

Crystal structure of the apatite-like compound $K_3Ca_2(SO_4)_3F$

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ABSTRACT

The compound $K_3Ca_2(SO_4)_3F$, which is found in coatings of heat-recovery cyclones in portland-cement kilns, crystallizes in space group $Pn2_1a$, pseudo $Pnma$, with $a = 13.415(7)$, $b = 10.493(8)$, $c = 9.127(5)$ Å. The structure was refined to $R = 0.105$ based on 1102 observed reflections. It is a very distorted analogue of apatite, $M_3(YO_4)_3X$. Both the $K_3Ca_2(SO_4)_3F$ and apatite structures can be described as parallel columns of central F atoms oriented along the pseudo-screw axis and the 6, c axis, respectively, surrounded by levels of three M polyhedra enclosing SO_4 or PO_4 groups. The main difference is that in apatite, the M_3 triangular cation coordination of X imposes a trigonal symmetry for the three surrounding Ca₉ cages, whereas in $K_3Ca_2(SO_4)_3F$, the Ca_2K_2 tetrahedral cation coordination of F leaves a pseudo-mirror symmetry for the surrounding M_8 and $2M_7$ cages. Different F columns are related by parallel screw-axes or inversion centers as in apatite.

INTRODUCTION

$K_3Ca_2(SO_4)_3F$ has been identified by Triviño-Vázquez (1985) in coatings of the heat-recovery cyclones used in the portland-cement manufacturing process. Kreidler and Hummel (1970) had previously reported this phase in a study of the structure fields of fluor- and chlorapatites. Compounds having the general formula $M_3(YO_4)_3X$, where M = Ca, Sr, Ba, Pb; Y = P, As, V; and X = F, Cl, were reported as hexagonal apatite structures for all chemical combinations. When Y = S, mixed-metal fluorapatites such as $Na_3Ca_2(SO_4)_3F$ and $Na_3Pb_2(SO_4)_3F$ were also described as apatite structures, but mixed-metal compounds of the type $K_3M_2(SO_4)_3F$ were reported as not having the apatite structure when M = Ca, Cd, Sr, Pb, Ba. The subject of the present report is one of the latter group. In addition, the same authors reported compounds such as $Ca_3(CrO_4)_3F$ and $Na_3Pb_2(SO_4)_3Cl$, which were considered to have slightly deformed apatite structures.

In the present paper, the crystal structure of $K_3Ca_2(SO_4)_3F$ is deduced from an X-ray diffraction study of a synthetic single crystal and is compared with the hexagonal apatite structure.

EXPERIMENTAL DETAILS

Single crystals were obtained by firing stoichiometric mixtures of $CaSO_4$, K_2SO_4 , and CaF_2 , together with 3% excess CaF_2 and K_2SO_4 , at 960°C for 17 h followed by quenching in water. Substantial yields of the phase $K_3Ca_2(SO_4)_3F$ were obtained, but other phases were always present.

Precession photos showed observed reflections allowed in space groups $Pnma$ or $Pn2_1a$. A cell with parameters $a = 13.415(7)$, $b = 10.493(8)$, and $c = 9.127(5)$ Å and $Z = 4$ was chosen and

refined by least-squares using 25 suitable reflections measured on an automated single-crystal diffractometer. Intensity data for 2988 independent reflections to $2\theta = 70^\circ$ were obtained from a tabular crystal; all crystals examined gave quite broad intensity profiles. The $\omega/2\theta$ scan mode with monochromatic $MoK\alpha$ radiation was used. Two standard reflections monitored during the data collection showed no significant intensity variations. Integrated intensities were corrected for Lorentz-polarization effects but not for absorption. The CRYSTALS package of Watkin et al. (1985) was used for all calculations except direct methods, for which the program MITHRIL (Gilmore, 1983) was employed.

