Table 2. *Bond lengths and angles*

Zr(1)–Zr(2)	3·546 (3) Å	O(1)–Zr(1)–O(7′)	92 (2)°
Zr(1)–Zr(3)	3·553 (3)	O(1)–Zr(1)–O(6)	88 (1)
Zr(2)–Zr(3)	3·552 (2)	O(1)–Zr(1)–O(6′)	92 (1)
		O(2)–Zr(1)–O(6′)	118 (1)
Zr(1)–O(2)	2·16 (1)	O(2)–Zr(1)–O(6)	70 (1)
Zr(2)–O(2)	2·19 (1)	O(2)–Zr(1)–O(7)	138 (2)
Zr(2)–O(3)	2·23 (3)	O(2)–Zr(1)–O(7′)	151 (2)
Zr(3)–O(2)	2·19 (1)	O(7)–Zr(1)–O(6)	91 (2)
Zr(3)–O(3)	2·15 (1)	O(7)–Zr(1)–O(6′)	81 (2)
		O(6)–Zr(1)–O(6′)	172 (1)
Zr(1)–O(1)	2·21 (1)		
Zr(1)–O(6)	2·19 (1)	O(2)–Zr(2)–O(2′)	70 (1)
Zr(3)–O(1)	2·12 (3)	O(2)–Zr(2)–O(2)	71 (1)
Zr(3)–O(4)	2·17 (2)		
		O(2)–Zr(3)–O(3)	72 (1)
Zr(1)–O(7)	2·03 (6)	O(1)–Zr(3)–O(4)	172 (1)
Zr(3)–O(5)	2·00 (2)	O(1)–Zr(3)–O(2)	70 (1)
		O(1)–Zr(3)–O(3)	118 (1)
O(1)–C(1)	1·38 (7)	O(1)–Zr(3)–O(5)	87 (1)
O(4)–C(4)	1·47 (4)	O(1′)–Zr(3)–O(5)	87 (1)*
O(5)–C(5)	1·39 (6)	O(1)–Zr(3)–O(4′)	87 (1)
O(6)–C(6)	1·52 (4)	O(1)–Zr(3)–O(1′)	92 (1)
O(7)–C(7)	1·34 (9)	O(2)–Zr(3)–O(4)	117 (1)
		O(3)–Zr(3)–O(4)	69 (1)
O(2)–Zr(1)–O(2′)	71 (1)°	O(5)–Zr(3)–O(3)	142 (1)
O(1)–Zr(1)–O(1)	174 (1)	O(5)–Zr(3)–O(2)	146 (1)
O(1)–Zr(1)–O(2)	69 (1)	O(5)–Zr(3)–O(4)	86 (1)
O(1)–Zr(1)–O(2′)	116 (1)	O(5)–Zr(3)–O(4)	86 (1)*
O(1)–Zr(1)–O(7)	83 (2)	O(1)–Zr(3)–O(4′)	172 (1)*

* Symmetry equivalent to a value listed; fractional parts of errors involving light atoms (<0·5) have been rounded up to (1).

Å), four bridging methoxide (2·12–2·21 Å), and one terminal methoxide group (2·00 and 2·03 Å). The coordination about these two Zr atoms is quite similar as can be seen by inspecting the angles in Table 2 (ordered for such comparison). In fact, the molecule deviates only slightly from $m3m$ (O_h) symmetry. The thermal parameters are consistent with the bonding behavior for the Zr–O skeleton, although rigid-body motion could account for part of this motion.

The disordering of C(7) appears to result from packing considerations. In the present results, the nearest-neighbor molecular contacts between closest symmetry-related positions of C(7) involve 3·66 Å separations; should C(7) not be disordered, this separation decreases below 2·80 Å, depending on the C–O separation used, with the O–C vectors pointing directly at each other. The shortest molecular contacts are between C(5) and two C(1)'s on a $\frac{2}{3},\frac{1}{3},\frac{1}{3}$-related molecule with 3·02 Å separations and O(5)–C(5)···C(1) angles of 120° as well as a symmetry-related C(5′) with a 3·13 Å separation and an O(5)–C(5)···C(5′) angle of 77°. Thus, C(5) is wedged between the three methyl groups on the adjacent molecule [and lies at a z coordinate above that for C(5′) of the molecule at $\frac{2}{3},\frac{1}{3},\frac{1}{3}$]. Hence, even though the molecules are large symmetric units, their close packing is considerably reduced from that of ideal spheres ($c/a = 3\sqrt{3}/2$) with $c/a = 1{\cdot}603$.

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New compounds with glaserite and Na_2SO_4(I) structures.

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New compounds with glaserite and Na_2SO_4(I) structures were crystallized from the melt and by solid-state reactions. The lattice parameters are reported. Superstructures and monoclinic deformations were observed.

The typical high-temperature modification of compounds A_2BX_4 with tetrahedral BX_4 complexes and medium-size to large cations A has the structure of Na_2SO_4(I) (or high-K_2SO_4) with the proposed space group $P6_3mc$ (Eysel & Hahn, 1970). Among the many low-temperature forms the glaserite structure (space group $P\bar{3}m1$) is unique since it occurs only in solid solutions with two cations of distinctly different size.

