Crystal Chemistry of the System Na₂SO₄–K₂SO₄–K₂CrO₄–Na₂CrO₄ and of the Glaserite Phase

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Abstract

A phase diagram for the system Na₂SO₄–K₂SO₄–K₂CrO₄–Na₂CrO₄ has been worked out particularly with respect to the regions of solid solutions of the six phases: High-K₂SO₄, low-K₂SO₄, (Na,K)₂SO₄(glaserite), Na₂SO₄(II), Na₂SO₄(III) and Na₂SO₄(V). In all of them SO₄ can be completely or partially replaced by CrO₄. With the exception of Na₂SO₄(V) the crystal structures are more or less related. It is demonstrated that the glaserite structure occurs only in solid solutions $(A,C)_2BX_4$ with cations A and C of different sizes; it is not isostructural with the hexagonal high-K₂SO₄ type, as assumed in many investigations of A_2BX_4 compounds. The nature of the glaserite phase and of the high-K₂SO₄ type is discussed.

Introduction

The system Na₂SO₄–K₂SO₄–K₂CrO₄–Na₂CrO₄ represents a reciprocal salt pair, parts of which have a close bearing on phases in certain natural salt deposits. The following minerals are phases in the system: thenardite (Na₂SO₄V), arcanite (low-K₂SO₄), glaserite or aphtitalite (a solid solution of Na₂SO₄ and K₂SO₄) and tarapacaite (low-K₂CrO₄). The system was originally investigated by Flach (1912), using optical microscopy and thermal analysis. Later investigations dealt with parts of the system, particularly with Na₂SO₄ and its polymorphism, the glaserite phase, and the binary systems Na₂SO₄–K₂SO₄ and Na₂CrO₄–K₂CrO₄. The system is characterized by the existence of several related crystal structures. All phases form at least limited solid solutions. Of particular structural interest are the glaserite and the high-K₂SO₄ solid solutions. Before presenting the complete system and its crystal chemistry, the components and the limiting binary systems will be described.

The Components

The polymorphism of sodium sulfate has been discussed recently by Eysel (1972) and is shown[1] in

Figure 1. Three of the four modifications, I, III, and V, are stable forms whereas Na₂SO₄(II) is possibly metastable. The complicated polymorphism is caused by the narrow stability field of this form II and by the sluggishness of the transition V-III, resulting in a metastable preservation of V up to the melting temperature and of III to room temperature. DTA tracings of pure Na₂SO₄ are shown in Figure 2 with the characteristic features outlined in Table 1. Structural data are given in Table 2.

Na₂CrO₄ reveals only two modifications, low-Na₂CrO₄ (isostructural with Na₂SO₄(III); Miller, 1936; Niggli, 1954) and high-Na₂CrO₄ (isostructural with Na₂SO₄(I); Goldberg *et al*[2]). Both K₂SO₄ and K₂CrO₄ have two modifications each. Low-K₂CrO₄ (Zachariasen and Ziegler, 1931) and low-K₂SO₄ (Robinson, 1958) are isostructural as well as high-K₂CrO₄ (Pistorius, 1962) and high-K₂SO₄ (Fischmeister, 1962). The latter two are isostructural with Na₂SO₄(I) and high-Na₂CrO₄ (Table 2).

For K₂SO₄ some further, extremely weak transformations have been reported in the temperature range of the low-form (Bernard and Jaffray, 1956; Fischmeister, 1962; Moreau, 1963; Majumdar and Roy, 1965). One of these transitions has also been confirmed by a very weak DTA signal at 450°C during this investigation. The corresponding structural changes must be minute. In this paper only the two well established modifications, high- and low-K₂SO₄ are considered.

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[1] This is only a rough transformation scheme. The polymorphism is under further investigation (B. N. Mehrotra, H. Arnold, W. Eysel, Th. Hahn, in preparation).

[2] Goldberg, A., W. Eysel, and Th. Hahn, Phase diagram and crystallography of the system Na₂CrO₄–K₂CrO₄ (*Neues Jahrb. Mineral. Monatsch.*, in press).
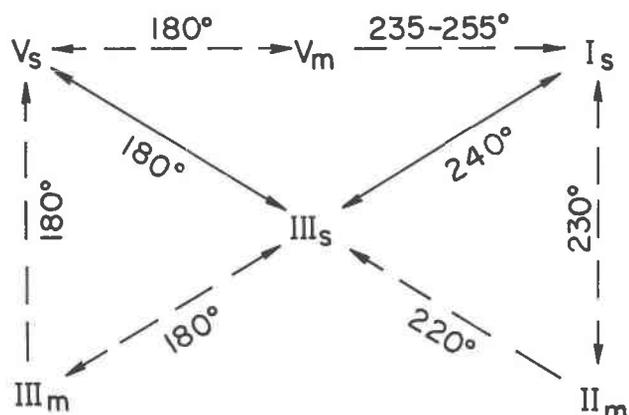
FIG. 1. Polymorphism of Na_2SO_4. s = stable (heavy lines), m = metastable (dashed lines).

The Systems Na_2SO_4–K_2SO_4 and Na_2CrO_4–K_2CrO_4

The phase diagram of the system Na_2SO_4–K_2SO_4 was investigated by Nacken (1910a,b), Jaenecke (1908), and Perrier and Bellance (1940). The high temperature equilibria in the binary system Na_2SO_4–K_2SO_4 (Eysel, 1972) are shown in Figure 3. Complete solid solubility exists for Na_2SO_4(I) and high-K_2SO_4 and limited solubility for Na_2SO_4(III), $(Na,K)_2SO_4$ (glaserite) and low-K_2SO_4. The solid solutions of Na_2SO_4(II), which have been discussed by Eysel (1972) have been omitted from the phase diagram.

The low temperature regions of the phase diagram were established as follows: The extensions of the glaserite field and miscibility gap G + L were determined from melted and quenched samples kept at 425° and 310°C until equilibrium was reached (Figs. 4 and 5). In the sodium rich part broad X-ray peaks occurred and the lattice parameters vary due to sluggish exsolutions and to transformations on cooling. Thus, it was not possible to determine the phase boundaries exactly. Figure 5 also indicates that glaserite can be quenched from the melt metastably in a wider region than would be expected from the equilibrium diagram. It is interesting that the *a*-axis of these samples shows a break at about 72 percent K_2SO_4, while *c* continues to increase. This indicates an unknown structural variation.

