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Tychite, $\text{Na}_6\text{Mg}_2(\text{SO}_4)(\text{CO}_3)_4$: structure analysis and Raman spectroscopic data

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Tychite, $\text{Na}_6\text{Mg}_2(\text{SO}_4)(\text{CO}_3)_4$: structure analysis and Raman spectroscopic data

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Key indicators

Single-crystal X-ray study

$T = 298 \text{ K}$

Mean $\sigma(\text{S}-\text{O}) = 0.001 \text{ \AA}$

R factor = 0.023

wR factor = 0.076

Data-to-parameter ratio = 23.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Tychite, hexasodium dimagnesium sulfate tetracarbonate, is a member of the northupite $[\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}]$ group and has a framework structure consisting of four basic units: CO_3^{2-} groups (3 symmetry), SO_4^{2-} tetrahedra (23 symmetry), MgO_6 ($\bar{3}$ symmetry) and NaO_6 octahedra (2 symmetry). Among them, the CO_3^{2-} , SO_4^{2-} , and MgO_6 units are regular in shape, but the NaO_6 octahedron, showing three different Na–O bond lengths, is considerably distorted. The Na atoms in tychite are slightly overbonded relative to those in northupite. The Raman spectroscopic data show three and four vibration modes for the CO_3^{2-} and SO_4^{2-} groups, respectively; these are comparable to the corresponding Raman modes observed in other carbonates and sulfates.

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Comment

Tychite is a sodium–magnesium sulfate–carbonate mineral with the ideal chemical formula $\text{Na}_6\text{Mg}_2(\text{SO}_4)(\text{CO}_3)_4$ and occurs uncommonly in lake-bed evaporite deposits in nature (Anthony *et al.*, 1990). It forms a solid solution series with ferrotychite, $\text{Na}_6\text{Fe}_2(\text{SO}_4)(\text{CO}_3)_4$ and manganotychite, $\text{Na}_6\text{Mn}_2(\text{SO}_4)(\text{CO}_3)_4$ (Khomyakov *et al.*, 1990) and is a member of the northupite $[\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}]$ group of minerals. The crystal structure of tychite was first proposed by Shiba & Watanabé (1931) in space group $Fd\bar{3}m$ and with all atoms in special positions. In the same year, however, Gossner & Koch (1931) suggested space group $Fd\bar{3}$ for both tychite and northupite. Based on X-ray intensity data from powder

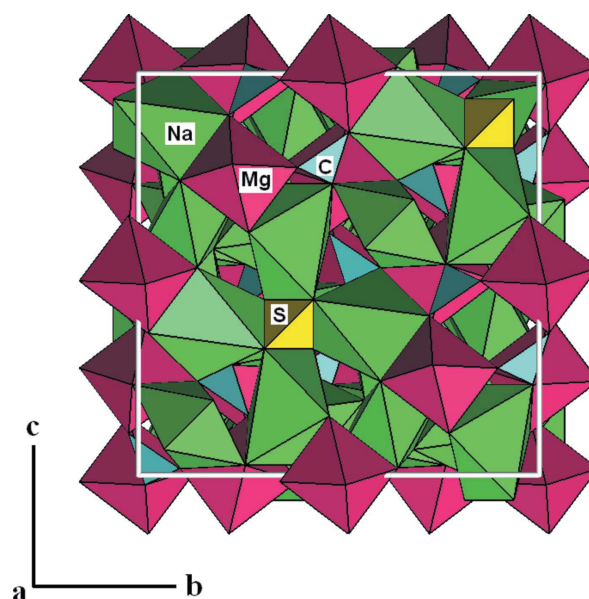


Figure 1
Polyhedral view of the crystal structure of tychite.

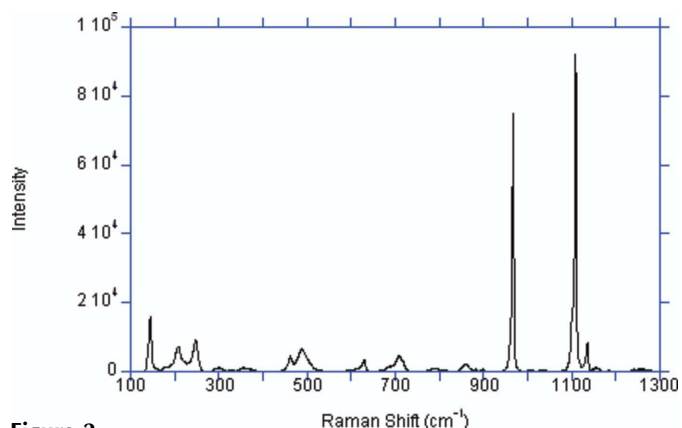


Figure 2
Raman spectrum of tychite.

diffraction and by using the Laue method, Watanabé (1933) solved the structures of tychite and northupite in space group $Fd\bar{3}$. While there have been subsequent refinements of the structures of northupite (Dal Negro *et al.*, 1975) and of a ferrotychite crystal with the composition $\text{Na}_6(\text{Fe}_{1.241}\text{Mn}_{0.358}\text{Mg}_{0.401})(\text{SO}_4)(\text{CO}_3)_4$ (Malinovskii *et al.*, 1979), which both confirmed space group $Fd\bar{3}$, no further structure analysis has been performed on tychite.

