $a_0 = 5.150(1)$, $c_0 = 17.290(3)$ Å, $Z = 3$ and $D_x = 2.79\,\mathrm{g\,cm^{-3}}$, and was refined to $R$ (unweighted) $= 0.057$ and $R$ (weighted) $= 0.036$ using 280 non-equivalent reflections. The compound is isostructural with buetschliite, $K_2Ca(CO_3)_2$. The structure consists of isolated $[CO_3]_2{}^-$ polyhedra (C–O distance 1.283 Å), $[MgO_6]$ octahedra (Mg–O distance 2.093 Å) and $[KO_9]$ polyhedra (K–O mean distance 2.801 Å). The $[CO_3]^{2-}$ group is non-planar and the distance of the carbon atom from the plane of the three oxygen atoms is 0.014(3) Å.

## Introduction

Double carbonates containing both alkalis and alkaline earths, with compositions $Na_2Mg(CO_3)_2$, $Na_2Ca(CO_3)_2$, $K_2Mg(CO_3)_2$ and $K_2Ca(CO_3)_2$ were synthesized by Eitel and Skaliks (1929). Whereas $K_2Ca(CO_3)_2$, buetschliite, and $Na_2Mg(CO_3)_2$, eitelite, were recognized as minerals by Milton and Axelrod (1947) and by Milton et al. (1955) respectively, $K_2Mg(CO_3)_2$ has not been found in nature. The structure of eitelite and buetschliite has been reported by Pabst (1973, 1974) and refined by Knobloch et al. (1980). In the present study it is demonstrated that $K_2Mg(CO_3)_2$ is isostructural to buetschliite as previously suggested by Simons and Sharma (1982a) and that the $[CO_3]^{2-}$ group is non-planar.

## Experimental

Single crystals of $K_2Mg(CO_3)_2$ were synthesized as follows:

Dried reagent-grade $K_2CO_3$ and natural magnesite rhombs from Brazil as source of $MgCO_3$ were mixed in equimolar proportions, ground for $^1/_2$ h under acetone in an agate mortar, kept at 383 K for 12 h, and 50 mg aliquots were pressed into Au capsules. These capsules were placed in a cold seal hydrothermal pressure vessel and subjected to 0.1 GPa using $CO_2$ as pressure transmitting medium. Temperature was raised to 1023 K and held constant for $^1/_4$ h. Under these conditions, the samples melt, and if rapidly quenched to room conditions they give clear transparent glasses. Such glasses have been investigated by Sharma and Simons (1980) and Simons and Sharma (1982b) by Raman spectroscopy. However, in the present study temperature was lowered to 573 K as fast as possible and pressure was lowered to 0.025 GPa simultaneously. These conditions were kept constant for 24 h yielding clear transparent crystal fragments.

A crystal measuring 0.04 × 0.04 × 0.15 mm was used for data collection on an automatic Philips PW 1100 four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å) and $\omega-2\theta$ scan ($\theta_{\max} = 40°$). The intensities of 1384 reflections were measured. Symmetry equivalent intensities were averaged to give 326 non-equivalent reflections; 280 of them had $|F_o| \geq 3\sigma$ ($|F_o|$) and were used for the subsequent refinement. The standard deviations, $\sigma(F_o)$, were estimated using the formula cited by Stout and Jensen (1968). Refined cell dimensions were determined with the program LAT written by Hornstra and Vossers (1973/74). Lorentz, polarization and absorption corrections (Busing and Levi, 1957) were applied [$\mu$(Mo$K\alpha$) = 18.51 cm$^{-1}$]. The structure was refined by full-matrix least-squares analysis with the program SHELX-76 (Sheldrick, 1976), starting with the atomic coordinates given by Pabst (1974) for buetschliite. The atomic scattering factors were taken from the International Tables for X-ray Crystallography, Vol. IV, 1974, for neutral atoms. Anisotropic refinement of the crystal structure converged at $R$ (unweighted) = 0.057 and $R$ (weighted) = 0.036 $\{R\ (\text{weighted}) = [\Sigma w(|F_o|-|F_c|)^2]^{1/2}/(\Sigma w F_o^2)^{1/2}$, $w = 1/\sigma^2\}$. Final atomic parameters are given in Table 1, bond lengths and angles in Table 2. A list of observed and calculated structure factors can be obtained from the authors.

