

THE CRYSTAL STRUCTURE OF SABINAITE, $\text{Na}_4\text{Zr}_2\text{TiO}_4(\text{CO}_3)_4$

ANDREW M. McDONALD¹

Department of Earth Sciences, Laurentian University, Sudbury, Ontario P3E 2C6

ABSTRACT

The crystal structure of sabinaité, $\text{Na}_4\text{Zr}_2\text{TiO}_4(\text{CO}_3)_4$, has been determined and refined to residuals of $R = 2.1\%$ and $wR^2 = 5.7\%$ using material from Mont Saint-Hilaire, Quebec. The structure is monoclinic, $C2/c$, with cell parameters a 10.196(1), b 6.616(1), c 17.958(3) Å, β 94.14(1)°, V 1208.2(3) Å³, and with $Z = 4$. The structure analysis indicates complete ordering of Zr^{4+} and Ti^{4+} and confirms that sabinaité is anhydrous. The crystal structure is strongly layered and is dominated by a slab composed of ZrO_8 and TiO_6 polyhedra. The ZrO_8 polyhedra form infinite zig-zag chains along [100]. These chains are cross-linked along [010] by sharing polyhedral edges with like polyhedra in adjacent chains and by sharing edges and corners with TiO_6 octahedra that occupy gaps between the chains. The chains of ZrO_8 polyhedra strongly influence the observed morphology and optical properties of sabinaité. Two distinct carbonate groups are present, one acting as a bidentate ligand in the ZrO_8 polyhedra and the other linking vertices between ZrO_8 and TiO_6 polyhedra. The remaining oxygen atoms from these carbonate groups are shared with the NaO_6 and NaO_8 polyhedra and link the Zr–Ti–O slabs together along [001]. This bonding is relatively weak and thus results in the pronounced {001} cleavage observed in the mineral.

Keywords: sabinaité, titanium zirconium carbonate, crystal structure, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La structure cristalline de la sabinaité, $\text{Na}_4\text{Zr}_2\text{TiO}_4(\text{CO}_3)_4$, a été affinée jusqu'à un résidu R de 2.1% ($wR^2 = 5.7\%$) en utilisant un cristal du mont Saint-Hilaire, Québec. Il s'agit d'une structure monoclinique, $C2/c$, dont les paramètres réticulaires sont: a 10.196(1), b 6.616(1), c 17.958(3) Å, β 94.14(1)°, V 1208.2(3) Å³, pour $Z = 4$. L'analyse structurale indique une mise en ordre complète des atomes Zr^{4+} and Ti^{4+} , et confirme que cette espèce est anhydre. La structure montre une structure en plan; l'élément dominant est une couche de polyèdres ZrO_8 et TiO_6 . Les polyèdres ZrO_8 sont agencés en chaînes le long de [100]. Ces chaînes sont liées le long de [010] par partage d'arêtes de polyèdres avec celles des chaînes adjacentes, et par partage d'arêtes et de coins d'octaèdres TiO_6 disposées entre les chaînes. Les chaînes de polyèdres ZrO_8 exercent une influence marquée sur la morphologie observée et sur les propriétés optiques de la sabinaité. Deux groupes de carbonate sont distincts, un de ceux-ci agissant comme ligand bidentée dans le polyèdre ZrO_8 , et l'autre joignant les extrémités apicales des polyèdres ZrO_8 et TiO_6 . Les autres atomes d'oxygène de ces groupes de carbonate participent à des liaisons avec les polyèdres NaO_6 et NaO_8 et joignent les panneaux à Zr–Ti–O le long de [001]. Ces liaisons sont relativement faibles, et rendent compte du clivage {001} prononcé de cette espèce.

(Traduit par la Rédaction)

Mots-clés: sabinaité, carbonate de titane et de zirconium, structure cristalline, mont Saint-Hilaire, Québec.