Below 300°C no equilibrium was reached in annealing experiments. Therefore, aqueous solutions were evaporated at about 110°C and the limits of solid solution were determined using the lattice parameters. The most K-rich glaserite obtained at 110°C had the composition $(Na_{0.27}K_{0.73})_2SO_4$.
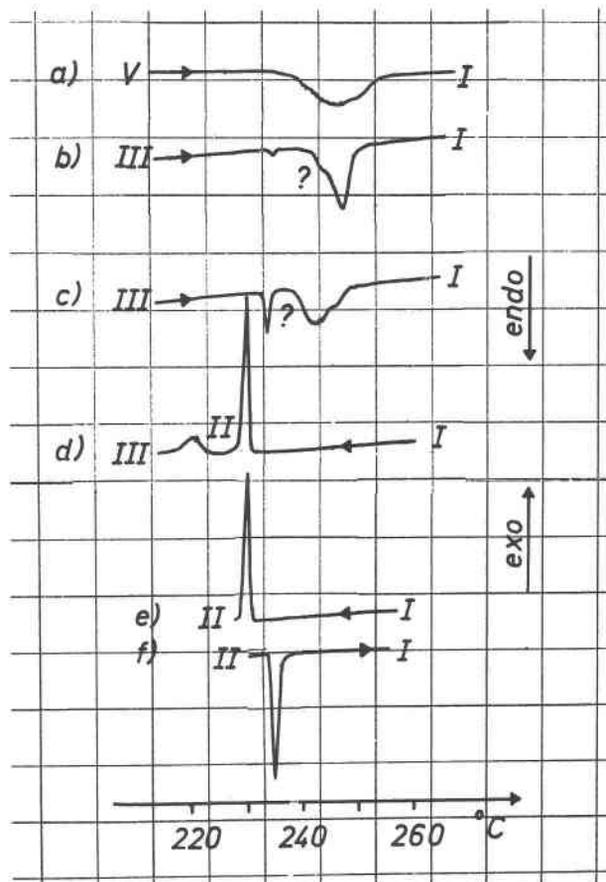

FIG. 2. DTA traces of Na_2SO_4. Samples 5 to 10 mg, Chromel/Alumel thermocouples, 2°C/min. Discussion in Table 1.

TABLE 1. Explanation of DTA-Traces of Figure 2

Starting modification	Traces in Fig.2	Observations[+]
V	a)	Heating: Broad, irreversible signal V→I
III	b) and c)	Heating: Usually two irreversible broad overlapping signals of varying sizes at about 244°C. Treated in Fig.1 as a single transition III→I.
		The small sharp signal II→I at 234°C occurs only if sample is reheated just after the cooling transition II→III (see below); indicates that II had not yet completely converted to III.
I	d)	Cooling: I→II→III. Narrow signal I→II; broad, small signal II→III.
II	e) and f)	Cooling and immediately reheating after transition I→II; proves reversibility of transition I↔II.

[+] The temperatures in Fig.2 do not fully agree with those in Fig.1, because the latter were calculated using both the heating and cooling data (Eysel, 1972).

TABLE 2.   Crystallographic Data for the Various Phases in the System Na_2SO_4–K_2SO_4–K_2CrO_4–Na_2CrO_4

Phase, °C	Space group	Pseudo-orthohexagonal cells a(Å)	b(Å)	c(Å)	a/b	References
Na_2SO_4(I), 270°	$P6_3mc$	9.39	5.42	7.24	$\sqrt{3}$=1.732	This paper
High-Na_2CrO_4, 420°	$P6_3mc$	9.85	5.69	7.37	$\sqrt{3}$	Goldberg et al.[+]
"High-Glaserite":						
$(Na_{0.8}K_{0.2})_2SO_4$, 500°	$P6_3mc$	9.60	5.54	7.39	$\sqrt{3}$	This paper
$(Na_{0.5}K_{0.5})_2SO_4$, 500°	$P6_3mc$	9.84	5.68	7.76	$\sqrt{3}$	This paper
High-K_2SO_4, 620°	$P6_3mc$	10.25	5.92	8.13	$\sqrt{3}$	This paper
High-K_2CrO_4, 680°	$P6_3mc$	10.61	6.12	8.22	$\sqrt{3}$	Goldberg et al.[+]
Glaserite:						
$(Na_{0.5}K_{0.5})_2SO_4$, 20°	$P\bar{3}m1$	9.711	5.607	7.177	$\sqrt{3}$	This paper
$(Na_{0.5}K_{0.5})_2SO_4$, 440°	$P\bar{3}m1$	9.86	5.69	7.42	$\sqrt{3}$	This paper
$(Na_{0.3}K_{0.7})_2SO_4$, 20°	$P\bar{3}m1$	9.809	5.663	7.298	$\sqrt{3}$	This paper
$(Na_{0.25}K_{0.75})_2CrO_4$, 20°	$P\bar{3}m1$	10.163	5.868	7.932	$\sqrt{3}$	Goldberg et al.[+]
$(Na_{0.70}K_{0.30})_2CrO_4$, 20°	$P\bar{3}m1$	9.923	5.729	7.214	$\sqrt{3}$	Goldberg et al.[+]
$(Na_{0.80}K_{0.20})_2CrO_4$, 20°	C2/m?	9.938	5.635	7.164 β =89017'	1.764	Goldberg et al.[+]
$(Na_{0.93}K_{0.07})_2SO_4$(II), 140°	Pnam?	9.53	5.35	7.11	1.781	This paper
Na_2SO_4(II)[++], 225°	Pnam?	9.51	5.33	7.16	1.784	This paper
Na_2SO_4(III), 20°	Ccmm	8.946	5.608	6.963	1.595	This paper
Low-Na_2CrO_4, 20°	Ccmm	9.253	5.854	7.142	1.581	Goldberg et al.[+]
Low-K_2SO_4, 20°	Pcmn	10.073	5.771	7.471	1.745	This paper
Low-K_2CrO_4, 20°	Pcmn	10.399	5.918	7.666	1.757	Goldberg et al.[+]
Na_2SO_4(V), 20°	Fddd	5.861	9.815	12.307	-	Mehrotra 1971[+++]

[+]   Goldberg, Eysel, Hahn (in preparation).
[++]   The first powder data of pure Na_2SO_4(II) were obtained by H.Arnold (private communication).
[+++]   B.N.Mehrotra, private communication.