Isotypic with ferrotychite (Malinovskii *et al.* 1979), the crystal structure of tychite consists of four different basic units: CO_3^{2-} groups, SO_4^{2-} tetrahedra, and MgO_6 and NaO_6 octahedra. The SO_4 , MgO_6 , and NaO_6 polyhedra share edges and corners, forming a three-dimensional framework, and the MgO_6 and NaO_6 octahedra are interlinked by the CO_3 groups (Fig. 1). All four types of bond distances (C—O, S—O, Mg—O, and Na—O) in tychite are consistent with the values reported in the literature. The principal difference between the structures of tychite and ferrotychite lies in the M —O bond lengths ($M = \text{Mg}$ and Fe), resulting from the substitution of Mg for Fe (Table 1).

However, there is a notable difference in the octahedral configuration around Na between tychite and northupite. In tychite, the Na atom is bonded to six O atoms with three different lengths, whereas it is coordinated by four O atoms and two Cl atoms in northupite. Relative to the bond distances within the Na octahedron in tychite (Table 1), those in northupite are not only longer, but also rather varied, from the shortest Na—O distance of 2.411 Å to the longest Na—Cl distance of 2.873 Å. The Na octahedral volumes in tychite and northupite are 16.75 and 20.48 Å³, respectively, indicating that the Na atom in tychite is more strongly bonded than that in northupite. The bond-valence sum (Brown, 2002) for Na is 1.04 v.u. (valence units) in tychite, whereas it is 0.99 v.u. in northupite.

The Raman spectrum measured between 100 and 1300 cm^{-1} for tychite is shown in Fig. 2, and the band assignments for the different vibrational modes are given in Table 2. Note that all vibrational modes for SO_4^{2-} and CO_3^{2-} groups in tychite compare very well with those observed in other sulfates, *e.g.* gypsum (Knittle *et al.*, 2001) and carbonates, *e.g.* calcite (Gabrielli *et al.*, 2000), respectively.

Experimental

A crystal from Searles Lake, Trona, San Bernardino County, California, was used for the data collection. The Raman spectrum was measured from a randomly oriented sample with nine scans and 30 s measuring time on a Thermo Almega microRaman system, using a solid-state laser with a frequency of 532 nm. The laser was partially polarized and collects a high resolution spectrum with a minimum lateral resolution of less than 5 μm .

Crystal data

$\text{Na}_6\text{Mg}_2(\text{SO}_4)(\text{CO}_3)_4$
 $M_r = 522.66$
Cubic, $Fd\bar{3}$
 $a = 13.9038$ (2) Å
 $V = 2687.82$ (7) Å³
 $Z = 8$

$D_x = 2.583$ Mg m^{-3}
Mo $K\alpha$ radiation
 $\mu = 0.63$ mm^{-1}
 $T = 298$ (2) K
Block, colourless
0.10 × 0.10 × 0.08 mm

Data collection

Bruker SMART APEX-II CCD diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2005)
 $T_{\min} = 0.939$, $T_{\max} = 0.951$

12979 measured reflections
570 independent reflections
505 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 36.6^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.076$
 $S = 1.01$
570 reflections
24 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.41$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.39$ e \AA^{-3}
Extinction correction: SHELXL97
Extinction coefficient: none

Table 1

Comparison of bond distances (Å) between tychite ($M = \text{Mg}$; this work) and ferrotychite ($M = \text{Fe}$; Malinovskii *et al.*, 1979).

Bonds	Tychite	Ferrotychite
S—O (×4)	1.4782 (10)	1.483 (1)
C—O (×3)	1.2857 (5)	1.287 (1)
Na—O1 (×2)	2.4994 (5)	2.485 (1)
Na—O2 (×2)	2.3915 (7)	2.388 (1)
Na—O2 (×2)	2.4124 (5)	2.409 (1)
M—O (×6)	2.0804 (5)	2.132 (1)

Table 2

Raman peak assignments for selected vibrational modes observed in tychite.

Peak Positions (cm^{-1})	Mode Assignments
144, 360	Lattice vibrations
493.8	ν_2 SO_4 symmetric bend
629.7	ν_4 SO_4 antisymmetric bending
708.7	ν_4 CO_3 in-plane bending
859.2	ν_2 CO_3 out-of-plane bending
967.1	ν_1 SO_4 primary internal stretching mode
1108.1	ν_1 CO_3 primary internal stretching mode
1136.6	ν_3 SO_4 antisymmetric stretching

For the present refinement, origin choice 2 of space group $Fd\bar{3}$ was used.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: Xtal-Draw (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

The sample of tychite was donated to the RRUFF Project (<http://rruff.geo.arizona.edu/rruff/>) by Excalibur Mineral Company.

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