

## Crystal Chemistry of the System $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-K}_2\text{CrO}_4\text{-Na}_2\text{CrO}_4$ and of the Glaserite Phase

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### Abstract

A phase diagram for the system  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-K}_2\text{CrO}_4\text{-Na}_2\text{CrO}_4$  has been worked out particularly with respect to the regions of solid solutions of the six phases: High- $\text{K}_2\text{SO}_4$ , low- $\text{K}_2\text{SO}_4$ ,  $(\text{Na},\text{K})_2\text{SO}_4$  (glaserite),  $\text{Na}_2\text{SO}_4$  (II),  $\text{Na}_2\text{SO}_4$  (III) and  $\text{Na}_2\text{SO}_4$  (V). In all of them  $\text{SO}_4$  can be completely or partially replaced by  $\text{CrO}_4$ . With the exception of  $\text{Na}_2\text{SO}_4$  (V) the crystal structures are more or less related. It is demonstrated that the glaserite structure occurs only in solid solutions  $(A,C)_2\text{BX}_4$  with cations *A* and *C* of different sizes; it is not isostructural with the hexagonal high- $\text{K}_2\text{SO}_4$  type, as assumed in many investigations of  $A_2\text{BX}_4$  compounds. The nature of the glaserite phase and of the high- $\text{K}_2\text{SO}_4$  type is discussed.

### Introduction

The system  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-K}_2\text{CrO}_4\text{-Na}_2\text{CrO}_4$  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 ( $\text{Na}_2\text{SO}_4$  V), arcanite (low- $\text{K}_2\text{SO}_4$ ), glaserite or aphtitalite (a solid solution of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ) and tarapacaite (low- $\text{K}_2\text{CrO}_4$ ). The system was originally investigated by Flach (1912), using optical microscopy and thermal analysis. Later investigations dealt with parts of the system, particularly with  $\text{Na}_2\text{SO}_4$  and its polymorphism, the glaserite phase, and the binary systems  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$  and  $\text{Na}_2\text{CrO}_4\text{-K}_2\text{CrO}_4$ . 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- $\text{K}_2\text{SO}_4$  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<sup>1</sup> in

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

<sup>2</sup> Goldberg, A., W. Eysel, and Th. Hahn, Phase diagram and crystallography of the system  $\text{Na}_2\text{CrO}_4\text{-K}_2\text{CrO}_4$  (*Neues Jahrb. Mineral. Monatsch.*, in press).

Figure 1. Three of the four modifications, I, III, and V, are stable forms whereas  $\text{Na}_2\text{SO}_4$  (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  $\text{Na}_2\text{SO}_4$  are shown in Figure 2 with the characteristic features outlined in Table 1. Structural data are given in Table 2.

$\text{Na}_2\text{CrO}_4$  reveals only two modifications, low- $\text{Na}_2\text{CrO}_4$  (isostructural with  $\text{Na}_2\text{SO}_4$  (III); Miller, 1936; Niggli, 1954) and high- $\text{Na}_2\text{CrO}_4$  (isostructural with  $\text{Na}_2\text{SO}_4$  (I); Goldberg *et al.*<sup>2</sup>). Both  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{CrO}_4$  have two modifications each. Low- $\text{K}_2\text{CrO}_4$  (Zachariasen and Ziegler, 1931) and low- $\text{K}_2\text{SO}_4$  (Robinson, 1958) are isostructural as well as high- $\text{K}_2\text{CrO}_4$  (Pistorius, 1962) and high- $\text{K}_2\text{SO}_4$  (Fischmeister, 1962). The latter two are isostructural with  $\text{Na}_2\text{SO}_4$  (I) and high- $\text{Na}_2\text{CrO}_4$  (Table 2).

For  $\text{K}_2\text{SO}_4$  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- $\text{K}_2\text{SO}_4$  are considered.

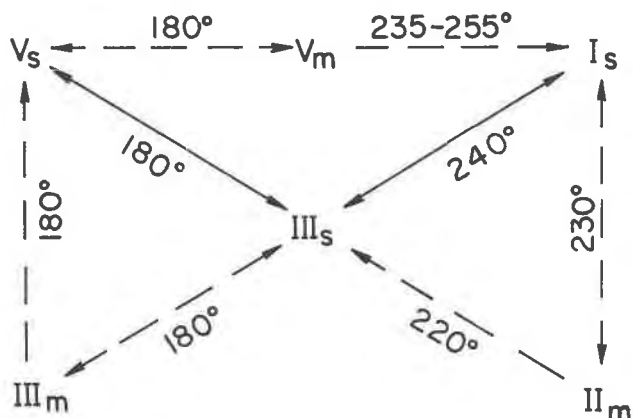


FIG. 1. Polymorphism of  $\text{Na}_2\text{SO}_4$ . s = stable (heavy lines), m = metastable (dashed lines).

### The Systems $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ and $\text{Na}_2\text{CrO}_4\text{-K}_2\text{CrO}_4$

The phase diagram of the system  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$  was investigated by Nacken (1910a,b), Jaenecke (1908), and Perrier and Bellance (1940). The high temperature equilibria in the binary system  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$  (Eysel, 1972) are shown in Figure 3. Complete solid solubility exists for  $\text{Na}_2\text{SO}_4$ (I) and high- $\text{K}_2\text{SO}_4$  and limited solubility for  $\text{Na}_2\text{SO}_4$ (III),  $(\text{Na,K})_2\text{SO}_4$  (glaserite) and low- $\text{K}_2\text{SO}_4$ . The solid solutions of  $\text{Na}_2\text{SO}_4$ (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  $425^\circ$  and  $310^\circ\text{C}$  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  $\text{K}_2\text{SO}_4$ , while  $c$  continues to increase. This indicates an unknown structural variation.

Below  $300^\circ\text{C}$  no equilibrium was reached in annealing experiments. Therefore, aqueous solutions were evaporated at about  $110^\circ\text{C}$  and the limits of solid solution were determined using the lattice parameters. The most K-rich glaserite obtained at  $110^\circ\text{C}$  had the composition  $(\text{Na}_{0.27}\text{K}_{0.73})_2\text{SO}_4$ .

