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	$14·92 = 2 \times 7·46$
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

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_2SO_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.

Table 2. *Materials with* Na_2SO_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_2SO_4	420	9·58	5·53	7·34	
High-Na_2SeO_4	20 (quenched)	9·507	5·489	7·217	
$(Na_{0·90}Zn_{0·05})_2SO_4$	20 (quenched)	9·265	5·348	7·121	$\beta = 92·62$
$(Na_{0·80}Ca_{0·10})_2SO_4$	20 (quenched)	9·246	5·338	7·137	$\alpha = 91·83$

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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_2SO_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_2SO_4 (or Na_2CrO_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

Table 1. *Lattice parameters and properties of vanthoffites*

Composition	Lattice parameters[1] a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	Reference	Decomposition point (°C)	Colour
$MgNa_6(SO_4)_4$	9·776	9·202	8·189	113·48	675·7	Calculated from Madsen (1966)	506	White
	9·797	9·217	8·199	113·50	679·0	Fischer & Hellner (1964)		
	9·779	9·190	8·196	113·55	675·2	Erd, 1973[2]		
$MnNa_6(SO_4)_4$	9·965	9·280	8·248	116·25	684·1	This paper	430	Pale pink
$FeNa_6(SO_4)_4$	9·94	9·41	8·24	116·2	691·5	This paper	?	Reddish brown[3]
$CoNa_6(SO_4)_4$	9·922	9·246	8·282	116·25	681·4	This paper	430	Purple
$NiNa_6(SO_4)_4$	9·883	9·176	8·207	115·41	672·3	This paper	420	Yellow
$ZnNa_6(SO_4)_4$	9·871	9·211	8·226	115·98	672·4	This paper	360	White
$ZnNa_6(SO_4)(CrO_4)_3$ [4]	10·13	9·54	8·38	116·5	724·8	This paper	?	Greenish brown[5]

(1) Mean standard deviation of lattice parameters is 0·005 Å; for $FeNa_6(SO_4)_4$ and for the chromate vanthoffite, 0·01 Å. (2) Private communication to K. L. Keester. (3) Colour probably due to some iron oxide present. (4) Approximate composition. (5) Some chromium oxide present.

even the substituted ions are similar in size. Correspondingly, the powder diagrams are closely related with respect to intensities and *d*-spacings.*

Because of experimental difficulties only partial replacement of SO_4 by CrO_4 was achieved. The large volume effect of this replacement is evident from Table 1. On the basis of crystal chemical considerations isostructural fluoroberyllates, tungstates, molybdates and selenates can be predicted to exist. Finally, it should be mentioned that Cu-vanthoffite could not be synthesized. The same applies to $ZrCa_6(SiO_4)_4$, which would have similar radius ratios, but doubled valencies.

* Complete powder data have been submitted to the Joint Committee on Powder Diffraction Standards for publication in the powder data file.

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Dibromo(1,4-dioxan)tin(II): the crystal structure.

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A full refinement ($R = 0·062$) of the title compound has been performed with diffractometer data and the positional parameters of the isostructural chloride. The crystal data are: space group $C2/c$, $a = 7·840$ (1), $b = 12·180$ (2), $c = 9·363$ (1) Å, $\beta = 95·65$ (1)°, $Z = 4$.

There is a complete lack of detailed information concerning the crystal structures of adducts of tin(II) bromide with neutral ligands other than water. We report here the results of a single-crystal X-ray structure determination of dibromo(1,4-dioxan)tin(II). This adduct was chosen in order to allow a direct comparison of the tin(II) environment and tin–halogen distances with those in the isostructural dichloro(1,4-dioxan)tin(II) reported recently (Hough & Nicholson, 1976).

The experimental procedure was identical with that described for the chloride. Crystal data in addition to those given above are: $D_m = 2·7$ (flotation), $D_c = 2·74$ g cm^{-3}, $F(000) = 672$, $M_r = 366·6$, μ(Mo $K\alpha$) = 53·7 cm^{-1}, $R = 0·062$ for 1225 measured reflexions (98 unobserved). The structure was refined to a conventional R of 0·062. The positional and thermal parameters are given in Table 1 and the interatomic distances and valence angles are contained in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31974 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.