# Investigation of Double Sulfates of Potassium and Rare Earth Elements with Composition $KRE(SO_4)_2$†

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We have established the formation of anhydrous double sulfates of $KRE(SO_4)_2$ for the entire series of rare earth elements, which crystallize in five different structural types. The parameters of the unit cells of the double sulfates $KRE(SO_4)_2$ ($RE =$ La–Tb) have been determined. The thermal stability and character of decomposition of the double sulfates of potassium and rare earth elements have been investigated.

Despite the large number of investigations devoted to the composition and properties of double sulfates of potassium and the rare earth elements, all as a rule are devoted not to the anhydrous compounds but to the hydrates. An analysis of the $K_2SO_4–RE_2(SO_4)_3–H_2O$ ($RE =$ La–Ho) systems has shown that for the entire series of rare earth elements, the formation of double sulfates $KRE(SO_4)_2 \cdot nH_2O$ is characteristic (1–7). According to (3, 5, 8) anhydrous double sulfates of composition $K_5RE(SO_4)_4$ (La–Sm) can be obtained from aqueous solutions. Previously we have made an X-ray analysis of double sulfates of composition $K_3RE(SO_4)_3$ ($RE =$ Sm–Lu, Y) (9). The purpose of the present work was to ascertain the possibility of synthesizing anhydrous double sulfates of potassium and rare earth elements with composition $KRE(SO_4)_2$ ($RE =$ La–Lu, Y).

Mixtures of stoichiometric quantities of the initial sulfates, which had first been annealed at 500°C to drive off the water of crystallization, were carefully and thoroughly ground and sintered in air at 500°C for 200–300 h. The formation of an individual phase was checked by X-ray in a Guiner–DeWolf camera using $CuK\alpha$ radiation. Thermographic and thermogravimetric analyses were carried out on a differential analyzer OD-103 and a Kurnakov pyrometer FRU-64 (platinum–platinorhodium thermocouple; accuracy of temperature measurement, $\pm10°C$).

Data from the X-ray analysis of the specimens obtained verified the formation of the double sulfates $KRE(SO_4)_2$ (Y, La–Lu), which agrees with results obtained from analysis of phase equilibrium diagrams of the $K_2SO_4–RE_2(SO_4)_3$ (Nd, Gd, Y) systems. We have established that the double sulfates $KRE(SO_4)_2$ crystallize in five structural types.

Double sulfates of La, Ce, Pr may provisionally be put in the first structural type. The double sulfates of the rare earth elements from Nd to Tb, inclusive, belong to the second type; Dy, Ho, Er, to the third. The compounds $KTm(SO_4)_2$ and $KY(SO_4)_2$ belong to the fourth structural type, and $KYb(SO_4)_2$ and $KLu(SO_4)_2$, to the fifth.

The analogous double sulfate of potassium and scandium described in Ref. (10–13) is isostructural with $KFe(SO_4)_2$ and $KV(SO_4)_2$ (14), as well as with a group of double sulfates of the type $NaM(SO_4)_2$ (15) $M =$ Al, Ga, Cr, V, Fe, Rh.

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Comparison of the X-ray data for the $KSc(SO_4)_2$ which we synthesized and for the double sulfates of $KRE(SO_4)_2$ indicated that the compounds are not isostructural. For further X-ray analyses of $KRE(SO_4)_2$, single crystals of the compounds $KPr(SO_4)_2$ and $KNd(SO_4)_2$, which belong to different structural types, were obtained. In studying these crystals by Laue, oscillation, and reciprocal-lattice photographs, we established that $KRE(SO_4)_2$ (Pr and Nd) belong to the triclinic class with unit-cell parameters as follows:

$KPr(SO_4)_2$, $a = 6.938$ Å, $b = 5.389$ Å, $c = 8.488$ Å, $\alpha = 91°27'$, $\beta = 93°51'$, $\gamma =$