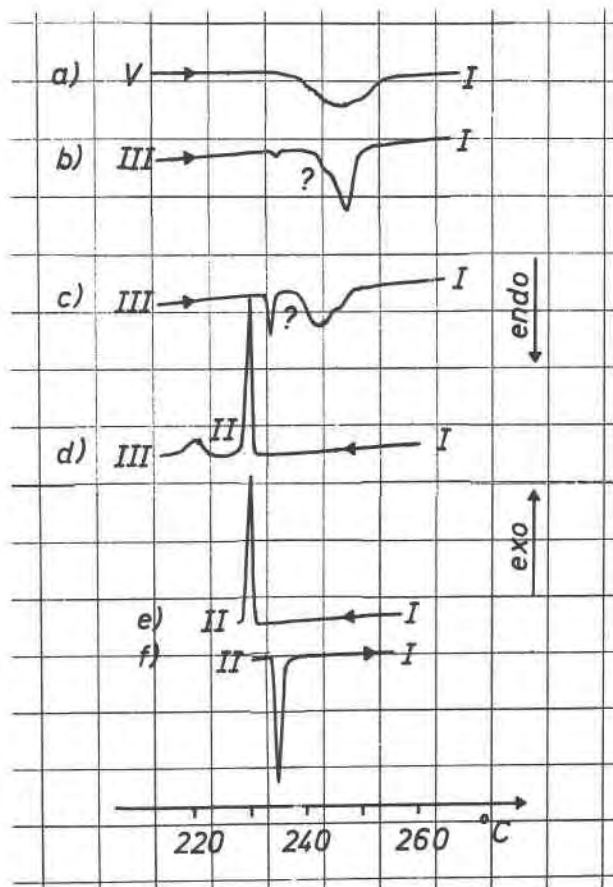


FIG. 2. DTA traces of  $\text{Na}_2\text{SO}_4$ . Samples 5 to 10 mg, Chromel/Alumel thermocouples,  $2^\circ\text{C}/\text{min}$ . Discussion in Table 1.

TABLE 1. Explanation of DTA-Traces of Figure 2

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

<sup>+</sup> 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  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-K}_2\text{CrO}_4\text{-Na}_2\text{CrO}_4$ 

Phase, °C	Space group	Pseudo-orthohexagonal cells			a/b	References
		a(Å)	b(Å)	c(Å)		
$\text{Na}_2\text{SO}_4$ (I), 270°	$P6_3mc$	9.39	5.42	7.24	$\sqrt{3}=1.732$	This paper
High- $\text{Na}_2\text{CrO}_4$ , 420°	$P6_3mc$	9.85	5.69	7.37	$\sqrt{3}$	Goldberg et al. <sup>+</sup>
"High-Glaserite":						
$(\text{Na}_{0.8}\text{K}_{0.2})_2\text{SO}_4$ , 500°	$P6_3mc$	9.60	5.54	7.39	$\sqrt{3}$	This paper
$(\text{Na}_{0.5}\text{K}_{0.5})_2\text{SO}_4$ , 500°	$P6_3mc$	9.84	5.68	7.76	$\sqrt{3}$	This paper
High- $\text{K}_2\text{SO}_4$ , 620°	$P6_3mc$	10.25	5.92	8.13	$\sqrt{3}$	This paper
High- $\text{K}_2\text{CrO}_4$ , 680°	$P6_3mc$	10.61	6.12	8.22	$\sqrt{3}$	Goldberg et al. <sup>+</sup>
Glaserite:						
$(\text{Na}_{0.5}\text{K}_{0.5})_2\text{SO}_4$ , 20°	$P\bar{3}m1$	9.711	5.607	7.177	$\sqrt{3}$	This paper
$(\text{Na}_{0.5}\text{K}_{0.5})_2\text{SO}_4$ , 440°	$P\bar{3}m1$	9.86	5.69	7.42	$\sqrt{3}$	This paper
$(\text{Na}_{0.3}\text{K}_{0.7})_2\text{SO}_4$ , 20°	$P\bar{3}m1$	9.809	5.663	7.298	$\sqrt{3}$	This paper
$(\text{Na}_{0.25}\text{K}_{0.75})_2\text{CrO}_4$ , 20°	$P\bar{3}m1$	10.163	5.868	7.932	$\sqrt{3}$	Goldberg et al. <sup>+</sup>
$(\text{Na}_{0.70}\text{K}_{0.30})_2\text{CrO}_4$ , 20°	$P\bar{3}m1$	9.923	5.729	7.214	$\sqrt{3}$	Goldberg et al. <sup>+</sup>
$(\text{Na}_{0.80}\text{K}_{0.20})_2\text{CrO}_4$ , 20°	$C2/m?$	9.938	5.635	7.164 $\beta = 89.017^\circ$	1.764	Goldberg et al. <sup>+</sup>
$(\text{Na}_{0.93}\text{K}_{0.07})_2\text{SO}_4$ (II), 140°	$Pnam?$	9.53	5.35	7.11	1.781	This paper
$\text{Na}_2\text{SO}_4$ (II) <sup>++</sup> , 225°	$Pnam?$	9.51	5.33	7.16	1.784	This paper
$\text{Na}_2\text{SO}_4$ (III), 20°	$Ccmm$	8.946	5.608	6.963	1.595	This paper
Low- $\text{Na}_2\text{CrO}_4$ , 20°	$Ccmm$	9.253	5.854	7.142	1.581	Goldberg et al. <sup>+</sup>
Low- $\text{K}_2\text{SO}_4$ , 20°	$Pcmm$	10.073	5.771	7.471	1.745	This paper
Low- $\text{K}_2\text{CrO}_4$ , 20°	$Pcmm$	10.399	5.918	7.666	1.757	Goldberg et al. <sup>+</sup>
$\text{Na}_2\text{SO}_4$ (V), 20°	$Fddd$	5.861	9.815	12.307	-	Mehrotra 1971 <sup>+++</sup>

<sup>+</sup> Goldberg, Eysel, Hahn (in preparation).