INTRODUCTION

Sabinaité is the only natural anhydrous carbonate known to contain both essential Zr and Ti. It was originally described by Jambor *et al.* (1980) from a silicocarbonatite sill at the Francon Quarry, Quebec, where it occurs as white, powdery coatings and chalky aggregates. Owing to the small size and poor crystallinity of the type material, only a partial

description was possible; the authors proposed a tentative chemical formula, $\text{Na}_9\text{Zr}_{4+x}\text{Ti}_2\text{O}_9(\text{CO}_3)_8$, and suggested a probable monoclinic symmetry. The mineral was subsequently discovered in large (up to 1.5 mm in length), euhedral crystals in cavities in sodalite syenite at Mont Saint-Hilaire, Quebec (Chao & Gu 1985). Analysis of sabinaité from Mont Saint-Hilaire by Chao & Gu (1985) led to a more complete characterization of the mineral, which included a more definite chemical formula, $\text{Na}_4\text{Zr}_2\text{TiO}_4(\text{CO}_3)_4$, and $C2/c$ as the most probable space-group. As part of a general study on the crystal chemistry of Ti-bearing phases from hyperalkaline rocks, the structure of

¹ E-mail address: amcdonal@nickel.laurentian.ca

sabinaite has been solved to verify its chemical formula, test the possibility of complete ordering of Ti and Zr, and determine its relationship to other Zr-carbonates.

EXPERIMENTAL

An optically homogeneous rhomb of sabinaite from Mont Saint-Hilaire was selected and cut in two to produce fragments of a size suitable for crystal-structure analysis. One of these fragments was mounted approximately parallel to c^* on an Enraf-Nonius CAD4 four-circle diffractometer equipped with monochromated $\text{MoK}\alpha$ X radiation. A set of 12 reflections ($36^\circ < 2\theta < 60^\circ$) permuted four ways ($\pm h$ at $\pm 2\theta$) was used to refine the cell dimensions, a 10.196(1), b 6.616(1), c 17.958(3) Å, β 94.14(1)°, and V 1208.2(3) Å³. A full sphere of data out to $2\theta = 60^\circ$ was collected and averaged to give 1745 unique reflections, of which 1564

were considered observed [$F_o > 6\sigma(F_o)$]. Data measurement and reduction (Lorentz, polarization, and scaling factors) were carried out using the NRCVAX package of computer programs (Gabe *et al.* 1989). Further data regarding data collection are given in Table 1.

The structure was solved using the program SHELX-90 (Sheldrick 1990) and refinement by means of the SHELXL-93 package (Sheldrick, in prep.). Scattering curves for neutral atoms and anomalous dispersion corrections were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The structure of sabinaite was solved in the space group $C2/c$ using direct methods. Space-group selection was made on the basis of $|E|$ -statistics and crystal morphology (Chao & Gu 1985), both of which strongly suggest $C2/c$ as the correct choice. From the E -map, the positions of Zr, Ti, and four O atoms were obtained. Subsequent difference-Fourier maps were used to locate the remaining cations and anions. Refinement of this model, which included conversion to anisotropic displacement-factors, introduction of a weighting scheme based on $[1/\sigma^2(F_o)]$, and refinement of site occupancies, converged to $R = 2.1\%$ and $wR^2 = 5.7\%$. An extinction correction was applied but did not improve the refinement. Refinement of site occupancies indicated all sites to be fully occupied, including those assigned to Zr and Ti. All maxima in the new difference-map calculated at this stage were found to be less than $1 e^-/\text{Å}^3$.

Final positional and displacement-factor parameters are given in Table 2, selected bond-lengths and distances in Table 3, and the calculated bond-valences in Table 4. The observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 1. MISCELLANEOUS DATA: SABINAITE

| | | | |
|------------------------------------|-----------|--|-----------------------------------|
| Space Group | $C2/c$ | Diffractometer | Enraf-Nonius CAD4 |
| a (Å) | 10.196(1) | Radiation | $\text{MoK}\alpha$ (50 kV, 20 mA) |
| b | 6.616(1) | Monochromator | Graphite |
| c | 17.958(3) | Crystal Shape | Equidimensional plate |
| β (°) | 94.14(1) | Crystal Size | $0.23 \times 0.23 \times 0.09$ mm |
| V (Å ³) | 1208.2(3) | μ (MoK α) | 4.23 cm ⁻¹ |
| Z | 4 | | |
| Chemical Formula | | $\text{Na}_2\text{Zr}_2\text{TiO}_4(\text{CO}_3)_4$ | |
| Intensity-Data Collection | | Θ - 2Θ scanning mode | |
| 2Θ Limit | | 60° | |
| No. of Unique Reflections | | 1745 | |
| No. of Observed Reflections | | 1564 | |
| Criterion for Observed Reflections | | $F_o > 6\sigma(F_o)$ | |
| R (observed)% | | 2.1 | |
| wR^2 (observed)% | | 5.7 | |
| Weighting Scheme | | $wR^2 = \frac{[\sum w(F_o^2 - F_c^2)^2]}{2[\sum w(F_o^2)^2]}$, $w = 1/\sigma^2(F_o)$ | |