The results of Nacken (1910a,b) and van t'Hoff and Barschall (1903) have been used to determine the glaserite field at low temperatures. In Na_2SO_4(V) no measurable amount of Na could be replaced by K. For low-K_2SO_4 no solid solutions were formed at 110° and 20°.

As mentioned, glaserite solid solutions can be quenched metastably in a broad range without decomposition into the phase V + G or G + L (Fig. 3), stable at room temperature. If such metastable glaserites with up to about 70 percent K_2SO_4 are kept at room temperature, the decomposition into Na_2SO_4(V) and glaserite slowly takes place within some weeks or months. According to the lattice parameters, the newly formed glaserite always has the formula $(Na_{0.30}K_{0.70})_2SO_4$, irrespective of the composition of the original quenched metastable glaserite. This composition was taken to be the Na-rich limit of solid solution at 20°C.

Considering the pinching out of the glaserite field towards low temperatures, the question arises whether the glaserite phase vanishes at about 0°C, with Na_2SO_4(V) and low-K_2SO_4 occurring as co-existing phases. To answer this question, quenched metastable glaserites containing 40 percent K_2SO_4 were decomposed by keeping them at 0 and − 12°C for two months. In all cases no low-K_2SO_4 was obtained, the decomposition products being Na_2SO_4 (V) and glaserite. Even though this is not conclusive, it indicates that glaserite of a narrow compositional range is stable down to these temperatures. Compositions and temperatures of specific points in the system Na_2SO_4–K_2SO_4 are given in Table 3.

The binary system Na_2CrO_4–K_2CrO_4 (Fig. 6) is very similar to the sulfate system. The transformation temperatures of the chromates are somewhat higher and the polymorphism of Na_2CrO_4 is simpler compared with that of Na_2SO_4. In a very small region with high Na-contents a monoclinically distorted chrome-glaserite has been found (Table 2). It is not yet clear whether it represents a stable or a metastable phase.
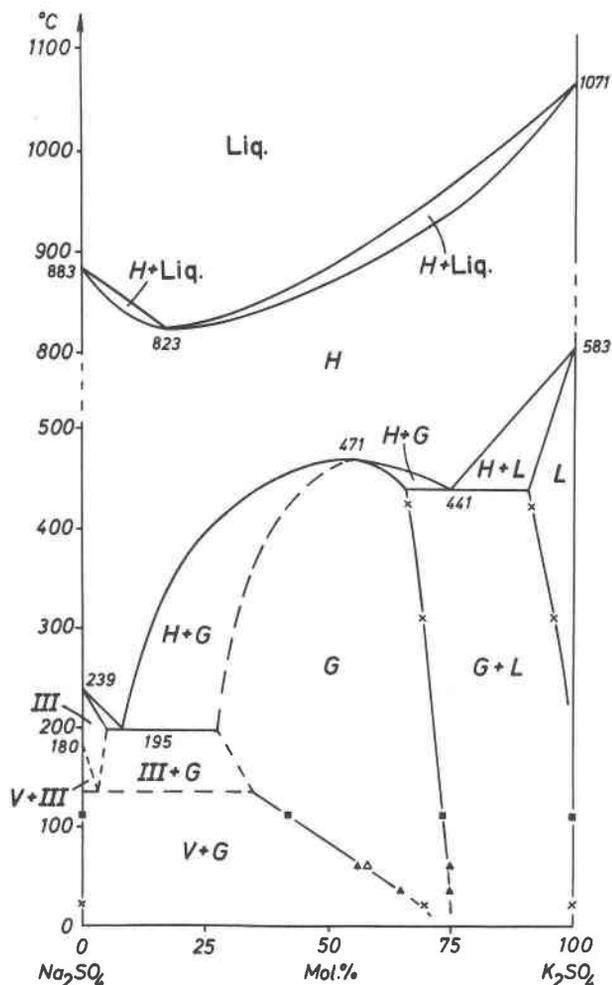
FIG. 3. Phase diagram of the system Na₂SO₄–K₂SO₄. Crosses = annealed and quenched samples, squares = samples from aqueous solutions, full triangles after Nacken (1910b) and open triangles after van't Hoff and Barschall (1903). In this and the next Figures the following symbols are used: H = high-K₂SO₄ structure type, L = low-K₂SO₄ type, G = glaserite type, III = Na₂SO₄(III) type and V = Na₂SO₄(V).

The Systems K₂CrO₄–K₂SO₄ and Na₂CrO₄–Na₂SO₄

The phase diagram of the system K₂CrO₄–K₂SO₄ has been described by Groschuff (1908), whose transformation curve L-H has been confirmed by several DTA runs (triangles in Fig. 7). Both low- and high-temperature modifications form unlimited solid solutions.

Complete solid solution exists between high-Na₂CrO₄ and Na₂SO₄(I) in the system Na₂CrO₄–Na₂SO₄. Similarly, samples quenched from high temperatures show complete solid solution for low-Na₂CrO₄ and Na₂SO₄(III) (Fig. 8), as pointed out

already by Fischmeister (1954). If kept at room-temperature, however, the solid solutions rich in sulfate decompose slowly into two phases—solid solutions of low-Na₂CrO₄ and solid solutions of Na₂SO₄(V). From the change of the lattice parameters it is estimated that Na₂SO₄(V) incorporates less than 5 percent of Na₂CrO₄. The phase diagram Na₂CrO₄–Na₂SO₄, originally given by Flach (1912), has been modified according to these results (Fig. 9), even though the determination of the exact extent of the miscibility gap V + III needs further work. Flach's transition curve H-III has been confirmed by DTA (triangles in Fig. 9).