Because of their very similar powder patterns the difference between these two structures was not recognized until recently. The crystal chemistry of both structure types, in-

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Table 1. *Materials with glaserite structure*

Complete powder data were submitted to the Joint Committee on Powder Diffraction Standards for publication in the powder data file. Mean standard deviation of lattice parameters is 0·004 Å, for low-NaK(SeO$_4$)$_2$ 0·01 Å; hexagonal axes, room-temperature data.

	a (Å)	c (Å)
Low-NaK$_3$(SeO$_4$)$_2$	5·85	14·92 = 2 × 7·46
Low-NaK$_3$(MoO$_4$)$_2$	6·001	7·528
Low-NaK$_3$(WO$_4$)$_2$	6·044	7·616
CdBa$_3$(SiO$_4$)$_2$	5·727	7·344
CdBa$_3$(GeO$_4$)$_2$	5·844	7·443

Table 2. *Materials with* Na$_2$SO$_4$(I) *structure*

Mean standard deviation of lattice parameters at elevated temperature is 0·01 Å, at room temperature 0·004 Å and 0·05°; orthohexagonal axes. t is the temperature at which the lattice parameters were determined.

	t (°C)	a(Å)	b(Å)	c(Å)	Angle (°)
High-NaK$_3$(SeO$_4$)$_2$	450	10·20	5·89	7·89	
High-NaK$_3$(MoO$_4$)$_2$	655	10·72	6·19	7·94	
High-NaK$_3$(WO$_4$)$_2$	625	10·82	6·25	7·98	
High-Ag$_2$SO$_4$	420	9·58	5·53	7·34	
High-Na$_2$SeO$_4$	20 (quenched)	9·507	5·489	7·217	
(Na$_{0·90}$Zn$_{0·05}$)$_2$SO$_4$	20 (quenched)	9·265	5·348	7·121	$\beta = 92·62$
(Na$_{0·80}$Ca$_{0·10}$)$_2$SO$_4$	20 (quenched)	9·246	5·338	7·137	$\alpha = 91·83$

cluding some slightly distorted derivatives was recently discussed by Eysel (1973). New structure determinations were carried out for a trigonal and a monoclinic glaserite (Christidis, Mehrotra & Hahn, 1976).

Several new representatives of both structure types were prepared (Tables 1 and 2). The silicates and germanates were synthesized by solid-state reactions, the other compounds by crystallization from the melt. Lattice parameters at room temperature were obtained from powder diffractometer patterns and at elevated temperatures from high-temperature Guinier patterns, using the lines of the Pt sample support for calibration.

Some points are noteworthy. The selenate-glaserite has a superstructure in the **c** direction. The two Na$_2$SO$_4$(I) phases stabilized by Zn and Ca represent slight monoclinic deformations of different types, one with the orthohexagonal angle β, the other with α deviating from 90°. All other compounds are either trigonal or hexagonal.

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New compounds MNa$_6$(SO$_4$)$_4$ with vanthoffite structure.

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New compounds MNa$_6$(SO$_4$)$_4$ with vanthoffite structure were prepared for M^{2+} = Mn, Fe, Co, Ni and Zn by solid-state reactions. Lattice parameters and thermal behaviour are reported.

Vanthoffite, MgNa$_6$(SO$_4$)$_4$, is a mineral occurring in oceanic salt deposits. The structure is monoclinic ($P2_1/c$) and consists of isolated SO$_4$ tetrahedra with Mg coordinated octahedrally by O atoms, whereas the different Na atoms have rather irregular six- to ninefold coordinations (Fischer & Hellner, 1964). The Mg vanthoffite was synthesized and investigated by Kühn (1958) and Madsen (1966).

New compounds isostructural with vanthoffite were obtained during a study of Na$_2$SO$_4$–MSO$_4$ systems (Keester, Eysel, Hahn & Ewald, 1976) with medium-size cations M = Mn^{2+}, Fe^{2+}, Co, Ni and Zn. Smaller cations (Be) and larger ones (Ca, Sr, Pb, Ba) are not capable of replacing Mg in vanthoffite. All compounds were prepared from Na$_2$SO$_4$ (or Na$_2$CrO$_4$) and divalent-metal sulphate hydrates. The stoichiometric mixtures were first dehydrated by heating, then melted in platinum crucibles and finally annealed to just below the decomposition point of the compound (Table 1). The reaction time varied with composition from days to weeks. The Fe-vanthoffite was synthesized in a sealed gold tube under a pressure of 2 kbar and at 700 °C to prevent oxidation and decomposition. Several of the compounds were not obtained in pure form and the samples contained additional phases (see footnotes to Table 1). On heating, all the compounds decompose in the solid state at rather low temperatures. Approximate decomposition temperatures are given in Table 1.

Lattice parameters were obtained by least-squares refinement of X-ray powder diffraction data. The cell parameters and cell volumes of the sulphates vary slightly owing to the fact that only one out of seven cations is exchanged and that