

STRUCTURAL CRYSTALLOGRAPHIC RELATION  
BETWEEN SODIUM SULFATE AND POTASSIUM  
SULFATE AND SOME OTHER SYNTHETIC  
SULFATE MINERALS\*†

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ABSTRACT

A study of the structural crystallographic relations between the following sulfate compounds has been made using  $x$ -ray methods as the main tool:  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4\text{-Li}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4\text{-Li}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4\text{-(NH}_4)_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4\text{-(NH}_4)_2\text{SO}_4$ .

Aphthitalite, a sodium potassium sulfate mineral, has been prepared in the laboratory from aqueous solutions as well as from fused melts of various sodium and potassium sulfate proportions.  $X$ -ray methods reveal that at high temperatures close to fusion, sodium sulfate and potassium sulfate are isomorphous and form a complete series of solid solutions. The same synthetic mineral, prepared from aqueous solutions, has been found by  $x$ -ray investigation and checked by chemical analysis to have a limited range of solid solution varying between the ratios of 1K:1Na to 5K:1Na when crystallized at 70° C. and limited to the almost invariable ratio of 3K:1Na at room temperature.

$X$ -ray powder data are given for  $\text{LiKSO}_4$  and  $\text{LiNaSO}_4$ , and also for the  $\text{NH}_4\text{KSO}_4$  member of the continuous series of crystalline solid solution  $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4$ . It is shown by the  $x$ -ray powder method that complete immiscibility exists between  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  at 70° C.

For  $\text{LiNaSO}_4$   $c_0=9.76 \text{ \AA} \pm 0.02$ ,  $a_0=7.64 \text{ \AA} \pm 0.02$ , space group  $P31c$ ,  $Z=6$ ,  $g.$  (determined) = 2.515,  $g.$  (calc.) = 2.527; basal twinning with 0001 as twinning plane is common.

INTRODUCTION

The study of the structural relation between sodium sulfate and potassium sulfate is of particular interest in the field of crystallography because of the fact that each compound occurs in more than one crystallographic modification (polymorph) and that there has been some controversy as to whether there exists a solid solution relationship or isomorphism, or both, between certain polymorphs of the two compounds. The existence of such solid solution or isomorphism, if any, is of special interest in structural crystallography because of the big difference in ionic radii between sodium (0.98 Å) and potassium (1.33 Å), which is equal to 0.35 Å or 35.7% of the smaller ion (sodium). Sodium and potassium are not generally grouped together in isomorphous series. Potassium is usually grouped with rubidium and cesium but not with sodium. Tutton (1922) in working out the isomorphous relationship between the alkali sulfates excluded sodium sulfate from his series.

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Aphthitalite (or glaserite) has for a long time been assigned the composition  $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$  or  $\text{K}_3\text{Na}(\text{SO}_4)_2$ . It has been shown by a number of investigators, Bücking (1889; Douglashall region in Germany), Teeple (1921; Searles Lake, California), Kurnakov, *et al.* (1936; Ural-Emba District, Russia), and Kurnakov, *et al.* (1938; Permian Sea and the salt lakes of Western Kazakhstan, Russia), to be widespread in saline deposits of lake basins. The mineral occurs also around volcanoes, e.g. Vesuvius, Scacchi (1875) and Bellanca (1942). Common among all these investigators, with the exception of Bellanca (1942), is the invariable composition  $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$  which they assigned to the mineral aphthitalite.

The composition and structure of aphthitalite have been the subject matter of argument and discussion since 1891. The problem is: Is there any crystallographic relation between sodium sulfate and potassium sulfate? Retgers (1891) stated that there is no isomorphism between sodium sulfate and potassium sulfate. He considered aphthitalite as a double salt of the composition  $3\text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ . Van't Hoff (1903), on the other hand, regarded aphthitalite as an isomorphous compound of the not closely investigated hexagonal modifications of both components. Gossner (1904) considered aphthitalite as a binary compound of a constant chemical composition,  $\text{NaK}_3(\text{SO}_4)_2$ . Van't Hoff and Barschall (1906) pointed to the existence of a series of solid solutions including the composition  $\text{NaK}_3(\text{SO}_4)_2$ . Druzhinin (1938), investigating the system  $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{H}_2\text{O}$  at the temperature of  $25^\circ \text{C}$ ., considered aphthitalite as a solid solution of the definite chemical compound  $\text{K}_3\text{Na}(\text{SO}_4)_2$  with  $\text{Na}_2\text{SO}_4$  and reported that the compound permits substitution of Na for K within the range  $\text{K}/\text{Na} = 2.44$  to  $3.00$ . Perrier and Bellanca (1940) and Bellanca (1942) using both thermal analysis technique and *x*-ray powder photographs believe that the compound is not  $\text{K}_3\text{Na}(\text{SO}_4)_2$  but rather  $\text{KNaSO}_4$ . This forms solid solutions with  $\text{K}_2\text{SO}_4$  (up to 73 mol per cent total content of the latter) and with  $\text{Na}_2\text{SO}_4$  (up to 75 mol per cent). Bredig (1942) states that aphthitalite should be considered simply as a solid solution of the high temperature forms of both potassium sulfate and sodium sulfate. Frondel (1950) gives the formula for aphthitalite as  $(\text{KNa})_3\text{Na}(\text{SO}_4)_2$ . Winchell (1951) considers aphthitalite,  $\text{NaK}_3(\text{SO}_4)_2$ , as "a double salt—not a crystal solution." He mentions that the Na:K ratio seems to vary from about 1:4 to about 1:1.

Sodium sulfate exists in five polymorphous modifications: I, (II), III, (IV), and V. Using the *x*-ray powder method, Kracek and Ksanda (1930) showed that  $\text{Na}_2\text{SO}_4$  I is stable above  $240^\circ \text{C}$ .,  $\text{Na}_2\text{SO}_4$  III is metastable below  $185^\circ \text{C}$ . but inert when dry at ordinary temperatures, and  $\text{Na}_2\text{SO}_4$  V is stable at ordinary temperatures. Polymorphs II and IV are unstable at ordinary pressure.  $\text{Na}_2\text{SO}_4$  V is equivalent to the natu-

rally occurring mineral thenardite, a rare salt lake deposit and also found near some volcanoes.