TABLE 2. POSITIONAL AND DISPLACEMENT-FACTOR PARAMETERS FOR SABINAITE

| | x | y | z | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} | U_{04} |
|-------|-----------|-----------|-----------|----------|----------|----------|----------|----------|----------|----------|
| Na(1) | 0.8971(1) | 0.5593(2) | 0.4184(1) | 179(5) | 162(5) | 160(5) | 5(4) | 8(4) | 16(4) | 167(2) |
| Na(2) | 0.8721(1) | 0.0874(2) | 0.4335(1) | 178(5) | 168(6) | 210(6) | -24(4) | -57(4) | 11(4) | 189(2) |
| Zr | 0.6916(1) | 0.3123(1) | 0.2478(1) | 49(1) | 45(1) | 63(1) | 1(1) | 6(1) | 1(1) | 52(1) |
| Ti | 0 | 0.3079(1) | 1/4 | 48(2) | 52(2) | 90(2) | 0 | 6(2) | 0 | 64(1) |
| C(1) | 0.1499(2) | 0.3512(4) | 0.3996(1) | 120(10) | 87(10) | 107(10) | 16(8) | 13(8) | 8(8) | 104(4) |
| C(2) | 0.5942(2) | 0.3353(3) | 0.3834(1) | 107(10) | 78(10) | 93(10) | -2(8) | 13(8) | 5(8) | 92(4) |
| O(1) | 0.0374(2) | 0.3073(3) | 0.3643(1) | 82(8) | 189(9) | 111(8) | 6(7) | 12(6) | 2(6) | 127(3) |
| O(2) | 0.7195(2) | 0.3316(3) | 0.3723(1) | 89(8) | 181(9) | 101(8) | 0(7) | 8(6) | -8(6) | 124(3) |
| O(3) | 0.1360(2) | 0.5034(3) | 0.2400(1) | 90(8) | 49(7) | 134(8) | 7(6) | 10(6) | 9(6) | 91(3) |
| O(4) | 0.8638(2) | 0.1207(3) | 0.2630(1) | 63(8) | 55(7) | 160(8) | -5(6) | -4(6) | -2(6) | 93(3) |
| O(5) | 0.1547(2) | 0.4306(4) | 0.4624(1) | 199(10) | 300(11) | 127(8) | -72(8) | 47(7) | -35(8) | 207(4) |
| O(6) | 0.5195(2) | 0.3091(3) | 0.3215(1) | 89(7) | 127(8) | 88(7) | -10(6) | 4(6) | -5(6) | 101(3) |
| O(7) | 0.2593(2) | 0.3159(3) | 0.3673(1) | 87(8) | 143(8) | 95(8) | 4(6) | 11(6) | 9(6) | 108(3) |
| O(8) | 0.5488(2) | 0.3568(3) | 0.4450(1) | 159(9) | 263(10) | 92(8) | -26(7) | 30(6) | 22(8) | 170(4) |

Note: Anisotropic displacement-factors have the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^{*2}b^{*2}U_{12})]$; all U values are in Å² × 10⁴; estimated standard deviations in parentheses.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN SABINAITE