<sup>++</sup> The first powder data of pure  $\text{Na}_2\text{SO}_4$ (II) were obtained by H. Arnold (private communication).

<sup>+++</sup> 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  $\text{Na}_2\text{SO}_4$ (V) no measurable amount of Na could be replaced by K. For low- $\text{K}_2\text{SO}_4$  no solid solutions were formed at 110° and 20°C.

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  $\text{K}_2\text{SO}_4$  are kept at room temperature, the decomposition into  $\text{Na}_2\text{SO}_4$ (V) and glaserite slowly takes place within some weeks or months. According to the lattice parameters, the newly formed glaserite always has the formula  $(\text{Na}_{0.30}\text{K}_{0.70})_2\text{SO}_4$ , 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  $\text{Na}_2\text{SO}_4$ (V) and low- $\text{K}_2\text{SO}_4$  occurring as co-existing phases. To answer this question, quenched metastable glaserites containing 40 percent  $\text{K}_2\text{SO}_4$  were decomposed by keeping them at 0 and -12°C for two months. In all cases no low- $\text{K}_2\text{SO}_4$  was obtained, the decomposition products being  $\text{Na}_2\text{SO}_4$ (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  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$  are given in Table 3.

The binary system  $\text{Na}_2\text{CrO}_4\text{-K}_2\text{CrO}_4$  (Fig. 6) is very similar to the sulfate system. The transformation temperatures of the chromates are somewhat higher and the polymorphism of  $\text{Na}_2\text{CrO}_4$  is simpler compared with that of  $\text{Na}_2\text{SO}_4$ . 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.

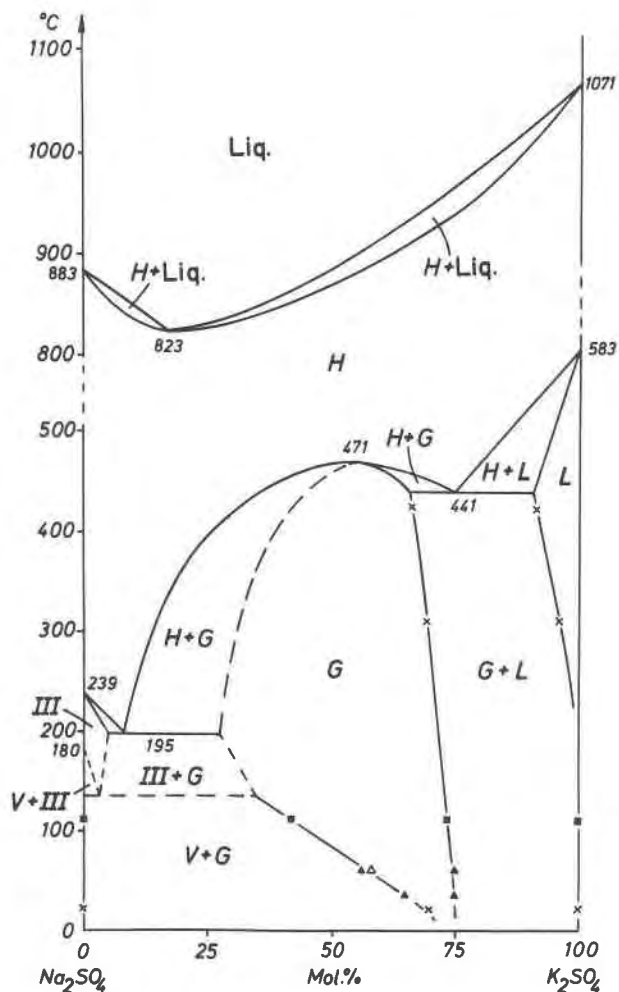


FIG. 3. Phase diagram of the system  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ . Crosses = annealed and quenched samples, squares = samples from aqueous solutions, full triangles after Nacken (1910b) and open triangles after van't Hoff and Barschall (1903). In this and the next Figures the following symbols are used: H = high- $\text{K}_2\text{SO}_4$  structure type, L = low- $\text{K}_2\text{SO}_4$  type, G = glaserite type, III =  $\text{Na}_2\text{SO}_4$ (III) type and V =  $\text{Na}_2\text{SO}_4$ (V).

### The Systems $\text{K}_2\text{CrO}_4\text{-K}_2\text{SO}_4$ and $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$

The phase diagram of the system  $\text{K}_2\text{CrO}_4\text{-K}_2\text{SO}_4$  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- $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{SO}_4$ (I) in the system  $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ . Similarly, samples quenched from high temperatures show complete solid solution for low- $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{SO}_4$ (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- $\text{Na}_2\text{CrO}_4$  and solid solutions of  $\text{Na}_2\text{SO}_4$ (V). From the change of the lattice parameters it is estimated that  $\text{Na}_2\text{SO}_4$ (V) incorporates less than 5 percent of  $\text{Na}_2\text{CrO}_4$ . The phase diagram  $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ , 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 $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-K}_2\text{CrO}_4\text{-Na}_2\text{CrO}_4$