The Systems Na₂SO₄–K₂SO₄–K₂CrO₄–Na₂CrO₄

Using the four binary systems described so far and additional results of Flach (1912), the phase diagram in Figure 10 has been constructed. In the high-temperature forms (H) both pairs, Na/K and
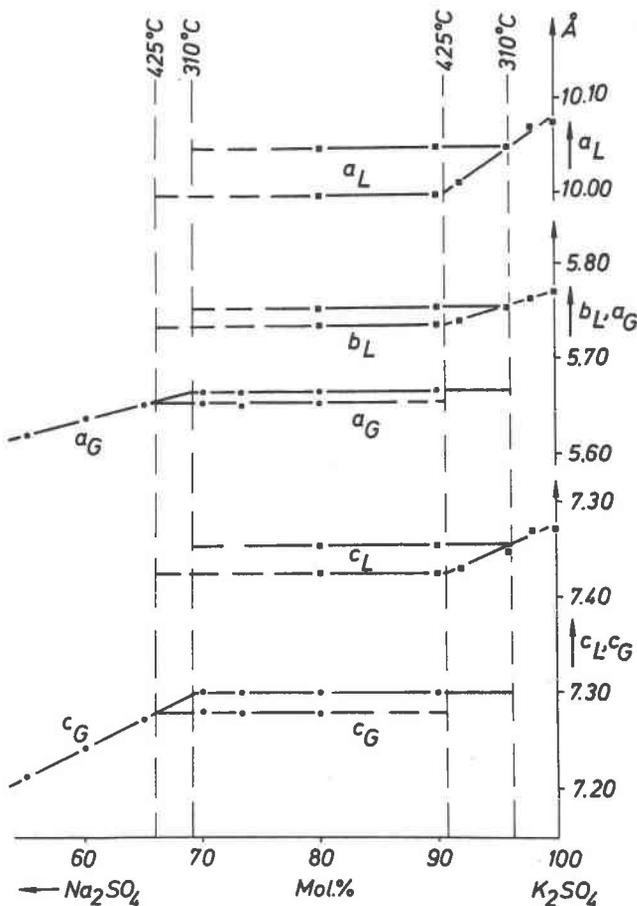

FIG. 4. Lattice parameters of K-rich samples quenched from 310 and 425°C. Squares = low-K₂SO₄ phase, dots = glaserite phase.

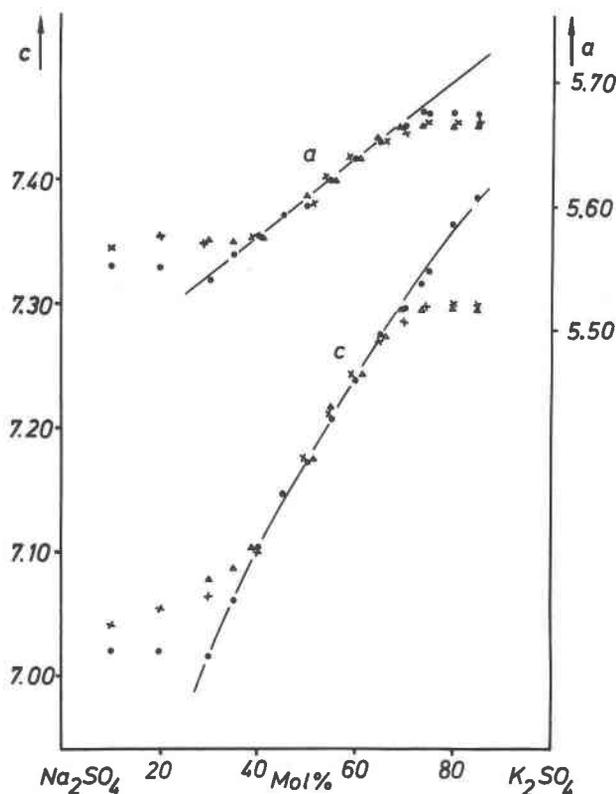FIG. 5. Lattice parameters of the glaserite phase in the system Na_2SO_4–K_2SO_4. Samples quenched from the melt in air (dots), slowly cooled from the melt (crosses), or annealed at 310°C and quenched (triangles).

SO_4/CrO_4, can replace each other completely. In three of the four low-temperature modifications (III, G and L), CrO_4 and SO_4 are completely, and Na and K only partly, miscible. In Na_2SO_4(V) only a few percent of SO_4 can be replaced by CrO_4 and no Na by K. These observations are in agreement with the similar size of the SO_4 (S–O = 1.58 Å) and CrO_4 (Cr–O = 1.67 Å) tetrahedra and the considerable difference in size of the Na^+ (0.98 Å) and K^+ (1.33 Å) ions.[3] Additional investigations are necessary to elucidate the phase relations near the sodium sulfate rich corner at low temperatures in Figure 10.

The Crystal Structures of High-K_2SO_4, Glaserite, and Na_2SO_4II

Structural data for the various phases are given in Table 2. For the high-temperature solid solution (high-K_2SO_4-type), the space group $P6_3mc$ is pro-

[3] Ionic radii after Goldschmidt.

TABLE 3. Compositions and Temperatures of Specific Points in the System Na_2SO_4–K_2SO_4 (Figure 3)

Temp. (°C)	Mol.% K_2SO_4	Temp. (°C)	Mol.% K_2SO_4
240	0	471	55
180	0	441	66
195	5	441	75
195	9	441	91
195	27	583	100

posed on the basis of powder data (Table 4). The occurrence of the c-glide during the transition glaserite → high-K_2SO_4 solid solution is apparent from Table 5. The discontinuous and reversible disappearance of the 111, 003 and 113 reflections could be