Potassium sulfate exists in two polymorphous modifications, namely: (1) a high-temperature modification, called alpha-K<sub>2</sub>SO<sub>4</sub>, stable above 590° C. and is uniaxial negative, and (2) a low-temperature modification called beta-K<sub>2</sub>SO<sub>4</sub>, stable at room temperature, orthorhombic, with the space group *Pmcn*. Arcanite is the name of the mineral having the composition K<sub>2</sub>SO<sub>4</sub> (equivalent to beta-K<sub>2</sub>SO<sub>4</sub>) and is said to be of very rare occurrence (Fron del, 1950).

Table 1 is a summary of the crystallographic data of the various sulfates mentioned above.

TABLE 1

| Substance  | System | Space Group                   | $a_0$ | $b_0$ | $c_0$ | Z | Ref. |
|--|--------|-------------------------------|-------|-------|-------|---|------|
| Na <sub>2</sub> SO <sub>4</sub>                  |        |                               |       |       |       |   |      |
| I  | Hex.   |                               | 5.39  |       | 7.25  | 2 | 1    |
| III  | Orth.  | <i>Pbnn</i>                   | 5.59  | 8.93  | 6.98  | 4 | 2    |
| V  | Orth.  | <i>Fddd</i>                   | 5.85  | 12.29 | 9.75  | 8 | 3    |
| K <sub>2</sub> SO <sub>4</sub>                   |        |                               |       |       |       |   |      |
| $\alpha$   | Hex.   |                               | 5.71  |       | 7.85  | 2 | 4    |
| $\beta$  | Orth.  | <i>Pmcn</i>                   | 5.77  | 10.06 | 7.52  | 4 | 5    |
| NaK <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> | Hex.   | <i>P<math>\bar{3}m</math></i> | 5.65  |       | 7.33  | 1 | 6    |
| Aphthitalite                                     |        |                               |       |       |       |   |      |
| NaKSO <sub>4</sub>                               | Hex.   | <i>P<math>\bar{3}m</math></i> | 5.643 |       | 7.259 | 2 | 7    |

1. Calculated from data of Kracek and Ksanda (1930).
2. Frevel (1940).
3. Zachariassen and Ziegler (1932).
4. Bredig (1942).
5. Strukturbericht (1937).
6. Gossner (1928).
7. Bellanca (1942).

#### THE RELATION BETWEEN SODIUM SULFATE AND POTASSIUM SULFATE

##### *The System Na<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub> (Fused samples)*

Samples were prepared by fusing mixtures of Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> ranging in molecular ratios from 4:1 to 1:4. These gave very similar powder photographs, and it seems apparent that when crystallizing from a melt, there is a continuous solid solution between the hexagonal forms of Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>. The pure end members always invert to a lower

symmetry modification upon cooling. On the other hand, there is a range of compositions between the end members in which the hexagonal form of the solid solution is stable. On either side of this stable range, as the end member is approached, the originally formed solid solution unmixes, yielding the pure end member, which inverts on cooling, and a stable solid solution phase containing a lower percentage of the end member than was present in the melt.

The limits of this range in which the solid solution is stable are difficult to determine in samples prepared from melts. The material is so fine grained, and the variation in refractive indices so slight, that optical differentiation of a pure end member and a solid solution close to that end member is impractical. The x-ray powder photographs of samples approaching the end members in composition show increasing evidence of a phase consisting of the inverted end member. But in the range of 3:1 to 1:3, or even 4:1 to 1:4, this unmixing and inversion is negligible. This difficulty in establishing definite limits for the stable range in material prepared by fusion is not encountered when using single crystals prepared from solution. These are discussed later.

The lattice constants,  $a_0$  and  $c_0$ , for some members of this high-temperature solid solution series of apthitalite, have been determined from the corresponding powder photographs. These are given, together with the published data on  $\text{Na}_2\text{SO}_4$  I (calculated from data of Kracek and Ksanda, 1930) and  $\alpha\text{-K}_2\text{SO}_4$  (Bredig, 1942), in Table 2. This table shows clearly the increase in the unit cell dimensions as the result of the substitution of potassium for sodium.

TABLE 2

|       | $\text{Na}_2\text{SO}_4$ I | $\text{Na}_4\text{K}$ | $\text{Na}_3\text{K}$ | $\text{NaK}$ | $\text{NaK}_3$ | $\text{NaK}_4$ | $\alpha\text{-K}_2\text{SO}_4$ |
|-------|----------------------------|-----------------------|-----------------------|--------------|----------------|----------------|--------------------------------|
| $a_0$ | 5.39                       | 5.49                  | 5.50                  | 5.64         | 5.66           | 5.67           | 5.710                          |
| $c_0$ | 7.25                       | 7.26                  | 7.265                 | 7.27         | 7.33           | 7.39           | 7.85                           |

Thin sections and crushed fragments showed apthitalite to be uniaxial positive. The values of  $\omega$  and  $\epsilon$  increase with higher content of potassium. They range from 1.485 to 1.493 for  $\omega$ , and from 1.492 to 1.500 for  $\epsilon$  (Na light; values  $\pm 0.002$ ). Winchell (1951) gives the range for  $\omega$  as 1.487 to 1.491, and for  $\epsilon$  1.492 to 1.499, in good agreement with the values found for the synthetic material. The general trend of increase of indices is shown graphically in Fig. 1.

Using the pycnometer method a general increase in the specific gravity was found in going from the high-sodium members to the high-potassium members. The determined specific gravity values range from 2.68 (for

$\text{Na}_4\text{K}$ ) to 2.71 (for  $\text{NaK}_4$ ) with an experimental error of  $\pm 0.01$ . Winchell (1951) gives the specific gravity of 2.7 for apthitalite of the composition  $\text{NaK}_3(\text{SO}_4)_2$ . Gossner (1928) gave the value of 2.697 for the same composition. The specific gravity of apthitalite from Vesuvius was reported by Bellanca (1943) to be 2.697. The determined specific gravities were found to be in general agreement with those calculated according to the increasing lattice constants given in Table 2.