## Description of the structure and results

The structure of $K_2Mg(CO_3)_2$ consists of [$MgO_6$] octahedra, [$KO_9$] polyhedra and isolated $[CO_3]^{2-}$ groups. Mg – O distance is 2.093 Å and the O – Mg – O angles direct to a slightly distorted [$MgO_6$] octahedron (88.79–91.21°). The K – O distance averages 2.801 Å (Table 2). The $[CO_3]^{2-}$ groups form double layers in which two opposite groups are twisted with respect to each other by an angle of 60°. The structure is isotypical to buetschliite, $K_2Ca(CO_3)_2$ (Pabst, 1974), and displays a C – O distance of 1.283 Å. Since the C atom is located on a three-fold axis, the three C – O distances are equal and the O – C – O angles are 119.99°. As has been reported for buetschliite the $[CO_3]^{2-}$ group has been observed to be slightly pyramidal in the present structure as well. The C atom lies 0.014(3) Å out of the plane of the three O atoms, and pointing to the Mg atom. This distance is less than that observed for buetschliite with 0.038(9) Å by Knobloch et al. (1980). However, comparable distances for the out-of-plane C atom as in the $K_2Mg(CO_3)_2$

**Table 1.** Positional and thermal parameters with standard deviations. The anisotropic temperature factors have the form. $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}\,hka^*b^* + 2U_{13}\,hla^*c^* + 2U_{23}\,klb^*c^*)]$

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ |
|---|---|---|---|---|---|
| K | 0 | 0 | 0.2103(1) | 0.0103(4) | 0.0103(4) |
| Mg | 0 | 0 | 0 | 0.0082(8) | 0.0082(8) |
| C | 0 | 0 | 0.5961(1) | 0.0096(12) | 0.0096(12) |
| O | 0.1438(4) | 0.8562(4) | 0.5953(1) | 0.0128(6) | 0.0128(6) |

| | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|
| K | 0.0190(5) | 0 | 0 | 0.0051(2) |
| Mg | 0.0105(10) | 0 | 0 | 0.0041(4) |
| C | 0.0055(16) | 0 | 0 | 0.0048(6) |
| O | 0.0167(7) | 0.0004(4) | −0.0004(4) | 0.0095(7) |

**Table 2.** Interatomic distances (Å) and angles (°)

| C–O polyhedra | | | K–O polyhedra | | |
|---|---|---|---|---|---|
| C–O | 1.283(1) | ×3 | K–O | 2.733(1) | ×6 |
| O–O | 2.222(1) | ×3 | | 2.938(2) | ×3 |
| O–C–O | 119.99(1) | ×3 | mean | 2.801 | |

Distance O plane – C atom 0.014(3) Å

| Mg–O polyhedra | | |
|---|---|---|
| Mg–O | 2.093(1) | ×6 |
| O–Mg–O | 88.79(6) | ×6 |
| | 91.21(6) | ×6 |
| | 180.00(0) | ×3 |

structure have been observed for eitelite, $Na_2Mg(CO_3)_2$, with 0.018(5) Å by Knobloch et al. (1980), for ankerite, $FeCa(CO_3)_2$, with 0.011(3) Å by Beran and Zemann (1977), and for dolomite, $CaMg(CO_3)_2$, with 0.018(1) Å by Effenberger et al. (1981), respectively for northupite, $Na_3Mg(CO_3)_2Cl$, with 0.015(3) Å by Dal Negro et al. (1975) (calculated by Zemann, 1981) and for Fe-tychite, $Na_6Fe_2(CO_3)_4SO_4$ with 0.016(4) Å by Malinowsky et al. (1979) (calculated by Zemann, 1981).

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