| | | | |
|-----------------------|-----------|-----------------------|-----------|
| Na(1) - O(5)f | 2.243(2) | O(8)i - Na(2) - O(8)j | 78.91(8) |
| - O(7)g | 2.348(2) | O(8)i - Na(2) - O(2) | 119.21(8) |
| - O(1) | 2.443(2) | O(8)j - Na(2) - O(5)c | 97.10(8) |
| - O(2) | 2.453(2) | O(8)j - Na(2) - O(1) | 99.66(8) |
| - O(8)h | 2.527(2) | O(8)j - Na(2) - O(7)c | 83.96(8) |
| - O(6)h | 2.763(2) | O(8)j - Na(2) - O(5)c | 113.02(9) |
| - O(5) | 2.819(2) | O(8)j - Na(2) - O(1) | 83.51(7) |
| - O(3)a | 2.866(2) | O(7)c - Na(2) - O(2) | 90.30(7) |
| <Na(1)-O> | 2.558 | O(7)c - Na(2) - O(1) | 118.98(7) |
| | | O(2) - Na(2) - O(5)c | 79.94(7) |
| Na(2) - O(8)i | 2.300(2) | O(2) - Na(2) - O(1) | 80.17(7) |
| - O(8)j | 2.358(2) | <O - Na(2) - O> | 94.98 |
| - O(7)c | 2.401(2) | | |
| - O(2) | 2.448(2) | O(4)b - Zr - O(7)a | 88.88(7) |
| - O(5)c | 2.535(2) | O(4)b - Zr - O(3)a | 69.90(6) |
| - O(1) | 2.609(2) | O(4)b - Zr - O(2) | 92.90(7) |
| <Na(2)-O> | 2.442 | O(4)b - Zr - O(6) | 81.43(6) |
| | | O(4)b - Zr - O(6)d | 74.89(6) |
| Zr - O(4)b | 2.123(2) | O(3)c - Zr - O(7)a | 91.56(7) |
| - O(3)c | 2.123(2) | O(3)c - Zr - O(4) | 69.84(6) |
| - O(7)a | 2.163(2) | O(3)c - Zr - O(2) | 97.73(7) |
| - O(3)a | 2.164(2) | O(3)c - Zr - O(6) | 79.36(6) |
| - O(4) | 2.167(2) | O(3)c - Zr - O(6)d | 74.51(6) |
| - O(2) | 2.237(2) | O(7)a - Zr - O(3)a | 81.20(7) |
| - O(6) | 2.273(2) | O(7)a - Zr - O(4) | 83.41(7) |
| - O(6)d | 2.407(2) | O(7)a - Zr - O(6)d | 76.49(6) |
| <Zr - O> | 2.207 | O(3)a - Zr - O(4) | 71.56(7) |
| | | O(3)a - Zr - O(2) | 79.75(7) |
| Ti - O(4) x2 | 1.888(2) | O(3)a - Zr - O(6) | 127.07(6) |
| - O(3) x2 | 1.914(2) | O(4) - Zr - O(2) | 82.17(7) |
| - O(1) x2 | 2.061(2) | O(4) - Zr - O(6) | 125.02(6) |
| <Ti - O> | 1.954 | O(2) - Zr - O(6)d | 124.17(6) |
| | | <O - Zr - O> | 87.99 |
| C(1) - O(5) | 1.242(3) | O(4) - Ti - O(4)a | 98.02(11) |
| - O(1) | 1.302(3) | O(4) - Ti - O(3) x2 | 83.54(7) |
| - O(7) | 1.314(3) | O(4) - Ti - O(1)a x2 | 92.16(7) |
| <C(1) - O> | 1.286 | O(4) - Ti - O(1)a x2 | 87.71(7) |
| | | O(3) - Ti - O(3)a | 94.95(10) |
| C(2) - O(8) | 1.239(3) | O(3) - Ti - O(1) x2 | 90.65(7) |
| - O(2) | 1.308(3) | O(3) - Ti - O(1)a x2 | 89.48(7) |
| - O(6) | 1.313(3) | <O - Ti - O> | 90.00 |
| <C(2) - O> | 1.287 | | |
| O(5)f - Na(1) - O(7)g | 100.12(8) | O(5) - C(1) - O(1) | 120.7(2) |
| O(5)f - Na(1) - O(1) | 125.81(9) | O(5) - C(1) - O(7) | 119.8(2) |
| O(5)f - Na(1) - O(2) | 96.99(8) | O(1) - C(1) - O(7) | 119.3(2) |
| O(5)f - Na(1) - O(8)h | 88.83(8) | <O - C(1) - O> | 120.0 |
| O(5)f - Na(1) - O(5) | 91.20(7) | | |
| O(7)g - Na(1) - O(2) | 84.60(7) | O(8) - C(2) - O(2) | 124.8(2) |
| O(7)g - Na(1) - O(8)h | 81.45(7) | O(8) - C(2) - O(6) | 122.7(2) |
| O(1) - Na(1) - O(2) | 83.43(7) | O(2) - C(2) - O(6) | 112.3(2) |
| O(1) - Na(1) - O(8)h | 103.81(7) | <O - C(2) - O> | 120.0 |
| O(1) - Na(1) - O(6)h | 81.57(7) | | |
| O(2) - Na(1) - O(6)h | 120.69(7) | | |
| O(2) - Na(1) - O(5) | 123.98(8) | | |
| O(8)h - Na(1) - O(3)a | 108.33(7) | | |
| O(6)h - Na(1) - O(5) | 84.43(6) | | |
| O(5) - Na(1) - O(3)a | 106.21(6) | | |
| <O - Na(1) - O> | 98.76 | | |