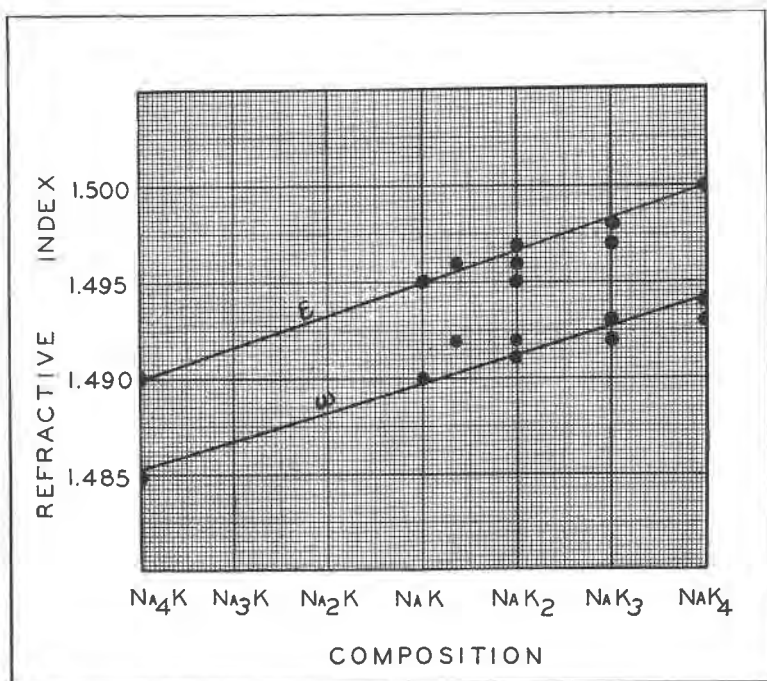


FIG. 1

*The System  $\text{Na}_2\text{SO}_4\text{—K}_2\text{SO}_4\text{—H}_2\text{O}$  (Aqueous solutions)*

X-ray powder photographs of crystals grown from aqueous solutions of various molecular ratios of sodium sulfate and potassium sulfate proved to be similar to those taken for the fused apthitalites. Also powder photographs of crystals obtained from aqueous solution and then fused were found to be similar to those of the unfused ones. This indicates that the crystals grown from aqueous solutions at the temperatures of  $70^\circ$ ,  $50^\circ$ ,  $35^\circ$  and  $20^\circ$  C. are anhydrous. Weissenberg photographs of these crystals showed the hexagonal symmetry and yielded the space group of  $P3m$ , in agreement with that given by Gossner (1928) and Bellanca (1943). The powder photographs of the various crystals, formed at the

same temperature but grown from solutions of different composition show either the apthitalite type of pattern or that of the end members,  $\text{Na}_2\text{SO}_4$  V or  $\beta\text{-K}_2\text{SO}_4$ . It is quite apparent that the crystals do not have the same chemical composition as that of the solution from which they crystallize. Table 3 shows the results of the chemical analyses in terms

TABLE 3

| Composition of Solution  |                         | Temperature | K determined quantitatively | Type of $\alpha$ -ray powder pattern | Composition of Crystals Produced |                         |
|--------------------------|-------------------------|-------------|-----------------------------|--------------------------------------|----------------------------------|-------------------------|
| $\text{Na}_2\text{SO}_4$ | $\text{K}_2\text{SO}_4$ |             |                             |                                      | $\text{Na}_2\text{SO}_4$         | $\text{K}_2\text{SO}_4$ |
| %                        |                         |             | %                           |                                      | %                                |                         |
| 75.0                     | : 25.0                  | 70° C.      | —                           | $\text{Na}_2\text{SO}_4$ V           | 100.0                            | : —                     |
| 66.7                     | : 33.3                  | 70° C.      | 28.0                        | Apthit.                              | 42.0                             | : 58.0                  |
| 50.0                     | : 50.0                  | 70° C.      | 31.6                        | Apthit.                              | 33.0                             | : 67.0                  |
| 33.3                     | : 66.7                  | 70° C.      | 39.2                        | Apthit.                              | 12.9                             | : 87.1                  |
| 25.0                     | : 75.0                  | 70° C.      | 45.1                        | $\beta\text{-K}_2\text{SO}_4$        | —                                | : 100.0                 |
| 20.0                     | : 80.0                  | 70° C.      | 45.1                        | $\beta\text{-K}_2\text{SO}_4$        | —                                | : 100.0                 |
| 66.7                     | : 33.3                  | 50° C.      | 34.6                        | Apthit.                              | 26.0                             | : 74.0                  |
| 50.0                     | : 50.0                  | 50° C.      | 35.8                        | Apthit.                              | 23.0                             | : 77.0                  |
| 33.3                     | : 66.7                  | 50° C.      | 40.5                        | Apthit.                              | 12.0                             | : 88.0                  |
| 25.0                     | : 75.0                  | 50° C.      | 45.5                        | $\beta\text{-K}_2\text{SO}_4$        | —                                | : 100.0                 |
| 20.0                     | : 80.0                  | 50° C.      | 45.5                        | $\beta\text{-K}_2\text{SO}_4$        | —                                | : 100.0                 |
| 66.7                     | : 33.3                  | 35° C.      | 34.0                        | Apthit.                              | 27.0                             | : 73.0                  |
| 50.0                     | : 50.0                  | 35° C.      | 35.8                        | Apthit.                              | 23.0                             | : 77.0                  |
| 33.3                     | : 66.7                  | 35° C.      | 40.6                        | Mixture                              | 11.0                             | : 89.0                  |
| 25.0                     | : 75.0                  | 35° C.      | 45.0                        | $\beta\text{-K}_2\text{SO}_4$        | —                                | : 100.0                 |
| 20.0                     | : 80.0                  | 35° C.      | 45.0                        | $\beta\text{-K}_2\text{SO}_4$        | —                                | : 100.0                 |
| 66.7                     | : 33.3                  | 20° C.      | 35.6                        | Apthit.                              | 24.0                             | : 76.0                  |
| 50.0                     | : 50.0                  | 20° C.      | 36.4                        | Apthit.                              | 22.0                             | : 78.0                  |
| 33.3                     | : 66.7                  | 20° C.      | 45.5                        | $\beta\text{-K}_2\text{SO}_4$        | —                                | : 100.0                 |
| 25.0                     | : 75.0                  | 20° C.      | 45.5                        | $\beta\text{-K}_2\text{SO}_4$        | —                                | : 100.0                 |
| 20.0                     | : 80.0                  | 20° C.      | 45.5                        | $\beta\text{-K}_2\text{SO}_4$        | —                                | : 100.0                 |