RESULTS

The Patterson peak at (0, V, 0) was nonspherical, having dimensions of 0.25 Å in the a direction and 0.60 Å in the c direction. This was interpreted as being due to the presence of a pseudo-mirror plane; i.e., the space group is $Pn2_1a$ instead of $Pnma$, a conclusion supported by statistical tests based on $N(Z)$ and $|E|^2$ distributions, which indicated the structure to be acentric.

Both possible space groups were tried during the structure solution by Patterson and direct methods. The same centrosymmetrical model was obtained for both space groups. In this model, three metal cations, as well as the F atom and one S atom, lie on the mirror plane. Another S atom with its four oxygen atoms and another metal cation were placed off of the mirror plane. The refinement of this model in $Pnma$ did not progress satisfactorily.

$Pn2_1a$ refinement

The structure could be better refined in the space group $Pn2_1a$. After an isotropic refinement, K and Ca were distinguished by geometrical considerations. This model was then refined using anisotropic temperature factors for K and Ca atoms and isotropic ones for the rest. Subsequently, eight oxygen atoms around S2 (S in the pseudo-mirror plane) were found by a difference synthesis. These were

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Table 1. Fractional atomic coordinates and thermal parameters ($\text{\AA}^2 \times 10^3$) in $K_3Ca_2(SO_4)_3F$

| Atom | x | y | z | U_{iso} |
|------|---------|----------|----------|-----------|
| K1 | 5735(8) | 5415(12) | 6939(11) | 23(5)* |
| K2 | 7128(4) | 2500(19) | 3481(8) | 29(4)* |
| K3 | 7755(4) | 2472(19) | 8055(9) | 33(4)* |
| Ca1 | 5763(7) | -475(10) | 6897(13) | 25(4)* |
| Ca2 | 9873(3) | 1/4 | 5128(6) | 21(3)* |
| F1 | 903(1) | 272(2) | 302(2) | 21(3) |
| S2 | 1027(1) | 237(1) | 901(2) | 8(3) |
| O12 | 994(3) | 282(3) | 755(3) | 19(9) |
| O22 | 1114(3) | 153(4) | 883(6) | 99(32) |
| O32 | 947(3) | 168(4) | 979(5) | 49(16) |
| O42 | 1053(3) | 353(3) | 988(4) | 26(10) |
| S21 | 1025(1) | 268(2) | 924(2) | 27(5) |
| O121 | 991(4) | 210(4) | 784(4) | 48(16) |
| O221 | 1126(2) | 317(4) | 899(4) | 23(9) |
| O321 | 958(4) | 371(4) | 971(6) | 20(41) |
| O421 | 1028(3) | 166(3) | 1036(4) | 42(13) |
| S1 | 841(1) | 535(1) | 546(1) | 25(2) |
| O11 | 861(2) | 398(3) | 591(3) | 35(6) |
| O21 | 913(3) | 613(3) | 632(4) | 59(9) |
| O31 | 744(2) | 579(2) | 589(3) | 27(5) |
| O41 | 857(3) | 571(4) | 407(5) | 74(12) |
| S11 | 853(1) | -32(1) | 579(1) | 16(1) |
| O111 | 854(2) | 102(3) | 540(3) | 37(7) |
| O211 | 932(3) | -81(3) | 680(4) | 58(9) |
| O311 | 755(2) | -61(3) | 652(3) | 44(7) |
| O411 | 877(3) | -103(3) | 436(4) | 58(9) |

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|----------|----------|----------|----------|----------|----------|
| K1 | 23(4) | 42(6) | 27(4) | -23(4) | -4(3) | 11(4) |
| K2 | 11(2) | 59(4) | 51(4) | 19(7) | 4(2) | -6(6) |
| K3 | 14(2) | 63(4) | 60(4) | 31(7) | 6(3) | 1(6) |
| Ca1 | 15(3) | 17(4) | 70(6) | -14(4) | -4(4) | 0(3) |
| Ca2 | 11(2) | 45(3) | 36(3) | -26(5) | -2(2) | 5(5) |

Note: Coordinates of K and Ca atoms are multiplied by 10^4 ; those of the remaining atoms are multiplied by 10^3 . The thermal parameters are of the form $\exp(-2\pi^2 \sum U_{ij} h_i a_i^* a_j^*)$. The U_{iso} of starred atoms are calculated as $U_{eq} = 1/3 \sum \sum U_{ij} a_i^* a_j^* a_i a_j$. E.s.d.'s are in parentheses.

interpreted as two statistically disordered tetrahedra, $S2(O2)_4$ and $S21(O21)_4$, which are related by the pseudo-mirror plane and which are each half-occupied.