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

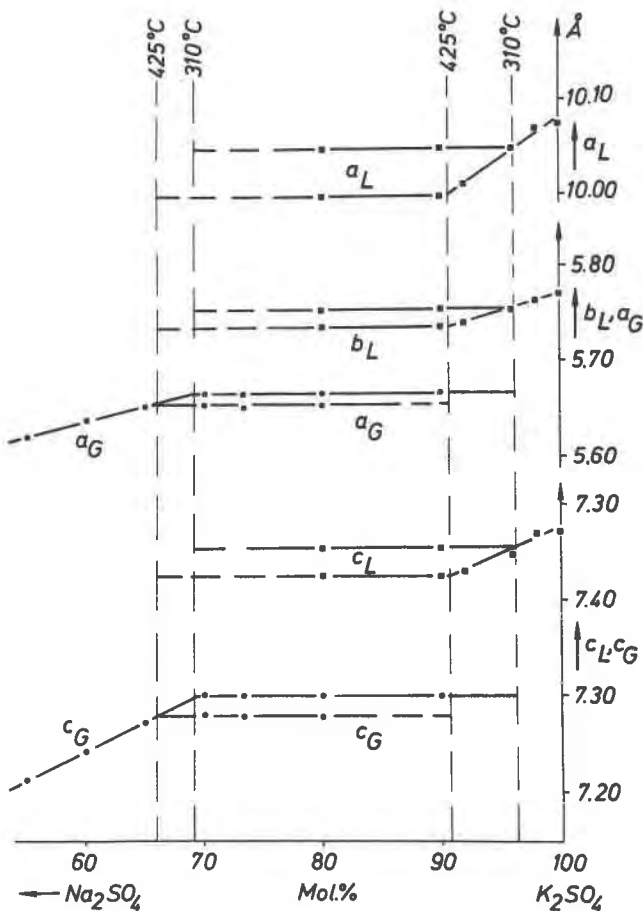


FIG. 4. Lattice parameters of K-rich samples quenched from 310 and 425°C. Squares = low- $\text{K}_2\text{SO}_4$  phase, dots = glaserite phase.

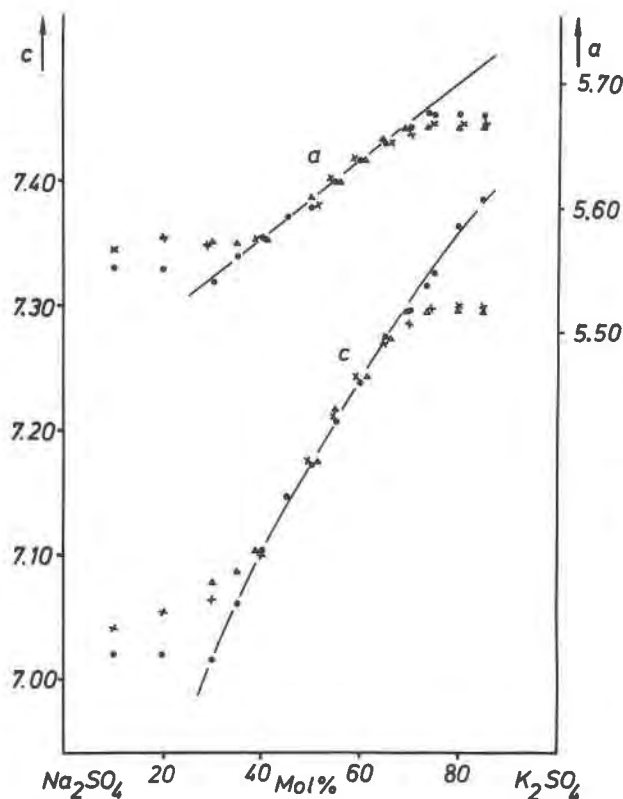


FIG. 5. Lattice parameters of the glaserite phase in the system  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ . Samples quenched from the melt in air (dots), slowly cooled from the melt (crosses), or annealed at  $310^\circ\text{C}$  and quenched (triangles).

$\text{SO}_4/\text{CrO}_4$ , can replace each other completely. In three of the four low-temperature modifications (III, G and L),  $\text{CrO}_4$  and  $\text{SO}_4$  are completely, and Na and K only partly, miscible. In  $\text{Na}_2\text{SO}_4$  (V) only a few percent of  $\text{SO}_4$  can be replaced by  $\text{CrO}_4$  and no Na by K. These observations are in agreement with the similar size of the  $\text{SO}_4$  ( $\text{S-O} = 1.58 \text{ \AA}$ ) and  $\text{CrO}_4$  ( $\text{Cr-O} = 1.67 \text{ \AA}$ ) tetrahedra and the considerable difference in size of the  $\text{Na}^+$  ( $0.98 \text{ \AA}$ ) and  $\text{K}^+$  ( $1.33 \text{ \AA}$ ) ions.<sup>8</sup> 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- $\text{K}_2\text{SO}_4$ , Glaserite, and $\text{Na}_2\text{SO}_4$ II

Structural data for the various phases are given in Table 2. For the high-temperature solid solution (high- $\text{K}_2\text{SO}_4$ -type), the space group  $P6_3mc$  is pro-

<sup>8</sup> Ionic radii after Goldschmidt.

TABLE 3. Compositions and Temperatures of Specific Points in the System  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$  (Figure 3)

Temp. ( $^\circ\text{C}$ )	Mol. % $\text{K}_2\text{SO}_4$	Temp. ( $^\circ\text{C}$ )	Mol. % $\text{K}_2\text{SO}_4$
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  $\rightarrow$  high- $\text{K}_2\text{SO}_4$  solid solution is apparent from Table 5. The discontinuous and reversible disappearance of the 111, 003 and 113 reflections could be