of the percentage of potassium in each crystal and the corresponding composition of the crystal in terms of the molecular percentage of the two end members. The chemical analyses, made by the periodate method (Willard, Boyle 1941), are within the range of experimental error of  $\pm 1.0\%$ . The values in Table 3 were then used in the construction of Fig. 2 which shows the relationship between the composition of the crystals and that of the solutions from which they were grown at the various temperatures of 70°, 50°, 35°, and 20° C. The results of the chemical analyses are in agreement with those of  $\alpha$ -rays.

The range of the limited solid solution series of apthitalite, formed from the pure compounds dissolved in distilled water, is shown in Fig.

3, based on the results of both chemical analyses and powder photographs. It is interesting to note that the range of the solid solution decreases with decrease in temperature until it finally shrinks to a very small range at 20° C. At this temperature apththitalite acts like a compound of fixed composition, and explains why many previous investiga-

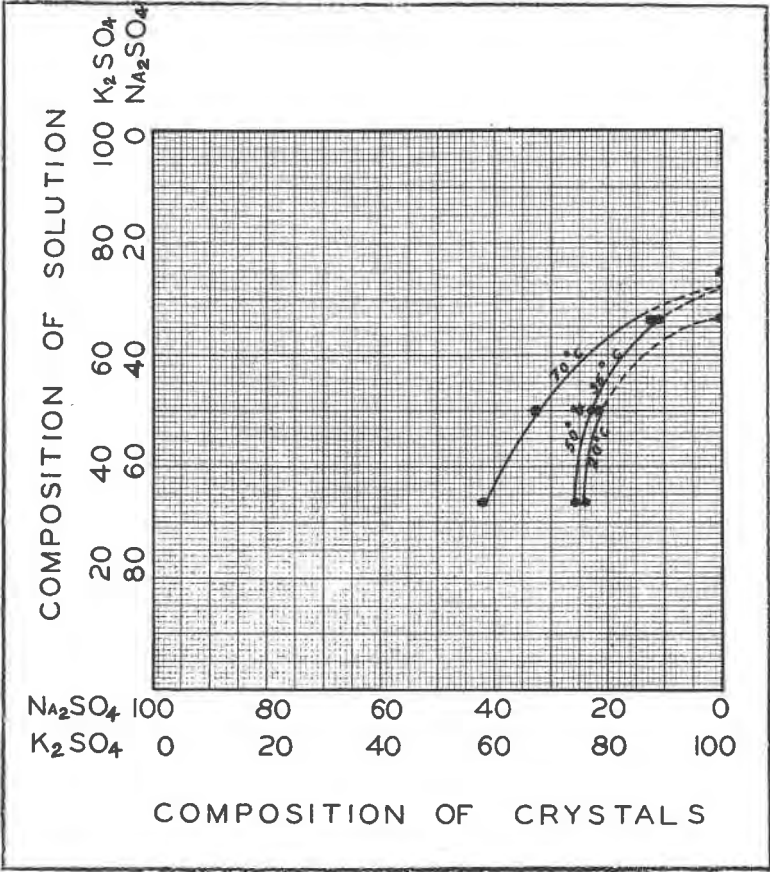


FIG. 2

tors had so regarded it. Perrier and Bellanca (1940) stated that apththitalites of volcanic origin occur in nature with the ratio of  $K_2SO_4$  to  $Na_2SO_4$  varying from 3:1 to 1:3. When formed from aqueous solutions, on the other hand (artificially or in salt deposits), it always shows the ratio approximately 3:1. This last statement seems to be true only at temperatures of 30° or lower.

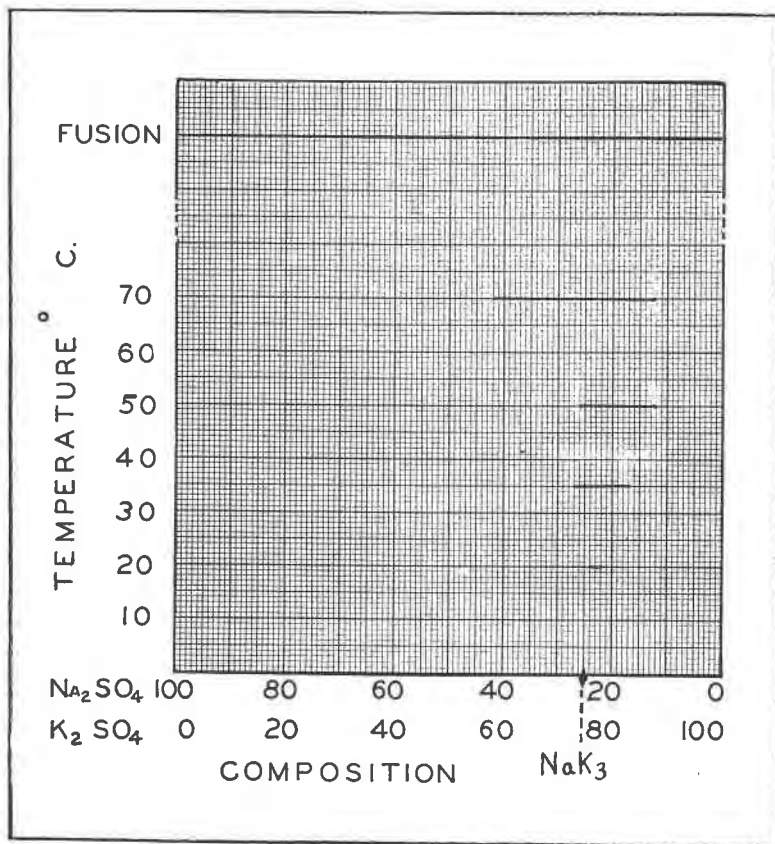


FIG. 3

*The Crystal Structure of the Isomorphous Series  $\text{Na}_2\text{SO}_4$  I, Aphthalite, and  $\beta\text{-K}_2\text{SO}_4$*