The final refinement including these oxygens (which were refined with isotropic temperature factors) was done under the following conditions, applied in order to avoid singularities in the matrix due to the pseudo-mirror plane: (1) reparameterization to $(y1 + y1')$ and $(y1 - y1')$ for the mirror-related atoms instead of $y1$ and $y1'$, respectively (Prince, 1982); (2) geometrical constraints of $S-O = 1.48 \pm 0.02 \text{ \AA}$ and $O-S-O = 110 \pm 2^\circ$ for both $S2(O2)_4$ and $S21(O21)_4$ groups. In the last stages of the refinement, 20 reflections with $|F_o| < 0.75 |F_c|$ were omitted. The final R factor was 0.105 for 1102 reflections with $I > 5\sigma_I$.

Geometrically, the metal atoms on the pseudo-mirror plane do not deviate significantly from this "plane," although they were refined with freedom of movement (except Ca2 to fix the origin) in this space group. The F atom moves 0.23 \AA out of the "plane." The two disordered S2 atoms move, after refinement, 0.15 \AA to each side of the plane. Table 1 shows the fractional coordinates and thermal parameters for all atoms after the last cycle of re-

finement. The structure factor table (Table 2) is deposited as supplementary material.¹

Pnma refinement

In order to confirm the space group, the noncentrosymmetric model obtained from the $Pn2_1a$ refinement was reduced to its centrosymmetric equivalent by (1) placing on the mirror plane all the atoms that are near it and (2) situating one atom at the mean distance to the plane for every pair of mirror-related atoms. The refinement of this model in $Pnma$ was done first varying positional parameters, then isotropic temperature factors, and finally mixed isotropic and anisotropic temperature factors. There were two problems with the model: (1) For metal atoms lying on the mirror plane, the only thermal parameters that could be refined successfully were U_{11} , U_{22} , and U_{33} . (2) Metal atoms not on the plane would not refine anisotropically. For this model the final value of R was 0.235 for 1125 reflections having $I > 5\sigma_I$.

In summary, it can be said that the structure is very close to being centrosymmetric, with deviations large enough to give a better fit in the noncentrosymmetric space group $Pn2_1a$. Some significant interatomic distances and angles from the latter refinement are given in Table 3.

DISCUSSION

Geometrical considerations

The greater radius of K relative to Ca is evident in Table 3 for K2, K3, and Ca2, so there is no doubt about these site assignments. The difference is not so clear for K1 and Ca1, although the given attribution seems to be more probable if more weight is assigned to the distances to F and the nonconstrained oxygen atoms. However, the distance K1-O31 is very short, and this could be explained by some (Ca,K) substitution in this position. Unfortunately, the thermal parameters were of no help in this regard. On the other hand, the possible (Ca,K) substitution would have to be accompanied by (O,F) substitution. The Ca-F distances of ca. 2.20 \AA shown in Table 3 are closer to those expected for Ca-F (2.33 \AA) than for Ca-O (2.40 \AA) for a similar atomic arrangement (Fayos et al., 1985). Hence, there is no crystallographic evidence for (O,F) substitution.