TABLE I

RESULTS OF INDEXING X-RAY PATTERNS OF $KPr(SO_4)_2$

| $I/I_0$ | $h\,k\,l$ | $1/d^2 \times 10^4_{exp}$ | $1/d^2 \times 10^4_{theor}$ |
|---|---|---|---|
| 5 | 0 0 1 | 138.2 | 140.0 |
| 10 | 1 0 0 | 207.8 | 208.4 |
| 100 | 1 0 $\bar{1}$ | 325.6 | 325.8 |
| 70 | 1 0 1 | 371.4 | 371.0 |
| 40 | 0 1 $\bar{1}$ | 473.6 | 474.3 |
| 30 | 0 1 1 | 493.3 | 494.9 |
| 15 | 1 1 0 | 537.8 | 540.0 |
| 15 | 0 0 2 | 559.8 | 560.7 |
|  | $\bar{1}$ 1 0 |  | 565.9 |
| 30 | $\bar{1}$ 1 1 | 693.1 | 693.6 |
| 30 | 1 0 $\bar{2}$ | 719.1 | 723.2 |
|  | 1 $\bar{1}$ 1 |  | 712.9 |
|  | 1 1 1 |  | 718.3 |
| 80 | 2 0 0 | 833.7 | 833.7 |
| 10 | 0 1 $\bar{2}$ | 882.8 | 884.0 |
| 100 | 2 0 $\bar{1}$ | 925.2 | 928.4 |
|  | 0 1 2 |  | 925.2 |
| 5 | 2 0 1 | 1019 | 1019 |
| 100 | 1 1 $\bar{2}$ | 1034 | 1034 |
| 2 | $\bar{1}$ 1 2 | 1100 | 1101 |
| 90 | 2 1 0 | 1151 | 1152 |
|  | 1 $\bar{1}$ 2 |  | 1151 |
| 90 | 1 1 2 | 1163 | 1166 |
| 2 | $\bar{2}$ 1 0 | 1204 | 1204 |
| 2 | 2 0 $\bar{2}$ | 1306 | 1303 |
|  | $\bar{2}$ 1 1 |  | 1309 |
| 70 | 2 1 1 | 1345 | 1348 |
| 90 | 0 2 0 | 1377 | 1378 |
|  | 2 $\bar{1}$ 1 |  | 1379 |
| 5 | 1 0 3 | 1535 | 1536 |
|  | 0 2 1 |  | 1539 |
| 5 | 0 1 $\bar{3}$ | 1572 | 1574 |
| 5 | $\bar{1}$ 2 0 | 1611 | 1613 |
| 10 | 1 2 $\bar{1}$ | 1657 | 1657 |
| 2 | 1 $\bar{2}$ 1 | 1752 | 1755 |
|  | $\bar{1}$ 2 1 |  | 1751 |
| 15 | 1 1 3 | 1899 | 1899 |
|  | 0 2 $\bar{2}$ |  | 1897 |
| 5 | 2 0 $\bar{3}$ | 1957 | 1958 |
| 2 | 3 0 1 | 2087 | 2084 |