Gossner (1928) described a structure for  $\text{NaK}_3(\text{SO}_4)_2$ , and Bellanca (1943) reported a closely related structure for  $\text{NaKSO}_4$ . Bredig (1941) proposed a structure type  $\text{A}_2\text{XO}_4$ , with a hexagonal unit cell  $P\bar{3}m1$  and  $Z=2$ , for a series of compounds, principally at high temperatures. These included  $\text{CaSiO}_4$  and alkaline earth phosphates, as well as alkali sulfates. No atomic positions were suggested.

In the space group  $P\bar{3}m1$ , the positions of the 4 metal atoms are not all structurally equivalent. Two occur at  $\pm\frac{1}{3}\frac{2}{3}z$ ; one at 000 and one at  $00\frac{1}{2}$ . In these three types of positions the number and arrangement of the oxygen atoms surrounding the metal atoms are different. For the structures of  $\text{NaK}_3(\text{SO}_4)_2$  and  $\text{NaKSO}_4$ , as determined by Gossner and Bellanca,



respectively, the distances from the metal to oxygen vary considerably. In all cases they are greater than the sum of the commonly used values of the ionic radii, and for one position considerably greater. This could account for the unusually small changes in unit cell dimensions with marked changes in the relative proportions of Na and K, and also offers an explanation of why these two elements, which do not usually replace each other in solid solution series, do so in this case.

It would seem most probable that the replacement of Na by K is selective, rather than occurring randomly over the 2+1+1 metal positions. If, starting with a low K content, additional K ions can replace Na ions in positions where the Na to O distance is greater than necessary (in so far as required by Na radius+O radius), the impact on unit cell dimensions will not be appreciable until these positions are filled. This would explain the comparatively small changes in the values of  $a_o$  and  $c_o$  until outside the 4:1 and 1:4 range of Na and K. The comparatively large change in  $c_o$  at the K end of the series occurs when even the positions with least room, originally filled by Na, must now be occupied by K. The smaller change, chiefly in  $a_o$ , at the Na end of the series may be attributed to the fact that here the cell dimensions are chiefly controlled by the close packing of O atoms.

#### THE RELATION BETWEEN LITHIUM SULFATE AND POTASSIUM SULFATE

##### *The System $\text{Li}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ (Aqueous solutions)*

$\text{Li}_2\text{SO}_4$  is not known to occur as a natural mineral. It is monoclinic and may be prepared by fusion of the common reagent salt,  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , which is also monoclinic. The ionic radii of  $\text{Li}^+$  and  $\text{K}^+$  are 0.78 Å and 1.33 Å, respectively. The earliest investigation of the compound  $\text{LiKSO}_4$  goes back to Schabus (1855) who erroneously described it as an isomorphous mixture of  $\text{Li}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ . Later the substance was investigated by Rammelsberg (1866), Scacchi (1867), Wyruboff (1880, 1882 and 1890), Wulff (1890, 1893), and Traube (1892 and 1894). Their descriptions were concerned with the morphology of the crystals which were found to be hexagonal pyramidal, with  $a:c=1:1.6755$  (Traube, 1892).

During the crystallization of mixtures of lithium sulfate and potassium sulfate from aqueous solutions, the common reagent salt  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  was used. Two types of solutions were prepared, namely, neutral (i.e. the pure salts dissolved in distilled water) and acidic (i.e. a few drops of concentrated  $\text{H}_2\text{SO}_4$  were added to the solution in distilled water). Crystallization was made at room temperature and at 70° C. ( $\pm 3^\circ$ ). The compositions of the solutions were in the following molecular ratios

when calculated in terms of  $\text{Li}_2\text{SO}_4:\text{K}_2\text{SO}_4=4.30:1$ ,  $3.44:1$ ,  $2.58:1$ ,  $1.72:1$ ,  $0.86:1$ ,  $1:2.32$ , and  $1:3.48$ , respectively. Platy hexagonal crystals, with well developed basal pinacoids, were formed from most of the solutions. Laue photographs show hexagonal symmetry, and Weissenberg photographs yielded the space group  $P6_3$ , with  $a_0=5.13\text{\AA}$  and  $c_0=8.60$  ( $\pm 0.02\text{\AA}$ ), in agreement with the data of Bradley (1925) for  $\text{LiKSO}_4$ . Powder photographs of crystals grown from the various solutions at two different temperatures were made, with the results shown in Table 4.

TABLE 4

| Mol. ratio of<br>$\text{Li}_2\text{SO}_4:\text{K}_2\text{SO}_4$<br>in solution | Type of x-ray powder photographs of crystals formed               |   |                               |                               |
|--|---|---|-------------------------------|-------------------------------|
|  | at 70° C.   |   | at 20° C.                     |                               |
|  | From<br>Neut. sol.  | Acid sol.   | Neut. sol.                    | Acid sol.                     |
| 4.30:1.0   | $\text{LiKSO}_4$  | mixture of<br>$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$<br>and $\text{LiKSO}_4$ | $\text{LiKSO}_4$              | $\text{LiKSO}_4$              |
| 3.44:1.0   | $\text{LiKSO}_4$  | $\text{LiKSO}_4$  | $\text{LiKSO}_4$              | $\text{LiKSO}_4$              |
| 2.58:1.0   | $\text{LiKSO}_4$  | $\text{LiKSO}_4$  | $\text{LiKSO}_4$              | $\text{LiKSO}_4$              |
| 1.72:1.0   | $\text{LiKSO}_4$  | $\text{LiKSO}_4$  | $\text{LiKSO}_4$              | $\text{LiKSO}_4$              |
| 0.86:1.0   | $\text{LiKSO}_4$  | $\text{LiKSO}_4$  | $\beta\text{-K}_2\text{SO}_4$ | $\beta\text{-K}_2\text{SO}_4$ |
| 1.00:2.32  | mixture of<br>$\beta\text{-K}_2\text{SO}_4$ &<br>$\text{LiKSO}_4$ | $\text{LiKSO}_4$  | $\beta\text{-K}_2\text{SO}_4$ | $\beta\text{-K}_2\text{SO}_4$ |
| 1.00:3.48  | $\beta\text{-K}_2\text{SO}_4$                                     | $\beta\text{-K}_2\text{SO}_4$   | $\beta\text{-K}_2\text{SO}_4$ | $\beta\text{-K}_2\text{SO}_4$ |