Description of the structure

The crystal structure can be described in terms of the packing of cation-polyhedral cages enclosing the SO_4 and F anions. Figure 1 shows the arrangement of these polyhedra. The F atoms are located at the center of Ca_2K_2 tetrahedra, which form columns along the pseudo-screw axis parallel to a . (These exist in the $Pnma$ pseudosymmetry.) Around each column, one CaK edge of the tetrahedron is shared with a Ca_3K_3 polyhedron, which en-

¹ To obtain a copy of Table 2, order Document AM-87-328 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

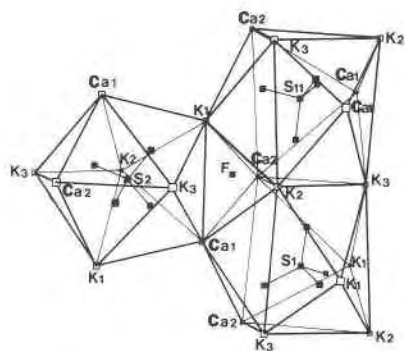


Fig. 1. The cation-polyhedra arrangement surrounding the anions SO_4 and F (both in full squares) in $K_3Ca_2(SO_4)_3F$ structure. Only one, half-populated S_2O_4 tetrahedron has been represented.

closes a statistically disordered SO_4 group. (Only one is shown.) The two tetrahedral faces Ca_2K_1 and Ca_1K_2 not containing that edge are shared by two Ca_4K_5 and Ca_3K_6 polyhedra, each of which encloses another SO_4 group. These two M_3 polyhedra are tricapped trigonal prisms, which are related by the pseudo-mirror plane and share a face. The whole group of three polyhedra that enclose the Ca_2K_2 tetrahedron is repeated every 6.74 \AA by the pseudo-screw axis parallel to a . The columns are related by parallel screw axes.

The distances between S and K or Ca atoms in a cage range from $3.14(2)$ to $4.09(2) \text{ \AA}$, with an average value of $3.6 \pm 0.2 \text{ \AA}$. The distances between cations in the same polyhedron range from $3.82(1)$ to $5.29(1) \text{ \AA}$, with an average of $4.4 \pm 0.5 \text{ \AA}$. The average cation-cation distance in the tetrahedron surrounding F has a smaller value of $3.9 \pm 0.2 \text{ \AA}$.

Relationship to the hexagonal apatite structure

The orthorhombic unit cell of $K_3Ca_2(SO_4)_3F$ has a volume almost double that of the hexagonal apatite with a

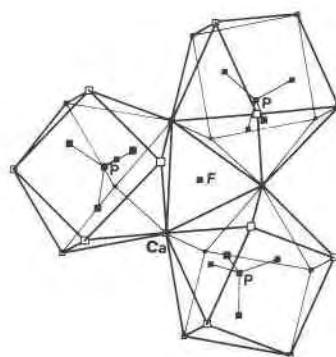


Fig. 2. The cation-polyhedra arrangement surrounding the anions PO_4 and F (both in full squares) in the apatite $(Ca_5(PO_4)_3F)$ structure.

similar formula, namely, $Na_3Ca_2(SO_4)_3F$, which has $a = 9.39$, $c = 6.89 \text{ \AA}$, and space group $P6_3/m$ (Kreidler and Hummel, 1970). In addition, both cells can be related through an intermediate cell, which has $a_{IN} = b_0 = 10.52$, $b_{IN} = -\frac{1}{2}b_0 - c_0 = 10.57$, $c_{IN} = \frac{1}{2}a_0 = 6.74 \text{ \AA}$, and $\gamma = 120.3^\circ$.

A parallel relationship between the crystal structure of $K_3Ca_2(SO_4)_3F$ and hexagonal apatite may therefore be expected. A previous crystallographic study of apatite structures of the type $Ca_5(PO_4)_3X$ ($X = F, Cl, OH$) (Wyckoff, 1965) shows that F atoms are in the center of Ca_3 triangles perpendicular to the c axis, and Cl or OH are ca. 0.5 \AA above and below that triangle.