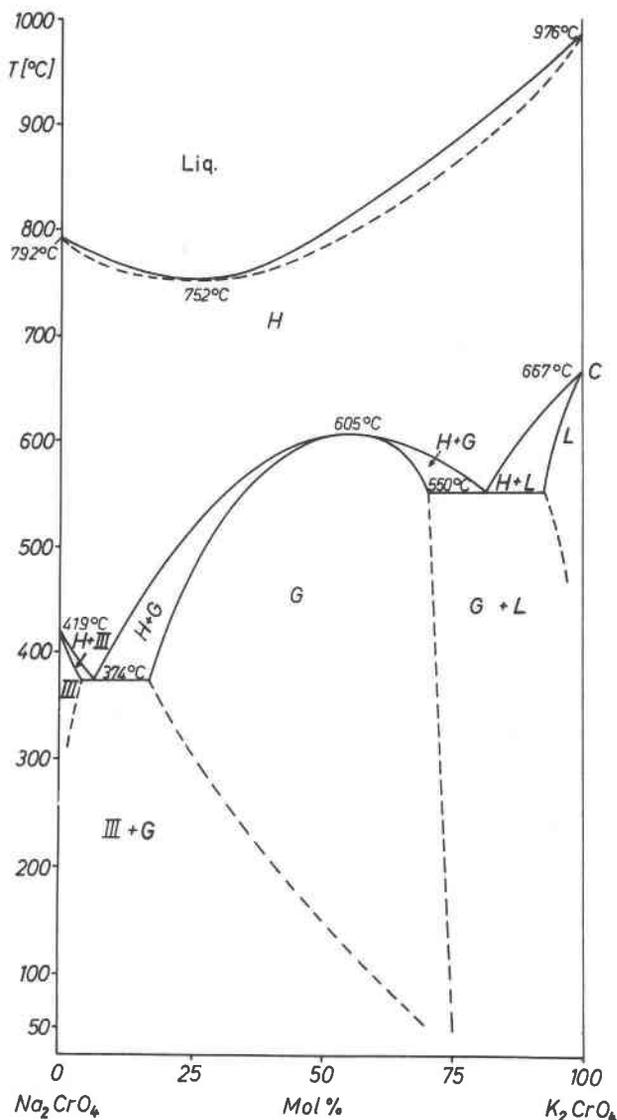FIG. 6. Phase diagram of the system Na_2CrO_4–K_2CrO_4 after Goldberg, Eysel, and Hahn (*Neues Jahrb. Mineral. Monatsh.*, in press).

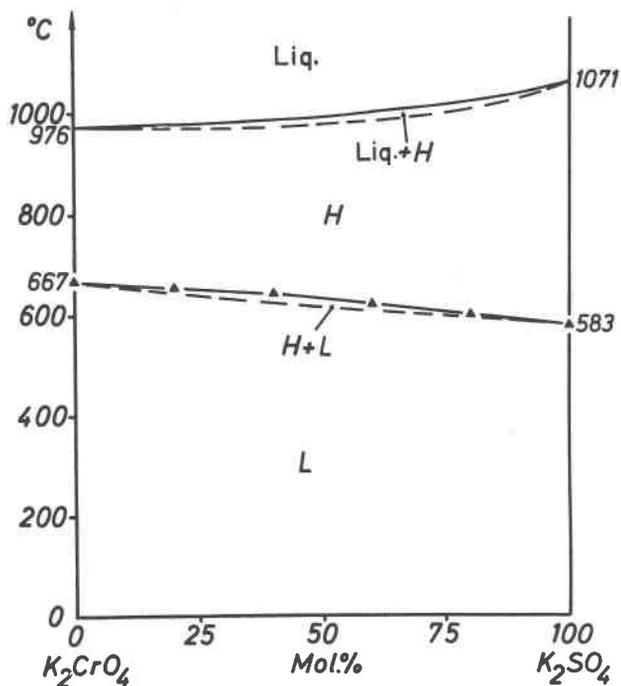FIG. 7. Phase diagram of the system K₂CrO₄–K₂SO₄. Triangles = DTA results.

definitely observed in the high temperature powder patterns.[4] The disappearance of 003 has been observed by Fischmeister (1962) but no structural conclusions were drawn.

The high-temperature solid solutions are thought to be isostructural with α-Ca₂SiO₄, for which a structure is proposed by Eysel and Hahn (1970) on the basis of powder and poor single crystal data as well as packing considerations. Since no investigation of a good single crystal has been carried out so far, slightly distorted structures (subgroup of $P6_3mc$) cannot be ruled out; they must, however, contain a c-glide or a pseudo c-glide. The following hexagonal and trigonal space groups fulfill this condition: $P6_3$, $P31c$, $P3m1$ and $P3$; not, however, the glaserite space group $P\bar{3}m1$. The main difference between the structures is that in the proposed high-K₂SO₄ structure the apices of all tetrahedra point in the same direction along c whereas in the glaserite type alternating tetrahedra point in opposite directions.

The glaserite structure, as originally determined

FIG. 8. Lattice parameters of quenched solid solutions in the system Na₂CrO₄–Na₂SO₄. Crosses = results of Fischmeister (1954).

by Gossner (1928) and confirmed later by Bellanca (1943) and Pontonnier *et al* (1972), was first suggested to be isostructural with high-K₂SO₄ by Bredig (1942). Later Bredig (1943) postulated rotating SO₄ groups for the high-K₂SO₄ structure, but Fischmeister (1962) demonstrated for the isostructural Na₂SO₄(I) that there is not enough space for rotation.[5] Instead, he discussed an orientational disorder of the tetrahedra, thus allowing also space group $P6_3/mmc$. Irrespective of these uncertainties the hexagonal high-temperature forms of a large number of compounds A_2BX_4 have been classified as isostructural with glaserite by many authors, even though Nacken (1910a,b) had earlier found a phase transition between glaserite and the high temperature solid solution of high-K₂SO₄ and Na₂SO₄(I). In ad-

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[4] It should be mentioned that in the system Ca₂SiO₄–Ba₂SiO₄ two phases isostructural with glaserite and high-K₂SO₄, respectively, have been found, also clearly showing the different extinctions (Eysel, 1971).
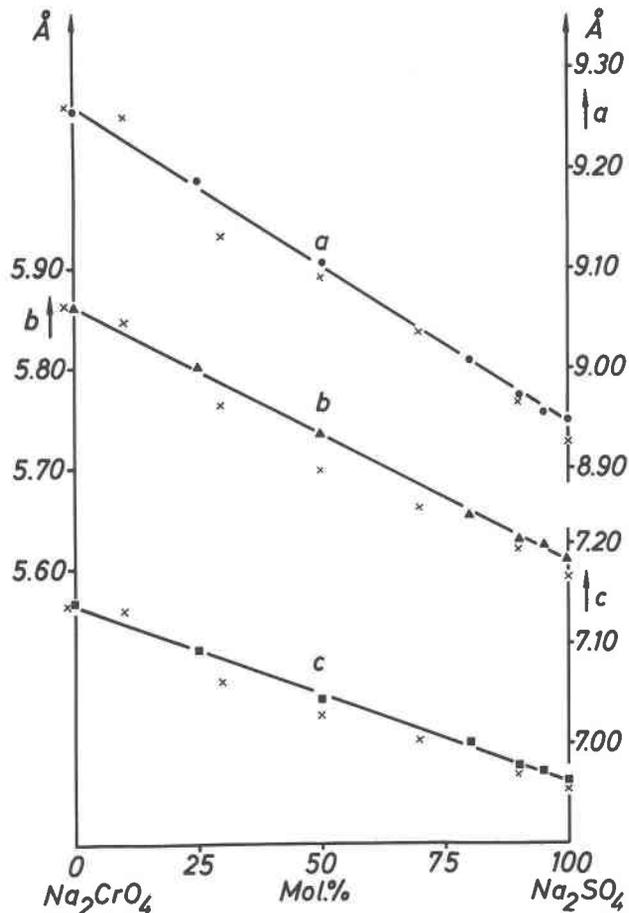
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[5] The rotation was reconsidered for K₂SO₄ by Watanabe *et al* (1972).