The powder pattern data are given in Table 5, There is no change in the spacings of the lines on the films, indicating that the crystals represent a compound of fixed chemical composition, with no solid solution relationship. As an additional check, chemical analyses were made. These are shown in Table 6, and the results show clearly that the potassium content in crystals grown from different solutions is almost constant, and corresponds to the 1:1 ratio of K:Li.

#### *The System $\text{Li}_2\text{SO}_4\text{-K}_2\text{SO}_4$ (Fused samples)*

Powder photographs of samples prepared by fusing mixtures of  $\text{Li}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  in various proportions likewise indicate clearly that there is no solid solution relationship. Only one mixture of the approximate ratio of 1:1 gave rise to the  $\text{LiKSO}_4$  pattern alone. All other mixtures gave the  $\text{LiKSO}_4$  pattern together with that of either  $\text{Li}_2\text{SO}_4$  or  $\text{K}_2\text{SO}_4$ , depending upon the proportions of the mixture. Thus even at the higher

TABLE 5. POWDER PHOTOGRAPH DATA FOR  $\text{LiKSO}_4$ 

| $d$<br>observed | $d$<br>calc. | $hk \cdot l$ | $I$<br>observed |
|-----------------|--------------|--------------|-----------------|
| 4.33 Å          | 4.31 Å       | 00·2         | 1               |
| 4.00            | 3.96         | 10·1         | 10              |
| 3.12            | 3.10         | 10·2         | 9               |
| 2.58            | 2.57         | 11·0         | 7               |
| 2.47            | 2.47         | 11·1         | 2               |
| 2.22            | { 2.225      | { 20·0       | 5               |
|                 | { 2.21       | { 11·2       |                 |
| 2.16            | { 2.165      | { 20·1       | 5               |
|                 | { 2.155      | { 00·4       |                 |
| 1.985           | 1.98         | 20·2         | 1               |
| 1.66            | { 1.655      | { 21·1       | 3               |
|                 | { 1.650      | { 11·4       |                 |
| 1.61            | 1.61         | 10·5         | 1               |
| 1.58            | 1.57         | 21·2         | 3               |
| 1.50            | 1.49         | 30·0         | 3               |
| 1.37            | 1.36         | 20·5         | 2               |

TABLE 6

| Composition of<br>solution in terms<br>of mol. ratio<br>$\text{Li}_2\text{SO}_4:\text{K}_2\text{SO}_4$ | Percentage of K<br>in crystals | Theoretical<br>percentage of<br>K in $\text{LiKSO}_4$ | Type of powder<br>pattern |
|--|--------------------------------|---|---------------------------|
| 3.44:1   | 27.8                           | 27.5  | $\text{LiKSO}_4$          |
| 2.58:1   | 27.0                           | 27.5  | $\text{LiKSO}_4$          |
| 1.72:1   | 27.7                           | 27.5  | $\text{LiKSO}_4$          |
| 0.86:1   | 28.6                           | 27.5  | $\text{LiKSO}_4$          |
| 3.44:1*  | 28.0                           | 27.5  | $\text{LiKSO}_4$          |
| 2.58:1*  | 28.2                           | 27.5  | $\text{LiKSO}_4$          |

\* Crystallized from slightly acid solution.

temperature near fusion, the  $\text{LiKSO}_4$  structure does not permit substitution of either Li or K for the other, unless there was unmixing during cooling. The cooling was relatively rapid, and if there was any tendency for a solid solution to form, it is probable that it would have persisted as a metastable phase, especially close to the 1:1 ratio.

THE RELATION BETWEEN LITHIUM SULFATE AND SODIUM SULFATE  
*The System  $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  (Aqueous solutions)*

The earliest investigation of crystals of  $\text{LiNaSO}_4$  found reported is

that of Scacchi (1867), who determined the axial ratio for the ditrigonal pyramidal crystals to be  $a:c=1:0.5624$ . Traube (1892) reported the specific gravity of  $\text{LiNaSO}_4$  as 2.369. This last value was not confirmed in the present study. The crystals used by these early investigators were obtained from aqueous solutions at about  $50^\circ \text{C}$ ., and also from acid solutions, with or without the addition of  $\text{NaCl}$ .

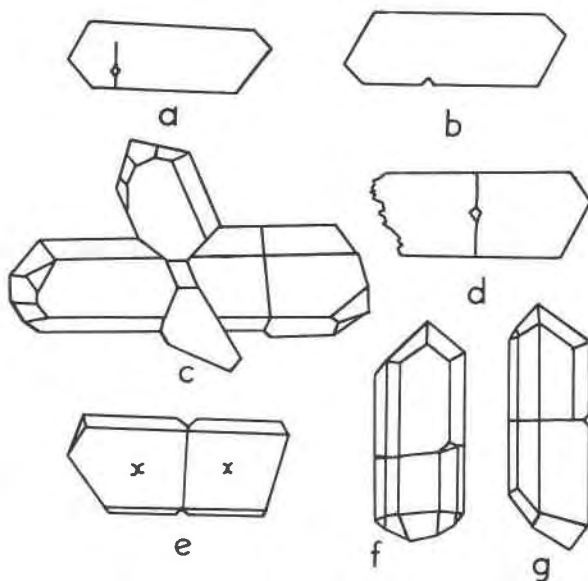


FIG. 4

Crystals were grown from solutions containing a wide range of ratios of  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ . Better crystals were obtained when a few drops of  $\text{H}_2\text{SO}_4$  were added to the solutions, and crystallization was carried out at about  $70^\circ \text{C}$ . Most of the crystals were elongated parallel to the  $c$  axis. A fairly common feature observed on these crystals is an equatorial marking around the prism zone. Figure 4 shows some free hand drawings of typical crystals as they appear under low magnification with the binoculars. In most cases the mark appears as an even straight line, which may completely surround the crystal (Fig. 4, *c*, *d*, *e*, *f* and *g*), or only partly surround it (Fig. 4*a*). Under higher magnification, this line shows as a series of tiny disconnected re-entrant angles. In many cases at the intersection of this line with an edge, there is a more prominent re-entrant angle (Fig. 4, *b*, *e* and *g*). On the two circle goniometer, the parts of a prism face on either side of the line either reflect light simultaneously, or else give signals separated by only a few minutes of arc. Usually the