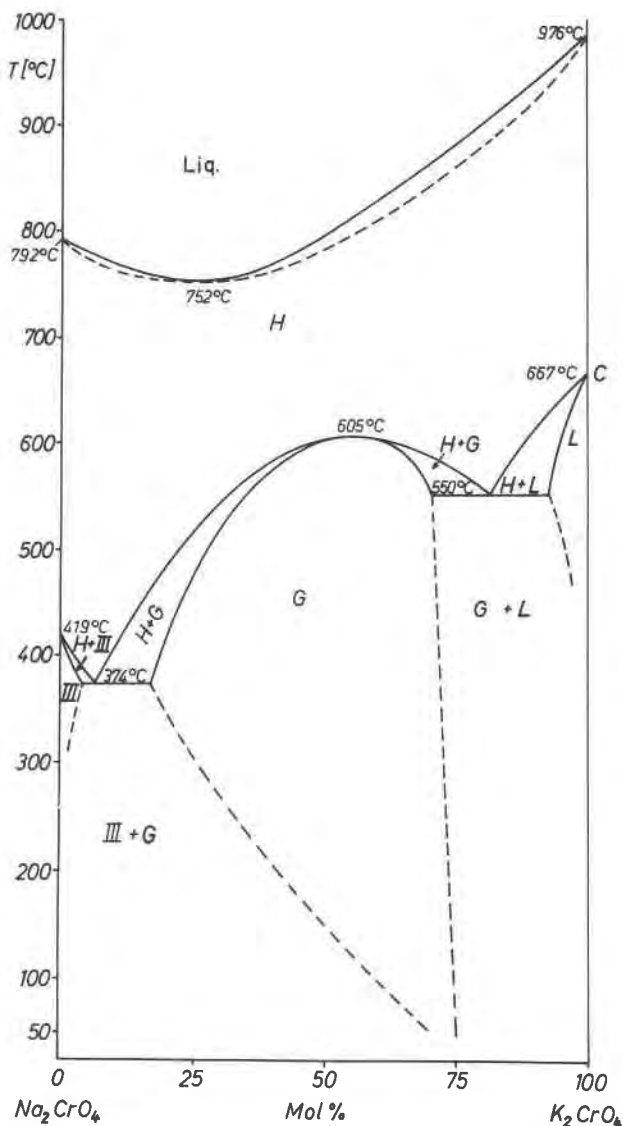


FIG. 6. Phase diagram of the system  $\text{Na}_2\text{CrO}_4\text{-K}_2\text{CrO}_4$  after Goldberg, Eysel, and Hahn (*Neues Jahrb. Mineral. Monatsh.*, in press).

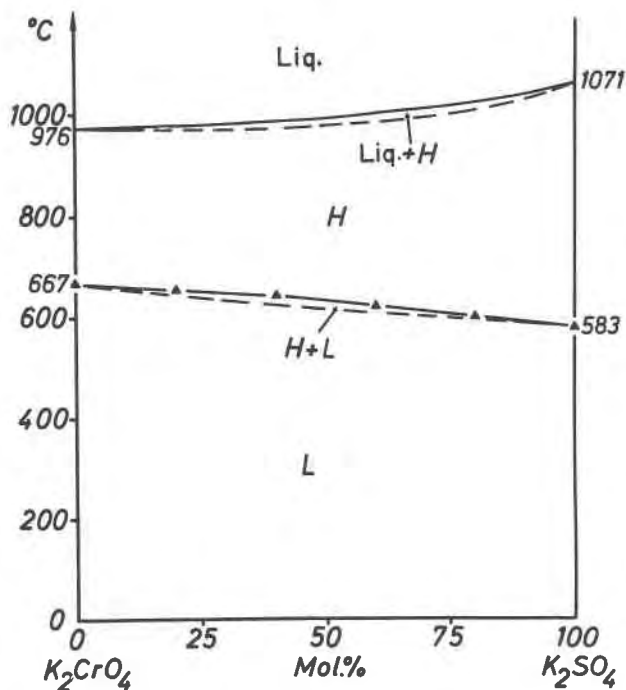


FIG. 7. Phase diagram of the system  $\text{K}_2\text{CrO}_4\text{-K}_2\text{SO}_4$ . Triangles = DTA results.

definitely observed in the high temperature powder patterns.<sup>4</sup> 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  $\alpha\text{-Ca}_2\text{SiO}_4$ , 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  $P3m1$ . The main difference between the structures is that in the proposed high- $\text{K}_2\text{SO}_4$  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

<sup>4</sup>It should be mentioned that in the system  $\text{Ca}_2\text{SiO}_4\text{-Ba}_2\text{SiO}_4$  two phases isostructural with glaserite and high- $\text{K}_2\text{SO}_4$ , respectively, have been found, also clearly showing the different extinctions (Eysel, 1971).

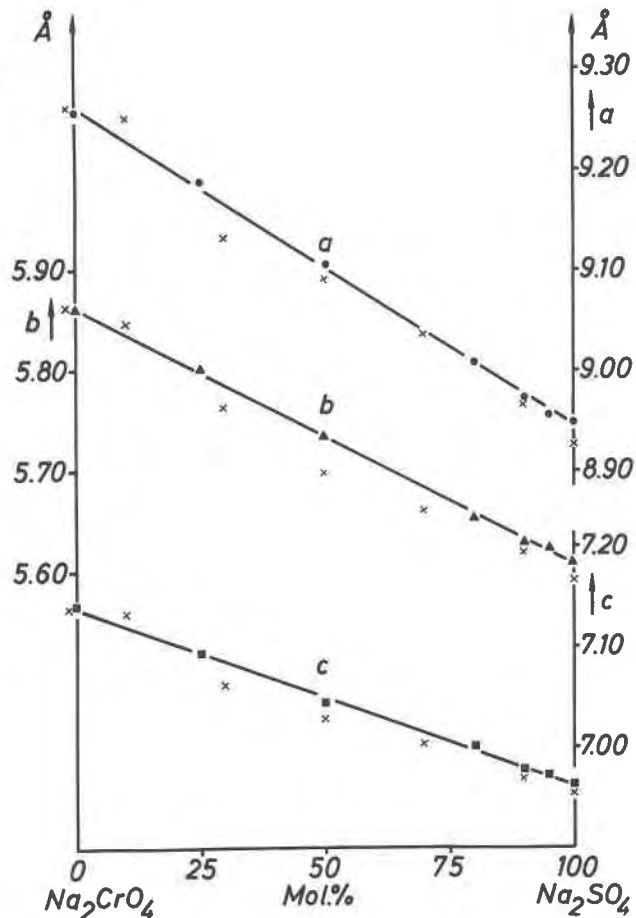


FIG. 8. Lattice parameters of quenched solid solutions in the system  $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ . Crosses = results of Fischmeister (1954).

by Gossner (1928) and confirmed later by Bellanca (1943) and Pontonnier *et al* (1972), was first suggested to be isostructural with high- $\text{K}_2\text{SO}_4$  by Bredig (1942). Later Bredig (1943) postulated rotating  $\text{SO}_4$  groups for the high- $\text{K}_2\text{SO}_4$  structure, but Fischmeister (1962) demonstrated for the isostructural  $\text{Na}_2\text{SO}_4(\text{I})$  that there is not enough space for rotation.<sup>5</sup> 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  $\text{A}_2\text{BX}_4$  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- $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4(\text{I})$ . In ad-

<sup>5</sup>The rotation was reconsidered for  $\text{K}_2\text{SO}_4$  by Watanabe *et al* (1972).