FIG. 9. Phase diagram of the system Na₂CrO₄–Na₂SO₄. Triangles = DTA-results.

TABLE 4. High-temperature Powder Data of Na₂SO₄ (I) and High-K₂SO₄

hkl[+]	Na₂SO₄(I)[++], 270°C			High-K₂SO₄[++], 620°C		
	I	$d_{obs.}$	$d_{calc.}$	I	$d_{obs.}$	$d_{calc.}$
100	20	4.71	4.69	10	5.13	5.12
101	100	3.94	3.93	35	4.348	4.335
002	30	3.610	3.619	35	4.062	4.066
102	90	2.865	2.864	100	3.187	3.185
110	90	2.703	2.709	70	2.963	2.960
200	20	2.346	2.345	5	2.563	2.562
201	20	2.226	2.229	20	2.443	2.445
112	3	2.166	2.168	-	-	-
103	3	2.145	2.145	-	-	-
202	30	1.9656	1.9681	50	2.1681	2.1686
004	10	1.8090	1.8090	5	2.0329	2.0325
211	2	1.7217	1.7217	-	-	-
212	20	1.5918	1.5925	15	1.7486	1.7489
300	15	1.5630	1.5634	15	1.7077	1.7086
114	15	1.5047	1.5040	20	1.6754	1.6754
302	3	1.4357	1.4351	-	-	-
213	3	1.4289	1.4285	2	1.5757	1.5761
220	10	1.3544	1.3542	5	1.4789	1.4796
222	8	1.2687	1.2682			

[+]   based on hexagonal cell.

[++]   lattice parameters and space group are given in Table 2.

dition, Nacken had characterized the two phases as trigonal and hexagonal, respectively.

So far no compound has been found for which the stability region of the high-K₂SO₄ type polymorph extends down to normal temperature. Quenching of this form to room temperature has been possible only for a few compounds and solid solutions, mostly in powder samples. The lack of suitable single crystals and the similarity of the trigonal and hexagonal powder diagrams—at room or elevated temperatures—are the main reasons for the confusion of these structures.

Investigations of various A_2BX_4 compounds and a check of high-temperature X-ray powder patterns in the literature revealed in all cases the presence of a c-glide, indicating space group $P6_3mc$ (Table 6). The absence of the c-glide, i.e., the glaserite structure type with space group $P\bar{3}m1$, was found only in $(A, C)_2BX_4$ solid solutions in which A and C are different medium- and large-size cations. Tables 2 and 7 contain the phases with glaserite structure which have been found so far. Some slightly deformed derivatives of both structure types are included in Tables 2, 6, and 7.

High temperature powder patterns have been obtained for solid solutions of Na₂SO₄(II) (Table 8), indicating the space group $Pnam$ (the same space group as for olivine but, because of somewhat different axial ratios, probably not the same structure) or $Pna2_1$. The powder diagram is very similar to that of Na₂SO₄(I) and only a slight deviation from

FIG. 10. The reciprocal salt pair Na₂SO₄–K₂SO₄–K₂CrO₄–Na₂CrO₄. Liquid surface after Flach (1912).

TABLE 5. Powder Data for the Solid Solution $(Na_{0.5}K_{0.5})_2SO_4$ at Different Temperatures

hkl[+]	Glaserite structure[++], 20°C			Glaserite structure[++], 440°C			High-K_2SO_4 type[++], 500°C		
	I	$d_{obs.}$	$d_{calc.}$	I	$d_{obs.}$	$d_{calc.}$	I	$d_{obs.}$	$d_{calc.}$
100	10	4.85	4.86	8	4.93	4.93	10	4.93	4.92
101	50	4.02	4.03	80	4.10	4.10	100	4.15	4.16
002	25	3.590	3.590	25	3.706	3.711	12	3.879	3.878
102	80	2.884	2.889	100	2.968	2.964	90	3.047	3.046
110	100	2.802	2.805	90	2.844	2.843	100	2.844	2.843
111[+++]	4	2.610	2.612	6	2.653	2.655	-	-	-
200	5	2.429	2.429	4	2.528	2.530	6	2.461	2.461
003[+++]	15	2.392	2.393	12	2.473	2.474	-	-	-
201	10	2.300	2.301	20	2.336	2.337	10	2.345	2.347
103	3	2.1459	2.1464	-	-	-	-	-	-
202	35	2.0115	2.0119	50	2.053	2.052	45	2.078	2.078
210	1	1.8353	1.8360	} 5	} 1.864	1.862	-	-	-
113[+++]	2	1.8198	1.8202			1.865	-	-	-
004	6	1.7947	1.7944	5	1.854	1.856	1	1.938	1.939
211	< 1	1.7781	1.7787	-	-	-	-	-	-
203	1	1.7041	1.7045	-	-	-	-	-	-
104	1	1.6834	1.6831	-	-	-	-	-	-
212	10	1.6345	1.6345	15	1.6639	1.6642	8	1.6777	1.6777
300	10	1.6192	1.6192	20	1.6417	1.6417	12	1.6407	1.6412
301	1	1.5790	1.5795	-	-	-	-	-	-
114	8	1.5114	1.5116	10	1.5546	1.5539	3	1.6027	1.6016
213	1	1.4562	1.4564	-	-	-	-	-	-
204	3	1.4435	1.4433	-	-	-	-	-	-
220	10	1.4022	1.4022	15	1.4215	1.4219	6	1.4215	1.4211
105	2	1.3773	1.3766	-	-	-	-	-	-
303	< 1	1.3409	1.3409	-	-	-	-	-	-

[+]   Based on trigonal and hexagonal cells.