prism faces continue uninterrupted on both sides of the line (Fig. 4, *d* and *e*), but in some cases the faces are interrupted, and different forms are shown on the two sides (Fig. 4, *c*, *f*, and *g*). Since the crystals of  $\text{LiNaSO}_4$  do not have a horizontal symmetry plane, it is believed that this line represents twinning on (0001).

No previous  $x$ -ray work has been reported on  $\text{LiNaSO}_4$ . Laue photographs at first glance appear to show a 6-fold axis of symmetry, but careful inspection reveals a few reflections which indicate the true symmetry to be 3-fold. (Laue symmetry  $\bar{3} 2/m$ ). This is verified by Weissenberg photographs. Lattice constants of the hexagonal unit cell ( $P$ ) were found to be  $a_0 = 7.64 \text{ \AA}$  and  $c_0 = 9.76 \text{ \AA}$  ( $\pm 0.02 \text{ \AA}$ ), giving an axial ratio of  $a:c = 1:1.277$ . The pyramidal faces gave poor reflections. Measurements on the two circle goniometer show two sets of pyramidal faces, separated by  $30^\circ$ , which in terms of the unit cell dimensions are  $10.2$  and  $11.4$ . If the latter were assumed to be the unit pyramid  $10.1$ , the derived axial ratio would be  $0.58$ , close to that given by Scacchi. The characteristic missing reflections on the Weissenberg photographs are  $hh2hl$  with  $l$  odd, indicating a  $c$  glide plane. In the Laue class  $\bar{3} 2/m$  the only possible space groups with a  $c$  glide are  $P\bar{3}1c$  and  $P31c$ . Since  $\text{LiNaSO}_4$  crystals are known to be pyroelectric (Traube, 1892), space group  $P\bar{3}1c$  is ruled out.

The specific gravity of the crystals was determined by diluting acetylene tetrabromide until they remained suspended in it. The specific gravity of the liquid was then found to be  $2.515$ , which is quite different from the value of  $2.369$  reported by Traube (1892). Because of this discrepancy, an approximate check was made with the Gladstone and Dale Law. Using the specific refractive energy values (Larsen and Berman, 1934) of  $\text{LiNaSO}_4$ , and the refractive indices, namely  $\epsilon = 1.495$  and  $\omega = 1.490$ , the specific gravity of this compound was determined to be  $2.54$ . Using the experimentally determined value of  $2.515$ , the number of formula weights of  $\text{NaLiSO}_4$  in the unit cell was found to be  $5.97 \cong 6$ .

Powder photograph data are given for  $\text{LiNaSO}_4$  in Table 7. No change in the spacings of the powder patterns of the various samples was found, indicating the absence of any solid solution relationship between  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ . Since these two compounds and the compound  $\text{LiNaSO}_4$  all crystallize in different systems, no extensive solid solution would be expected.

#### *The System $\text{Li}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ (Fused samples)*

X-ray powder photographs were made of samples prepared by fusing mixtures of varying proportions of  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ . Only one mixture of the approximate ratio  $1:1$  gave rise to a pattern consisting solely of

TABLE 7. POWDER PHOTOGRAPH DATA FOR  $\text{LiNaSO}_4$ 

| $d$<br>observed | $d$<br>calc. | $hk \cdot l$ | $I$<br>observed |
|-----------------|--------------|--------------|-----------------|
| 3.94 Å          | 3.95 Å       | 10·2         | 8               |
| 3.83            | 3.82         | 11·0         | 10              |
| 3.04            | 3.02         | 11·2         | 7               |
| 2.94            | 2.94         | 10·3         | 7               |
| 2.75            | 2.745        | 20·2         | 9               |
| 2.425           | { 2.445      | { 00·4       | 4               |
|                 | { 2.430      | { 12·1       |                 |
| 2.31            | 2.32         | 20·3         | 3               |
| 2.215           | { 2.23       | { 12·2       | 3               |
|                 | { 2.20       | { 30·0       |                 |
| 2.15            | 2.15         | 30·1         | 4               |
| 2.01            | 2.01         | 30·2         | 1               |
| 1.97            | 1.97         | 20·4         | 2               |
| 1.91            | 1.91         | 22·0         | 5               |
| 1.88            | 1.88         | 10·5         | 1               |
| 1.83            | { 1.83       | { 13·0       | 2               |
|                 | { 1.825      | { 30·3       |                 |
| 1.745           | 1.75         | 12·4         | 1               |
| 1.69            | 1.685        | 20·5         | 1               |
| 1.64            | { 1.65       | { 40·0       | 2               |
|                 | { 1.635      | { 40·1       |                 |
|                 | { 1.63       | { 00·6       |                 |
| 1.60            |              |              | 2               |
| 1.565           |              |              | 2               |
| 1.545           |              |              | 2               |
| 1.505           | 1.50         | 11·6         | 3               |
| 1.47            |              |              | 4               |
| 1.44            |              |              | 4               |

$\text{LiNaSO}_4$  lines. All other ratios gave the pattern of  $\text{LiNaSO}_4$  together with that of either  $\text{Li}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4$ , thus verifying the results obtained from the crystals. As was mentioned in the case of fused Li-K sulfate mixtures, there is the possibility of limited solid solution near the fusion temperature, with unmixing on cooling.