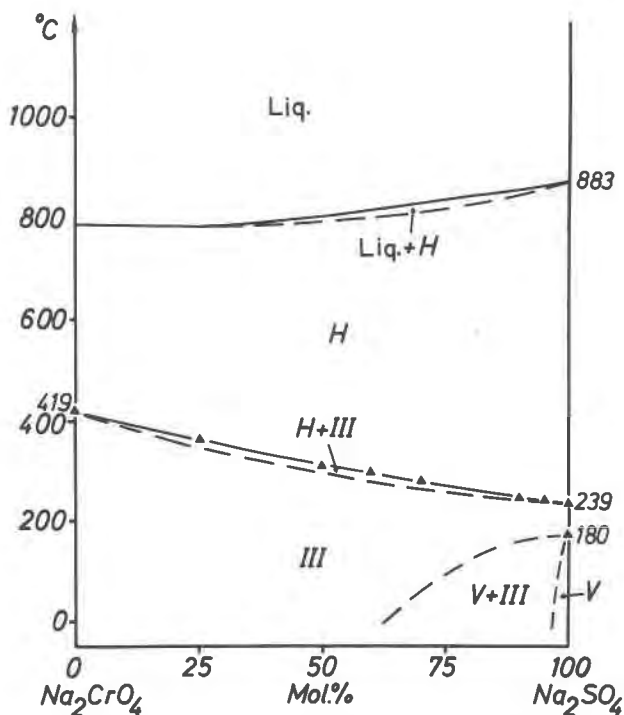


FIG. 9. Phase diagram of the system  $\text{Na}_2\text{CrO}_4$ - $\text{Na}_2\text{SO}_4$ . Triangles = DTA-results.

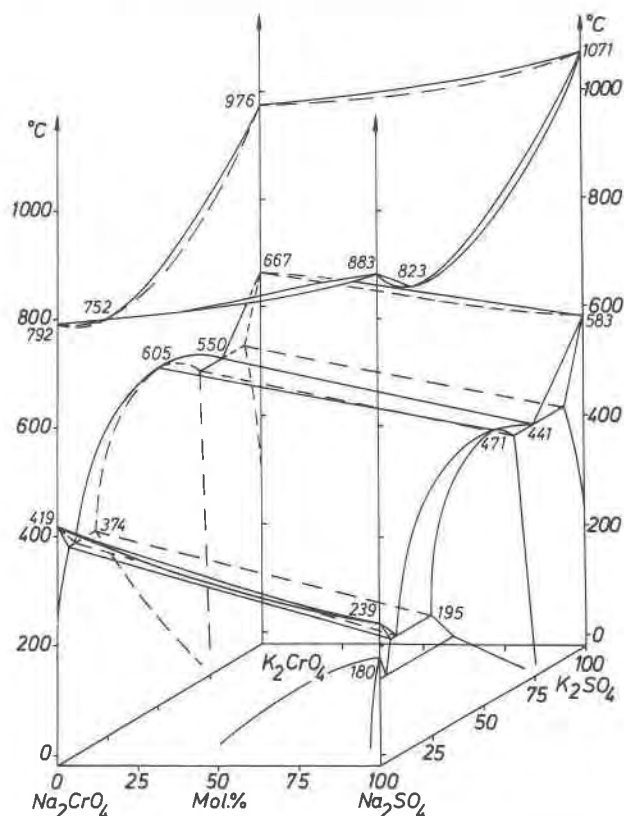


FIG. 10. The reciprocal salt pair  $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{K}_2\text{CrO}_4$ - $\text{Na}_2\text{CrO}_4$ . Liquid surface after Flach (1912).

TABLE 4. High-temperature Powder Data of  $\text{Na}_2\text{SO}_4$  (I) and High- $\text{K}_2\text{SO}_4$

hk1 <sup>+</sup>	$\text{Na}_2\text{SO}_4$ (I) <sup>++</sup> , 270°C			High- $\text{K}_2\text{SO}_4$ <sup>++</sup> , 620°C		
	I	d <sub>obs.</sub>	d <sub>calc.</sub>	I	d <sub>obs.</sub>	d <sub>calc.</sub>
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	-	-	-

<sup>+</sup> based on hexagonal cell.

<sup>++</sup> 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- $\text{K}_2\text{SO}_4$  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  $\text{Na}_2\text{SO}_4$ (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  $\text{Na}_2\text{SO}_4$ (I) and only a slight deviation from

TABLE 5. Powder Data for the Solid Solution  $(\text{Na}_{0.5}\text{K}_{0.5})_2\text{SO}_4$  at Different Temperatures

hkl <sup>+</sup>	Glaserite structure <sup>++</sup> , 20°C			Glaserite structure <sup>++</sup> , 440°C			High-K <sub>2</sub> SO <sub>4</sub> type <sup>++</sup> , 500°C		
	I	d <sub>obs.</sub>	d <sub>calc.</sub>	I	d <sub>obs.</sub>	d <sub>calc.</sub>	I	d <sub>obs.</sub>	d <sub>calc.</sub>
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 <sup>+++</sup>	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 <sup>+++</sup>	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	-	-	1.862	-	-	-
113 <sup>+++</sup>	2	1.8198	1.8202	5	1.864	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	-	-	-	-	-	-

<sup>+</sup> Based on trigonal and hexagonal cells.

<sup>++</sup> Lattice parameters and space groups are given in Table 2.

<sup>+++</sup> Reflexions hkl with  $l \neq 2n$ , indicating the difference between both structure types.