[++]   Lattice parameters and space groups are given in Table 2.

[+++]   Reflexions hhl with l≠2n, indicating the difference between both structure types.

TABLE 6. Some Compounds with High–K_2SO_4 Type Polymorphs[+]

Compound	°C	Orthohexagonal cells			References
		a(Å)	b(Å)	c(Å)	
$Na_2SeO_4(I)$	20	9.507	5.489	7.217	Mehrotra 1971[++]
α-Na_2BeF_4	450	9.13	5.27	6.96	Hahn 1953
High-Rb_2SO_4	660	10.616	6.129	8.421	Tabrizi et al. 1970
High-Tl_2SO_4	514	10.663	6.156	8.28	Majumdar et al. 1965
High-K_2MoO_4	480	10.966	6.331	8.07	V.d.Akker et al. 1970
High-Rb_2WO_4	495	11.376	6.568	8.411	V.d.Akker et al. 1970
High-$CaNaVO_4$	820	9.648	5.57	7.33	Klement et al. 1961
α-Ca_2SiO_4	1500	9.572	5.526	7.307	Regourd et al. 1968
α-$Ca_2(Si_{0.5}Ge_{0.5})O_4$	20	9.436	5.448	7.096	Eysel et al. 1970
α-$Ca_2GeO_4(+B_2O_3)$	20	9.556	5.517	7.164	Eysel et al. 1970
α-$(Ca_{0.7}Ba_{0.3})SiO_4$	20	9.660	5.577	7.136	Eysel 1971
41.5 wt.% Ca_2SiO_4 + 58.5 wt.% $Ca_3(PO_4)_2$	20	18.646 (=2×9.322)	10.765 (=2×5.382)	21.73 (≈3×7.24)	Saalfeld 1971

[+]   For further examples c.f. Table 2.

[++]   B.N.Mehrotra, private communication.

TABLE 7.   Solid Solutions with Glaserite Structure[+], 20°C

Solid solution	Space group	Pseudo-orthohexagonal axes a(Å)	b(Å)	c(Å)	β	a/b	References
$Na(K,NH_4)_3(SO_4)_2$	$P\bar{3}m1$	9.84	5.68	7.35		$\sqrt{3}$=1.732	Frondel (1950)
$(Na,Tl)_2SO_4$		9.84	5.68	7.35			Larsson (1971)[++]
$(Na_{0.25}K_{0.75})_2BeF_4$		9.682	5.590	7.159			Pontonnier et al. (1972)
$(Na_{0.3}Rb_{0.7})_2BeF_4$		9.982	5.763	7.512			Pontonnier et al. (1972)
$(Na_{0.38}Rb_{0.62})_2BeF_4$		9.94	5.74	7.49			Grebenshchikov et al. (1970)
$(Na_{0.25}(NH_4)_{0.75})_2BeF_4$		10.099	5.831	5.664			Pontonnier et al. (1972)
$(Na_{0.25}Tl_{0.75})_2BeF_4$		9.969	5.756	7.550			Pontonnier et al. (1972)
$(Ca_{0.40}Ba_{0.60})_2SiO_4$		9.925	5.730	7.283			Eysel (1971)
$(Ca_{0.38}Ba_{0.62})_2GeO_4$		10.141	5.855	7.37			Grebenshchikov et al. (1970)
$(Ca_{0.35}Ba_{0.65})_2SiO_4$	$P\bar{3}c1$[+++]	9.949	5.744	14.641 (=2×7.321)		$\sqrt{3}$=1.732	Eysel (1971)
$(Ca_{0.30}Ba_{0.70})_2SiO_4$	$C2/c$[+++]	9.975	5.760	14.714 (=2×7.357)	89.67°	1.732	Eysel (1971)
$MgCa_3(SiO_4)_2$ (Merwinite)	$P2_1/c$	9.328	5.293	13.254 (=2×6.627)	91.90°	1.762	Moore et al. (1972)

[+]   For further examples c.f. Table 2.

[++]   L.O. Larsson, private communication.

[+++]   From powder patterns and subgroup relations.

the hexagonal axial ratio $a/b = \sqrt{3}$ has been found. The lattice parameters of pure $Na_2SO_4(II)$ in Table 2 were derived by extrapolation from the solid solution.

With the exception of $Na_2SO_4(V)$ all crystal structures of the Na_2SO_4–K_2SO_4–K_2CrO_4–Na_2CrO_4 system have hexagonal or pseudo-hexagonal cells. Their structures can be deduced from a basic structure with space group $P6_3/mmc$, $Z = 2$, $a \approx 5.5$, and $c \approx 7.5$ Å on the basis of subgroup relations (Eysel, 1970, 1971). The structures differ predominantly by the sizes of the cations, *i.e.*, their coordination numbers. The structural differences, therefore, are more than just slight distortions. This is also apparent from the magnitudes of the transition enthalpies (Table

9). From the basic structure mentioned above, further structure types of A_2BX_4, A_2BX_3, ABX_4, ABX_3 compounds or similar compositions can be derived. These relationships will be discussed elsewhere (Eysel, in preparation).

The Glaserite Phase

Glaserite (also called aphthitalite) has been considered in the literature to be either a stoichiometric compound $NaK_3(SO_4)_2$ forming a solid solution with Na_2SO_4 or a compound $NaKSO_4$ forming solid solutions with Na_2SO_4 as well as with K_2SO_4. The same assumptions have been applied to chrome-glaserite. The phase diagram in Figure 3 indicates that at high temperatures the composition $NaK_3(SO_4)_2$ is part of the two phase region G + L and therefore cannot exist as a compound. The maximum in the transition curve glaserite-high temperature solid solution occurs at $(Na_{0.45}K_{0.55})_2SO_4$ and not at $NaKSO_4$. This implies a melting interval and not a melting point for the composition $NaKSO_4$. The same results are found in the chromate system (Fig. 6). At high temperatures, therefore, glaserite must be considered a solid solution and not a particular stoichiometric compound. Further support for this observation is supplied by Toropov *et al* (1964) who found a "glaserite" phase $(Ca,Ba)_2SiO_4$ in the system Ca_2SiO_4–Ba_2SiO_4 with the maximum in the melting curve at $(Ca_{0.40}Ba_{0.60})_2SiO_4$. In the system Na_2BeF_4–Rb_2BeF_4 glaserite type solid solutions extend from $(Na_{0.5}$