*The System  $(\text{NH}_4)_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$  (Aqueous solutions)*

Ammonium sulfate occurs in nature as the mineral mascagnite. Both mascagnite and arcanite ( $\beta\text{-K}_2\text{SO}_4$ ) are orthorhombic and have the space group  $Pm\bar{c}n$  (Winchell, 1951). Because of the isomorphism of the two compounds and the similarity of the ionic radii of  $\text{NH}_4$  and K (1.43 and 1.33Å, respectively) complete solid solution between the two would be expected. Such was reported by Fock (1892). *X*-ray evidence completely

substantiates this. Crystals formed from solutions of varying proportions do not have the same composition as the solution (Table 8), but are shown by both Weissenberg and powder photographs to be structurally alike, with gradual decrease in lattice constants with increasing potassium.

|                               | $a_0$  | $b_0$   | $c_0$  |
|-------------------------------|--------|---------|--------|
| $(\text{NH}_4)_2\text{SO}_4$  | 5.95 Å | 10.56 Å | 7.72 Å |
| $\text{NH}_4\text{KSO}_4$     | 5.84   | 10.08   | 7.52   |
| $\beta\text{-K}_2\text{SO}_4$ | 5.70   | 9.99    | 7.34   |

The measured spacings and intensities of the powder photograph lines of various  $\text{NH}_4\text{-K}$  sulfate solid solutions are in agreement with the published data for the mineral taylorite as given by Winchell and Benoit (1951).

The crystals obtained from the various solutions of mixtures of potassium and ammonium sulfates were chemically analyzed so as to determine potassium quantitatively. A known amount of the dry powdered material was ignited first to remove  $\text{NH}_3$  and the amount of potassium was then determined by the periodate method (Willard and Boyle, 1941). The results of the chemical analysis are given in Table 8. The table shows clearly how the composition of the crystals varies continuously with the change in the composition of the solution.

TABLE 8

| Comp. of solution<br>$\text{K}_2\text{SO}_4:(\text{NH}_4)_2\text{SO}_4$ | Temp. of<br>crystalliza-<br>tion | % K<br>determined<br>quant. | Type of x-ray<br>powder<br>pattern | Comp. of crystals<br>$\text{K}_2\text{SO}_4:(\text{NH}_4)_2\text{SO}_4$ |
|---|----------------------------------|-----------------------------|------------------------------------|---|
| 25.0:75.0   | 70° C.                           | 21.05                       | xtalline solid soln.               | 46.3:53.7   |
| 33.3:66.7   | 70° C.                           | 31.8                        | xtalline solid soln.               | 70.0:30.0   |
| 50.0:50.0   | 70° C.                           | 39.4                        | xtalline solid soln.               | 86.5:13.5   |
| 66.7:33.3   | 70° C.                           | 42.8                        | xtalline solid soln.               | 94.0: 6.0   |
| 75.0:25.0   | 70° C.                           | 43.2                        | xtalline solid soln.               | 95.0: 5.0   |

#### THE RELATION BETWEEN SODIUM SULFATE AND AMMONIUM SULFATE

##### *The System $\text{Na}_2\text{SO}_4\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$ (Aqueous solutions)*

No mineral having the composition of pure sodium ammonium sulfate has been reported. Ammonian apthitalite,  $(\text{KNH}_4)_3\text{Na}(\text{SO}_4)_2$ , from the Chincha Islands has been described by Frondel (1950). Although  $\text{Na}_2\text{SO}_4$  III,  $\text{Na}_2\text{SO}_4$  V and  $(\text{NH}_4)_2\text{SO}_4$  are all orthorhombic, their space groups are different. Since the ionic radii of  $\text{NH}_4$  and Na are quite different, no solid solution of the  $(\text{NH}_4)_2\text{SO}_4$  with either form of  $\text{Na}_2\text{SO}_4$  would be expected. This was verified by powder photographs of crystals obtained

from solutions of varying proportions of the two sulfates at 70° C. No evidence of solid solution was found. Samples could not be prepared by melting, since ammonium sulfate dissociates readily at higher temperatures.

#### SUMMARY AND CONCLUSIONS

1. Aphthitalite, a sodium potassium sulfate mineral, has been prepared in the laboratory from aqueous solutions as well as from fused melts of various sodium and potassium sulfate proportions. Using  $x$ -ray methods, powder, rotation and Weissenberg, it is revealed that at high temperatures close to fusion, sodium sulfate and potassium sulfate are isomorphous and form a complete series of solid solutions. The same synthetic mineral, prepared from aqueous solution has been found, by  $x$ -ray investigation and checked by chemical analysis, to have a limited range of solid solution varying between the ratios of 1K:1Na to 5K:1Na at 70° C. and is limited to the almost invariable ratio of 3K:1Na at room temperature. A gradual increase in the lattice constants as well as in the refractive indices has been observed, with increasing potassium content in the synthesized aphthitalites of the high-temperature complete solid solution series. It is concluded, therefore, that aphthitalite whether of composition  $\text{NaK}_3(\text{SO}_4)_2$  or  $\text{NaKSO}_4$  is to be considered simply as a solid solution member of the high temperature forms of sodium sulfate and potassium sulfate.

2.  $\text{LiKSO}_4$  and  $\text{LiNaSO}_4$ , both hexagonal but with different space groups (i.e. different structures), are found to represent double compounds between  $\text{Li}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  and  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ , respectively. No solid solution relationship was revealed by  $x$ -ray analysis.

3. The following data have been determined for  $\text{LiNaSO}_4$ :  $a_o = 7.64$ ,  $c_o = 9.76$  ( $\pm 0.02\text{\AA}$ );  $a_o:c_o = 1:1.277$ ;  $Z = 6$ ; space group  $P31c$ ; measured specific gravity 2.515, calculated specific gravity 2.527. Twinning on (0001) common.

4. Complete solid solution and isomorphous relationship between ammonium sulfate and potassium sulfate have been verified by  $x$ -ray methods.

5. There is no solid solution between sodium sulfate and ammonium sulfate at 70° C.

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