Symmetry operations: a: $-x, y, -z+1/2$; b: $-x-1/2, y+1/2, -z+1/2$; c: $x-1/2, y-1/2, z$; d: $-x-1, y, -z+1/2$; e: $-x-1/2, y-1/2, -z+1/2$; f: $-x, -y+1, -z+1$; g: $x-1/2, y+1/2, z$; h: $x+1/2, -y+1/2, z$; i: $-x-1/2, -y+1/2, -z$; j: $x+1/2, y-1/2, z$; k: $x, y-1, z$.

DISCUSSION AND DESCRIPTION OF THE STRUCTURE

The structure analysis confirms the chemical formula, $\text{Na}_4\text{Zr}_2\text{TiO}_4(\text{CO}_3)_4$, for sabinaitite. Bond-valence summations also confirm that both Zr and Ti are in the 4+ valence state and that there is no indication of hydroxyl or water in the mineral (Table 4).

TABLE 4. EMPIRICAL BOND-VALENCES* (ν) FOR SABINAITE

| | Na(1) | Na(2) | Zr | Ti | C(1) | C(2) | ΣV |
|------------|-------|-------|-------|---------------------|-------|-------|------------|
| O(1) | 0.175 | 0.112 | | 0.514 ³² | 1.269 | | 2.070 |
| O(2) | 0.171 | 0.174 | 0.444 | | | 1.248 | 2.037 |
| O(3) | 0.056 | | 0.605 | 0.765 ³² | | | 1.969 |
| | | | 0.543 | | | | |
| O(4) | | | 0.605 | 0.821 ³² | | | 1.963 |
| | | | 0.537 | | | | |
| O(5) | 0.303 | 0.137 | | 1.492 | | | 1.996 |
| | 0.064 | | | | | | |
| O(6) | 0.074 | | 0.403 | | | 1.228 | 1.986 |
| | | | 0.281 | | | | |
| O(7) | 0.227 | 0.197 | 0.543 | 1.225 | | | 2.192 |
| O(8) | 0.140 | 0.259 | | | | 1.508 | 2.128 |
| | | 0.221 | | | | | |
| ΣV | 1.210 | 1.100 | 3.961 | 4.200 | 3.986 | 3.984 | |

* parameters from Brese & O'Keeffe (1991).

There are two distinct Na positions in the structure, each of which occupies the general 8f position. Na(1) is coordinated by eight oxygen atoms in a distorted polyhedron [range: 2.242(2)–2.819(2) Å; <Na(1)–O> = 2.558 Å], whereas Na(2) is coordinated by six atoms of oxygen in a more regular octahedron [range: 2.300(2)–2.609 Å; <Na(2)–O> = 2.442 Å]. There is one distinct Zr position, which occupies the general 8f position. It is coordinated by eight atoms of oxygen, forming a polyhedron that may be described as a triangulated dodecahedron. The bond distances range from 2.123(2) to 2.407(2) Å, with the <Zr–O> distance being 2.207 Å. The average distance is considerably longer than the 2.140 Å observed in the Na–Zr carbonate phosphate voggite (Szymański & Roberts 1990), but is relatively close to the 2.254 Å observed in the Na–Sr–Zr carbonate weloganite (Grice & Perrault 1975). Ti occupies the special position 4e (0, y, 1/4) and is octahedrally coordinated by six oxygen atoms, with bond distances ranging from 1.888(2) to 2.061(2) Å [<Ti–O> = 1.954 Å], the octahedron being slightly elongate along [001]. The complete ordering of Zr and Ti is most likely caused by differences in ionic radii [$V_{II}r(\text{Ti}^{4+}) = 0.605$ Å versus $V_{II}r(\text{Zr}^{4+}) = 0.72$ Å; $V_{III}r(\text{Ti}^{4+}) = 0.74$ Å versus $V_{III}r(\text{Zr}^{4+}) = 0.84$ Å (Shannon 1976)]. There are two distinct C atoms, both in the general 8f position, that are coordinated by oxygen in a distorted trigonal planar configuration. Both carbonate groups have one shorter and two longer bond distances [C(1): 1.242(3) Å with 1.302(3) and 1.315(3) Å; C(2): 1.238(3) Å with 1.308(3) and 1.314(3) Å]. The mean bond-lengths for both