TABLE 6. Some Compounds with High-K<sub>2</sub>SO<sub>4</sub> Type Polymorphs<sup>+</sup>

Compound	°C	Orthohexagonal cells			References
		a(Å)	b(Å)	c(Å)	
Na <sub>2</sub> SeO <sub>4</sub> (I)	20	9.507	5.489	7.217	Mehrotra 1971 <sup>++</sup>
α-Na <sub>2</sub> BeF <sub>4</sub>	450	9.13	5.27	6.96	Hahn 1953
High-Rb <sub>2</sub> SO <sub>4</sub>	660	10.616	6.129	8.421	Tabrizi et al. 1970
High-Tl <sub>2</sub> SO <sub>4</sub>	514	10.663	6.156	8.28	Majumdar et al. 1965
High-K <sub>2</sub> MoO <sub>4</sub>	480	10.966	6.331	8.07	V.d.Akker et al. 1970
High-Rb <sub>2</sub> WO <sub>4</sub>	495	11.376	6.568	8.411	V.d.Akker et al. 1970
High-CaNaVO <sub>4</sub>	820	9.648	5.57	7.33	Klement et al. 1961
α-Ca <sub>2</sub> SiO <sub>4</sub>	1500	9.572	5.526	7.307	Regourd et al. 1968
α-Ca <sub>2</sub> (Si <sub>0.5</sub> Ge <sub>0.5</sub> )O <sub>4</sub>	20	9.436	5.448	7.096	Eysel et al. 1970
α-Ca <sub>2</sub> GeO <sub>4</sub> (+B <sub>2</sub> O <sub>3</sub> )	20	9.556	5.517	7.164	Eysel et al. 1970
α-(Ca <sub>0.7</sub> Ba <sub>0.3</sub> )SiO <sub>4</sub>	20	9.660	5.577	7.136	Eysel 1971
41.5 wt.% Ca <sub>2</sub> SiO <sub>4</sub> + 58.5 wt.% Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	20	18.646 (=2x9.322)	10.765 (=2x5.382)	21.73 (=3x7.24)	Saalfeld 1971

<sup>+</sup> For further examples c.f. Table 2.

<sup>++</sup> B.N.Mehrotra, private communication.



TABLE 7. Solid Solutions with Glaserite Structure<sup>+</sup>, 20°C

Solid solution	Space group	Pseudo-hexagonal axes			$\beta$	a/b	References
		a(Å)	b(Å)	c(Å)			
Na(K,NH <sub>4</sub> ) <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub>	P3m1	9.84	5.68	7.35		$\sqrt{3}=1.732$	Fronde! (1950)
(Na,Tl) <sub>2</sub> SO <sub>4</sub>		9.84	5.68	7.35			Larsson (1971) <sup>++</sup>
(Na <sub>0.25</sub> K <sub>0.75</sub> ) <sub>2</sub> BeF <sub>4</sub>		9.682	5.590	7.159			Pontonnier et al. (1972)
(Na <sub>0.3</sub> Rb <sub>0.7</sub> ) <sub>2</sub> BeF <sub>4</sub>		9.982	5.763	7.512			Pontonnier et al. (1972)
(Na <sub>0.38</sub> Rb <sub>0.62</sub> ) <sub>2</sub> BeF <sub>4</sub>		9.94	5.74	7.49			Grebenschikov et al. (1970)
(Na <sub>0.25</sub> (NH <sub>4</sub> ) <sub>0.75</sub> ) <sub>2</sub> BeF <sub>4</sub>		10.099	5.831	5.664			Pontonnier et al. (1972)
(Na <sub>0.25</sub> Tl <sub>0.75</sub> ) <sub>2</sub> BeF <sub>4</sub>		9.969	5.756	7.550			Pontonnier et al. (1972)
(Ca <sub>0.40</sub> Ba <sub>0.60</sub> ) <sub>2</sub> SiO <sub>4</sub>		9.925	5.730	7.283			Eysel (1971)
(Ca <sub>0.38</sub> Ba <sub>0.62</sub> ) <sub>2</sub> GeO <sub>4</sub>		10.141	5.855	7.37			Grebenschikov et al. (1970)
(Ca <sub>0.35</sub> Ba <sub>0.65</sub> ) <sub>2</sub> SiO <sub>4</sub>	P3c1 <sup>+++</sup>	9.949	5.744	14.641 (=2×7.321)		$\sqrt{3}=1.732$	Eysel (1971)
(Ca <sub>0.30</sub> Ba <sub>0.70</sub> ) <sub>2</sub> SiO <sub>4</sub>	C2/c <sup>+++</sup>	9.975	5.760	14.714 (=2×7.357)	89.67 <sup>o</sup>	1.732	Eysel (1971)
MgCa <sub>3</sub> (SiO <sub>4</sub> ) <sub>2</sub> (Merwinite)	P2 <sub>1</sub> /c	9.328	5.293	13.254 (=2×6.627)	91.90 <sup>o</sup>	1.762	Moore et al. (1972)

<sup>+</sup> For further examples c.f. Table 2.

<sup>++</sup> L.O.Larsson, private communication.

<sup>+++</sup> From powder patterns and subgroup relations.

the hexagonal axial ratio  $a/b = \sqrt{3}$  has been found. The lattice parameters of pure Na<sub>2</sub>SO<sub>4</sub>(II) in Table 2 were derived by extrapolation from the solid solution.

With the exception of Na<sub>2</sub>SO<sub>4</sub>(V) all crystal structures of the Na<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>CrO<sub>4</sub>-Na<sub>2</sub>CrO<sub>4</sub> 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 apthitalite) has been considered in the literature to be either a stoichiometric compound NaK<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub> forming a solid solution with Na<sub>2</sub>SO<sub>4</sub> or a compound NaKSO<sub>4</sub> forming solid solutions with Na<sub>2</sub>SO<sub>4</sub> as well as with K<sub>2</sub>SO<sub>4</sub>. The same assumptions have been applied to chrome-glaserite. The phase diagram in Figure 3 indicates that at high temperatures the composition NaK<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub> 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<sub>0.45</sub>K<sub>0.55</sub>)<sub>2</sub>SO<sub>4</sub> and not at NaKSO<sub>4</sub>. This implies a melting interval and not a melting point for the composition NaKSO<sub>4</sub>. 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)<sub>2</sub>SiO<sub>4</sub> in the system Ca<sub>2</sub>SiO<sub>4</sub>-Ba<sub>2</sub>SiO<sub>4</sub> with the maximum in the melting curve at (Ca<sub>0.40</sub>Ba<sub>0.60</sub>)<sub>2</sub>SiO<sub>4</sub>. In the system Na<sub>2</sub>BeF<sub>4</sub>-Rb<sub>2</sub>BeF<sub>4</sub> glaserite type solid solutions extend from (Na<sub>0.5</sub>