TABLE 8.   Powder Data for $(Na_{0.93}K_{0.07})_2SO_4(II)$ at 140°C[+]

hkl	I	$d_{obs.}$	$d_{calc.}$	hkl	I	$d_{obs.}$	$d_{calc.}$
200	8	4.78	4.77	312	10	2.1681	2.1661
110	10	4.68	4.67	022	5	2.1381	2.1381
201	25	3.953	3.959	203	8	2.1233	2.1223
111	65	3.909	3.904	402	25	1.9782	1.9790
002	30	3.564	3.556	222	20	1.9509	1.9509
202	100	2.848	2.850	313	5	1.7908	1.7901
112	65	2.832	2.832	004	20	1.7778	1.7778
310	50	2.731	2.732	123	3	1.7430	1.7446
020	15	2.676	2.677	204	4	1.6645	1.6656
120	7	2.5779	2.5772	413} 512}	10	1.6024	1.6031 1.6026
212	12	2.5162	2.5156	600	20	1.5885	1.5883
400	25	2.3812	2.3824	520	5	1.5520	1.5524
220	5	2.3339	2.3339	314	15	1.4895	1.4901
401	10	2.2586	2.2586	024	10	1.4807	1.4809
221	12	2.2160	2.2175	602	3	1.4497	1.4503

[+]   Based on cell parameters in Table 2.

TABLE 9. Transition Enthalpies ΔH in the System Na_2SO_4–Na_2CrO_4–K_2CrO_4–K_2SO_4[+]

Composition	Transition	°C	ΔH kcal/Mol.	References
Na_2SO_4	V⟶I, Fddd⟶P6₃mc	240–260	2.59	Eysel 1972
	V⟷III, Fddd⟷Ccmm	~180	1.01	Eysel 1972
	III⟶I, Ccmm⟶P6₃mc	240	1.58	Eysel 1972
	I⟷II, P6₃mc⟷Pnam	230	1.08	Eysel 1972
	II⟶III, Pnam⟶Ccmm	220	0.54	Eysel 1972
Na_2CrO_4	low⟷high, Ccmm⟷P6₃mc	419	2.12	Goldberg et al.[++]
Glaserite, $(Na_{0.45}K_{0.55})_2SO_4$	low⟷high, P3̄m1⟷P6₃mc	471	1.12	Eysel 1972
Chrome-glaserite, $(Na_{0.45}K_{0.55})_2CrO_4$	low⟷high, P3̄m1⟷P6₃mc	605	1.50	Goldberg et al.[++]
K_2SO_4	low⟷high, Pcmn⟷P6₃mc	583	~1.8	Eysel 1972
K_2CrO_4	low⟷high, Pcmn⟷P6₃mc	667	2.437	D'ans Lax 1967

[+] The results of other authors on Na_2SO_4 and K_2SO_4 are summarized by Eysel (1972).

[++] Goldberg, Eysel, Hahn (in preparation).

$Rb_{0.5})_2BeF_4$ to $(Na_{0.3}Rb_{0.7})BeF_4$ (Pontonnier *et al*, 1972).

From a structural point of view, Hilmy (1953), Dickens and Brown (1971) and Moore *et al* (1972, 1973)[6] have pointed out that the cations occupy three different sites. The octahedral site in 001/2 (1*b*, 3̄*m*, one quarter of the cations) should be occupied by the smaller cation.[7] The site of the trigonal axes (1/3 2/3*z*, 2*d*, 3*m*; one half of the cations, 10-co-ordinated) and the position in 000 with coordination number 6 + 6 (1*a*, 3̄*m*, one quarter of the ion) should be preferred by the larger cations. From these structural features, a maximum limit of solid solution can be predicted at $(Na_{0.25}K_{0.75})_2SO_4$ in the K-rich part of the system, and this composition has been found experimentally (Figs. 3 and 6). The phase diagrams in Figures 3 and 6 also indicate that at low temperatures, only this 1:3 composition is stable. It seems probable that here the glaserite phase is represented by a $NaK_3(SO_4)_2$ compound with an ordered distribution of Na (in position 1*b*) and K (in 1*a* and in 2*d*).

With increasing temperature, however, Na is increasingly capable of occupying also the 1*a*- and the 2*d*-positions, resulting in an extensive enlargement of the field of solid solution towards Na_2SO_4 (Fig. 3) and Na_2CrO_4 (Fig. 6), respectively. At the same time, the distribution of Na and K should become more and more disordered. At even higher temperatures the glaserite field decreases and vanishes be-cause the hexagonal high-temperature structure provides higher coordination numbers.[8] Thus, phases of the glaserite type are to be considered as solid solutions of medium- and large-size cations A and C in which the proportion of the cations A/C can vary from above 3 to 1/3, depending on temperature and the difference in the size of the cations. Site disordering to ordering of A and C can be expected. This needs to be proved by detailed structure determinations.

The glaserite structure and its deformed derivatives have been found or can be predicted for $(A, C)_2BX_4$ solid solutions with cations A = Na,Ag⁺, Mg, Ca, Cd; cations C = K, Rb, Cs, Tl⁺, NH₄, Sr, Ba, Eu²⁺ and with tetrahedral complexes BX_4 = BeF₄, SO₄, SeO₄, CrO₄, MoO₄, WO₄, PO₄, VO₄, AsO₄, SiO₄, GeO₄, *etc*. It should be mentioned that merwinite, $MgCa_3(SiO_4)_2$, has recently been found by Moore and Araki (1972) to have a deformed glaserite structure (Table 7). Mg and Ca are the smallest cations A and C found in this structure type so far.

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[6] A very interesting geometrical interpretation of the glaserite type and related structures is given by Moore (1973).

[7] For a more detailed description of the structure, *cf* Eysel *et al* (1970).

[8] Contrary to this picture, Förland (1959) concluded, on the basis of thermodynamical data, that the cations in the glaserite structure are ordered and become disordered during the transition into the high temperature form.

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