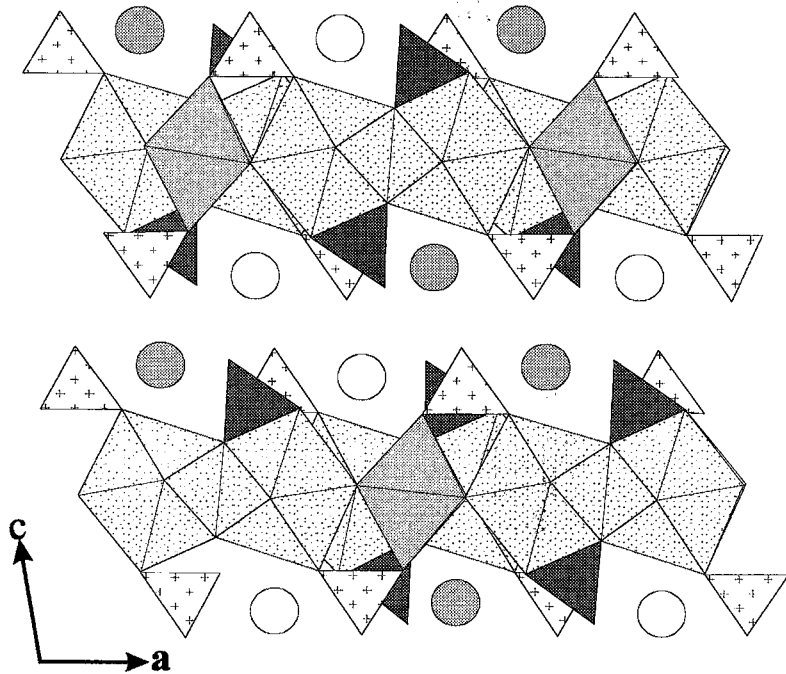


FIG. 1. The structure of sabinaitite projected parallel to $[010]$, showing the pronounced layering perpendicular to $[001]$. The ZrO_8 polyhedra are stippled, the TiO_6 octahedra are lightly shaded, the Na(1) atoms are open circles, the Na(2) atoms, shaded circles, the $C(1)O_3$ groups are heavily shaded, and the $C(2)O_3$ groups are filled with crosses.

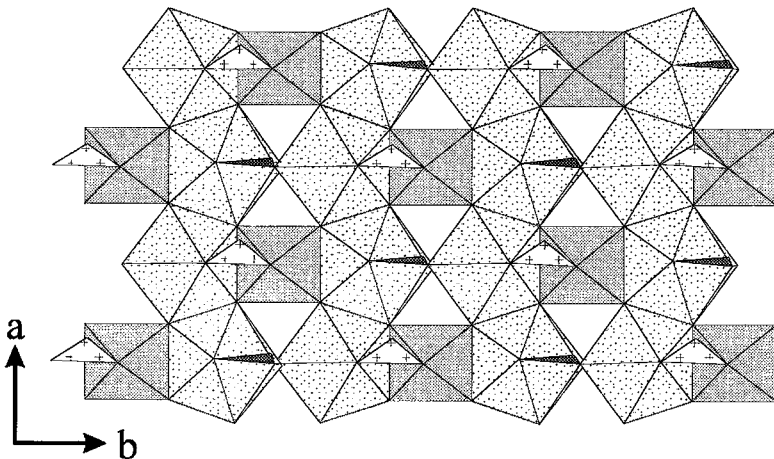


FIG. 2. The structure of sabinaitite projected parallel to $[001]$, showing the chains of edge-sharing ZrO_8 polyhedra with the TiO_6 octahedra filling voids between these chains. The $C(1)O_3$ and $C(2)O_3$ groups also are indicated. Shading as in Figure 1.

carbonate groups are quite normal [$\langle C(1)-O \rangle = 1.286 \text{ \AA}$ and $\langle C(2)-O \rangle = 1.287 \text{ \AA}$] and are consistent with those observed in voggite (1.287 Å; Szymański & Roberts 1990) and weloganite (1.29 Å; Grice & Perrault 1975).