TABLE 8. Powder Data for (Na<sub>0.68</sub>K<sub>0.07</sub>)<sub>2</sub>SO<sub>4</sub>(II) at 140°C<sup>+</sup>

hkl	I	d <sub>obs.</sub>	d <sub>calc.</sub>	hkl	I	d <sub>obs.</sub>	d <sub>calc.</sub>
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			1.6031
212	12	2.5162	2.5156	512	10	1.6024	1.6026
400	25	2.3812	2.3824	600	20	1.5885	1.5883
220	5	2.3339	2.3339	520	5	1.5520	1.5524
401	10	2.2586	2.2586	314	15	1.4895	1.4901
221	12	2.2160	2.2175	024	10	1.4807	1.4809
				602	3	1.4497	1.4503

<sup>+</sup> Based on cell parameters in Table 2.

TABLE 9. Transition Enthalpies  $\Delta H$  in the System  $\text{Na}_2\text{SO}_4\text{--Na}_2\text{CrO}_4\text{--K}_2\text{CrO}_4\text{--K}_2\text{SO}_4$ <sup>+</sup>

Composition	Transition	$^{\circ}\text{C}$	$\Delta H$ kcal/Mol.	References
$\text{Na}_2\text{SO}_4$	$\text{V} \rightarrow \text{I}$ , $\text{Fddd} \rightarrow \text{P6}_3\text{mc}$	240-260	2.59	Eysel 1972
	$\text{V} \leftrightarrow \text{III}$ , $\text{Fddd} \leftrightarrow \text{Ccm}$	$\sim 180$	1.01	Eysel 1972
	$\text{III} \rightarrow \text{I}$ , $\text{Ccm} \rightarrow \text{P6}_3\text{mc}$	240	1.58	Eysel 1972
	$\text{I} \leftrightarrow \text{II}$ , $\text{P6}_3\text{mc} \leftrightarrow \text{Pnam}$	230	1.08	Eysel 1972
	$\text{II} \rightarrow \text{III}$ , $\text{Pnam} \rightarrow \text{Ccm}$	220	0.54	Eysel 1972
$\text{Na}_2\text{CrO}_4$	low $\leftrightarrow$ high, $\text{Ccm} \leftrightarrow \text{P6}_3\text{mc}$	419	2.12	Goldberg et al. <sup>++</sup>
Glaserite, $(\text{Na}_{0.45}\text{K}_{0.55})_2\text{SO}_4$	low $\leftrightarrow$ high, $\text{P}\bar{3}\text{m1} \leftrightarrow \text{P6}_3\text{mc}$	471	1.12	Eysel 1972
Chrome-glaserite, $(\text{Na}_{0.45}\text{K}_{0.55})_2\text{CrO}_4$	low $\leftrightarrow$ high, $\text{P}\bar{3}\text{m1} \leftrightarrow \text{P6}_3\text{mc}$	605	1.50	Goldberg et al. <sup>++</sup>
$\text{K}_2\text{SO}_4$	low $\leftrightarrow$ high, $\text{Pcmn} \leftrightarrow \text{P6}_3\text{mc}$	583	$\sim 1.8$	Eysel 1972
$\text{K}_2\text{CrO}_4$	low $\leftrightarrow$ high, $\text{Pcmn} \leftrightarrow \text{P6}_3\text{mc}$	667	2.437	D'ans Lax 1967

<sup>+</sup> The results of other authors on  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  are summarized by Eysel (1972).

<sup>++</sup> Goldberg, Eysel, Hahn (in preparation).

$\text{Rb}_{0.5})_2\text{BeF}_4$  to  $(\text{Na}_{0.3}\text{Rb}_{0.7})\text{BeF}_4$  (Pontonnier *et al*, 1972).

From a structural point of view, Hilmy (1953), Dickens and Brown (1971) and Moore *et al* (1972, 1973)<sup>6</sup> have pointed out that the cations occupy three different sites. The octahedral site in 001/2 (*1b*,  $\bar{3}m$ , one quarter of the cations) should be occupied by the smaller cation.<sup>7</sup> The site of the trigonal axes ( $1/3\ 2/3z$ , *2d*,  $3m$ ; one half of the cations, 10-coordinated) and the position in 000 with coordination number  $6 + 6$  (*1a*,  $\bar{3}m$ , 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  $(\text{Na}_{0.25}\text{K}_{0.75})_2\text{SO}_4$  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  $\text{NaK}_3(\text{SO}_4)_2$  compound with an ordered distribution of Na (in position *1b*) and K (in *1a* and in *2d*).

With increasing temperature, however, Na is increasingly capable of occupying also the *1a*- and the *2d*-positions, resulting in an extensive enlargement of the field of solid solution towards  $\text{Na}_2\text{SO}_4$  (Fig. 3) and  $\text{Na}_2\text{CrO}_4$  (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.<sup>8</sup> 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  $(A, C)_2\text{BX}_4$  solid solutions with cations *A* = Na, Ag<sup>+</sup>, Mg, Ca, Cd; cations *C* = K, Rb, Cs, Tl<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Sr, Ba, Eu<sup>2+</sup> and with tetrahedral complexes  $\text{BX}_4 = \text{BeF}_4, \text{SO}_4, \text{SeO}_4, \text{CrO}_4, \text{MoO}_4, \text{WO}_4, \text{PO}_4, \text{VO}_4, \text{AsO}_4, \text{SiO}_4, \text{GeO}_4$ , etc. It should be mentioned that merwinite,  $\text{MgCa}_3(\text{SiO}_4)_2$ , 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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<sup>6</sup> A very interesting geometrical interpretation of the glaserite type and related structures is given by Moore (1973).

<sup>7</sup> For a more detailed description of the structure, cf Eysel *et al* (1970).

<sup>8</sup> 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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