The apatite structure, represented in Figure 2, can be described as columns of parallel Ca_3 triangles with F atoms in their centers, oriented along the c axis, which corresponds to the a axis of $K_3Ca_2(SO_4)_3F$. Surrounding each column and sharing the edges of the Ca_3 triangles, there are three equivalent Ca_9 polyhedral cages enclosing PO_4 groups. This structure is repeated by the 6_3 screw-axis every 3.5 \AA , half the period in the $K_3Ca_2(SO_4)_3F$

Table 3. Interatomic distances (\AA) and O-S-O bond angles ($^\circ$) in $K_3Ca_2(SO_4)_3F$

| Atom | K2 | K3 | K1 | Ca1 | Ca2 | S1 | S11 |
|---------------------------------------|---------|---------|---------|------------------------|---------|---------|---------|
| F | 2.59(2) | — | 2.63(2) | 2.17(2) | 2.24(2) | — | — |
| (O _{i2} , O _{i21}) | 2.9(1) | 3.0(1) | 2.6(3) | 2.9(5) | 2.4(2) | — | — |
| O11 | 3.36(3) | 2.77(3) | — | — | 2.40(3) | 1.52(3) | — |
| O21 | 2.97(4) | — | 2.77(4) | — | 2.37(4) | 1.49(4) | — |
| O31 | 3.02(3) | 3.15(3) | 2.51(3) | — | — | 1.44(2) | — |
| O41 | — | 2.72(4) | — | 2.51(4) | 2.91(4) | 1.34(4) | — |
| O111 | 3.02(3) | 3.05(3) | 3.37(3) | — | 2.38(3) | — | 1.45(3) |
| O211 | 3.05(4) | — | — | 2.30(4) | 2.72(3) | — | 1.49(4) |
| O311 | 2.70(3) | 3.54(3) | — | 2.43(3) | — | — | 1.50(3) |
| O411 | — | 2.84(4) | 2.76(4) | — | 2.44(4) | — | 1.54(4) |
| (O) | 3.0(2) | 3.0(3) | 2.9(4) | 2.4(1) | 2.5(2) | — | — |
| O11-S1-O21 = 105(2) | | | | O111-S11-O211 = 118(2) | | | |
| O11-S1-O31 = 113(1) | | | | O111-S11-O311 = 109(2) | | | |
| O11-S1-O41 = 120(2) | | | | O111-S11-O411 = 105(2) | | | |
| O21-S1-O31 = 105(2) | | | | O211-S11-O311 = 106(2) | | | |
| O21-S1-O41 = 104(2) | | | | O211-S11-O411 = 102(2) | | | |
| O31-S1-O41 = 108(2) | | | | O311-S11-O411 = 117(2) | | | |

Note: Average distances to oxygens are in the last row with their σ ($n - 1$) standard deviations $\{[n\sum x^2 - (\sum x)^2]/n(n - 1)\}^{1/2}$. Distances to the eight constrained O_{i2} and O_{i21} are averaged, their σ ($n - 1$) being in parentheses.

structure. The trigonal packing around the FCa_3 group allows closer packing between F atoms than in the compound described in this paper. Columns in the apatite structure are related by inversion centers. Accordingly, both structures can be described as parallel columns of central halide ions surrounded by the three-cation polyhedra, which, in turn, enclose tetrahedral groups. The Ca_3 trigonal cation coordination of the halide in apatite imposes a trigonal symmetry for the three Ca_9 cages, whereas the Ca_2K_2 tetrahedral cation coordination around F in $K_3Ca_2(SO_4)_3F$ produces pseudo-mirror symmetry for the M_8 and $2M_9$ cages.

The similarities between the apatite and $K_3Ca_2(SO_4)_3F$ structures are, however, not enough to identify the latter as apatite-related by inspection of its X-ray powder-diffraction pattern. A powder pattern calculated from the atomic coordinates in Table 1 confirms that fact.

ACKNOWLEDGMENTS

The authors thank Dr. G. W. Groves of the Department of Metallurgy and Science of Materials, Oxford University, for use of his laboratory facilities during the synthesis experiments.

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MANUSCRIPT RECEIVED DECEMBER 16, 1985

MANUSCRIPT ACCEPTED SEPTEMBER 2, 1986