The sabinaite structure is strongly layered perpendicular to [001] (Fig. 1). It is dominated by a Zr-Ti-O slab composed of edge-sharing ZrO_8 polyhedra that form infinite zig-zag chains extending parallel to [100] (Fig. 2). These chains are in turn cross-linked across [010] by both shared edges between adjacent ZrO_8 polyhedra from adjacent chains and TiO_6 octahedra, the latter occupying gaps between the ZrO_8 polyhedral chains (Fig. 2). These chains are of interest for two reasons: firstly, they seem to have a pronounced influence on the morphology of sabinaite, as the crystals are typically elongate along [100]; secondly, they in part control the optical properties of the mineral. Because these chains have the highest electron-density, they correspond approximately to the Z vibration direction. The carbonate groups decorate the edges of the Zr-Ti-O slab and are oriented with their planar surfaces parallel to [001]. Both crystallographically distinct carbonate groups are bidentate, with the two long C-O bonds in each group defining the edge of a carbonate triangle that is shared with the ZrO_8 polyhedron [via the O(1) and O(7) atoms for C(1)O₃] and the edge that links vertices between ZrO_8 and TiO_6 polyhedra [via O(2) and O(6) atoms for C(2)O₃]. The remaining oxygen atoms of the carbonate groups constitute part of the Na(1)O₈ and Na(2)O₆ coordination polyhedra. The Na-O polyhedra form layers between Zr-Ti-O slabs and serve to join adjacent layers along [001]. The Na-O bonds are relatively weak, and this results in the pronounced {001} cleavage observed in sabinaite.

At present, there are only two other minerals known to contain essential Zr and carbonate: weloganite, $Sr_3ZrNa_2(CO_3)_6 \cdot 3H_2O$, and voggite, $Na_2Zr(PO_4)(CO_3)(OH) \cdot 2H_2O$. Weloganite does not resemble sabinaite from a structural standpoint, as it is dominated by carbonate layers that lie with their planar surfaces oriented approximately perpendicular to c. Voggite has features somewhat reminiscent of those found in sabinaite. It consists of layers of seven-coordinated edge-sharing Zr-O pentagonal bipyramids, separated by layers of Na-O octahedra, the two alternating along [101]. As in sabinaite, the carbonate groups act as a bidentate ligands coordinated to the Zr-O polyhedra. Unlike sabinaite, a combination of $(PO_4)^{3-}$ groups and hydrogen bonds serves to link the layers of Zr-O and Na-O polyhedra together, producing a much more tightly bonded structure.

ACKNOWLEDGEMENTS

I thank J.T. Szymański of the Canada Centre for Mineral and Energy Technology, Ottawa, for assistance with the single-crystal diffractometer, G.Y. Chao for providing the specimen of sabinaite, and Drs. R.C. Rouse, J.M. Hughes and R.F. Martin for their editorial comments. This research was supported through grants from the Laurentian University Research Fund and NSERC, both of which are gratefully acknowledged.

REFERENCES

- BRESE, N.E. & O'KEEFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.
- CHAO, G.Y. & GU, JIEXANG (1985): Sabinaite: a new occurrence and new data. *Can. Mineral.* **23**, 17-19.
- CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.
- _____ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.
- GABE, E.J., LE PAGE, Y., CHARLAND, J.-P., LEE, F.L. & WHITE, P.S. (1989): NRCVAX - an interactive program system for structural analysis. *J. Appl. Crystallogr.* **22**, 384-387.
- GRICE, J.D. & PERRAULT, G. (1975): The crystal structure of triclinic weloganite. *Can. Mineral.* **13**, 209-216.
- JAMBOR, J.L., STURMAN, B.D. & WEATHERLY, G.C. (1980): Sabinaite, a new anhydrous zirconium-bearing carbonate mineral from Montreal Island, Quebec. *Can. Mineral.* **18**, 25-29.
- SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.
- SHELDRIK, G.M. (1990): Phase annealing in SHELX-90: direct methods for larger structures. *Acta Crystallogr.* **A46**, 467-473.
- SZYMAŃSKI, J.T. & ROBERTS, A.C. (1990): The crystal structure of voggite, a new hydrated Na-Zr hydroxide-phosphate-carbonate mineral. *Mineral. Mag.* **54**, 495-500.

Received November 21, 1995, revised manuscript accepted February 29, 1996.