TABLE II

RESULTS OF INDEXING X-RAY PATTERNS OF $KNd(SO_4)_2$

| $I/I_0$ | $h\,k\,l$ | $1/d^2 \times 10^4_{exp}$ | $1/d^2 \times 10^4_{theor}$ |
|---|---|---|---|
| 10 | 1 0 0 | 210.4 | 212.0 |
| 100 | 1 0 $\bar{1}$ | 295.9 | 297.1 |
| 50 | 1 0 1 | 375.2 | 374.9 |
| 70 | 0 1 $\bar{1}$ | 463.9 | 463.8 |
| 100 | 0 0 2 | 495.2 | 495.8 |
|  | 0 1 1 |  | 495.3 |
| 5 | $\bar{1}$ 1 0 | 556.6 | 557.4 |
| 5 | 1 1 0 | 575.7 | 577.8 |
| 5 | 1 1 $\bar{1}$ | 648.2 | 647.1 |
| 5 | $\bar{1}$ 1 1 | 657.4 | 658.2 |
| 5 | 1 1 1 | 760.0 | 756.4 |
| 5 | 1 0 2 | 788.3 | 785.7 |
| 40 | 0 1 $\bar{2}$ | 822.2 | 820.0 |
| 100 | 2 0 0 | 847.8 | 848.0 |
| 50 | 0 1 2 | 884.1 | 882.9 |
| 50 | 2 0 $\bar{1}$ | 893.4 | 894.0 |
| 80 | 1 1 2 | 965.9 | 964.2 |
| 50 | $\bar{1}$ 1 2 | 1007 | 1006 |
| 5 | 2 0 1 | 1050 | 1050 |
| 100 | 1 $\bar{1}$ 2 | 1103 | 1100 |
| 80 | 1 1 2 | 1184 | 1183 |
|  | 2 0 $\bar{2}$ |  | 1188 |
|  | 0 1 $\bar{2}$ |  | 1183 |
| 20 | 2 $\bar{1}$ 1 | 1369 | 1369 |
| 100 | 0 2 0 | 1419 | 1422 |
|  | 0 1 $\bar{3}$ |  | 1424 |
| 5 | 1 0 3 | 1442 | 1444 |
|  | 2 1 1 |  | 1441 |
| 5 | 1 1 $\bar{3}$ | 1533 | 1529 |
|  | 2 1 2 |  | 1533 |
| 20 | $\bar{2}$ 1 2 | 1556 | 1555 |
| 5 | $\bar{1}$ 2 0 | 1611 | 1614 |
| 5 | 1 2 0 | 1655 | 1655 |
| 10 | 1 2 $\bar{1}$ | 1701 | 1708 |
| 10 | 2 0 $\bar{3}$ | 1725 | 1730 |
|  | $\bar{1}$ 2 1 |  | 1731 |
| 10 | 0 2 $\bar{2}$ | 1854 | 1855 |
|  | 1 1 3 |  | 1857 |
| 5 | 3 0 0 | 1908 | 1908 |
|  | 3 0 $\bar{1}$ |  | 1915 |
|  | 2 1 2 |  | 1907 |
| 5 | 0 0 4 | 1981 | 1983 |
|  | 0 2 2 |  | 1981 |

## TABLE III

UNIT-CELL PARAMETERS OF COMPOUNDS $KRE(SO_4)_2$ BELONGING TO TWO DIFFERENT STRUCTURE TYPES

| Compound | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ | $\beta$ | $\gamma$ | $V/Z$ (Å³) |
|---|---|---|---|---|---|---|---|
| $KLa(SO_4)_2$ | 7.009 | 5.436 | 8.490 | 91°47′ | 93°30′ | 88°36′ | 161.343 |
| $KCe(SO_4)_2$ | 6.976 | 5.416 | 8.478 | 91°38′ | 93°40′ | 88°30′ | 159.754 |
| $KPr(SO_4)_2$ | 6.938 | 5.389 | 8.488 | 91°27′ | 93°51′ | 88°33′ | 158.235 |
| $KNd(SO_4)_2$ | 6.919 | 5.307 | 9.053 | 92°02′ | 96°52′ | 90°48′ | 164.891 |
| $KSm(SO_4)_2$ | 6.893 | 5.341 | 8.972 | 92°16′ | 97°23′ | 90°56′ | 163.597 |
| $KEu(SO_4)_2$ | 6.878 | 5.350 | 8.943 | 92°22′ | 97°30′ | 91°11′ | 162.908 |
| $KGd(SO_4)_2$ | 6.860 | 5.355 | 8.909 | 92°29′ | 97°33′ | 91°07′ | 162.009 |
| $KTb(SO_4)_2$ | 6.833 | 5.345 | 8.890 | 92°27′ | 97°37′ | 90°52′ | 160.696 |

88°33′, $Z = 2$, $\rho_{exp} = 3.81$, $\rho_{theor} = 3.90$, the space group $P1$;

$KNd(SO_4)_2$, $a = 6.919$ Å, $b = 5.307$ Å, $c = 9.053$ Å, $\alpha = 92°02′$, $\beta = 96°52′$, $\gamma = 90°48′$, $Z = 2$, $\rho_{exp} = 3.70$, $\rho_{theor} = 3.78$, the space group $P\bar{1}$.

Tables I and II give the indexing of the powder lines for these compounds as carried out with reference to the position and intensities of the X-ray reflections in the development of layer lines $h0l–h2l$. We have also indexed the X-ray patterns of the double sulfates $KLa(SO_4)_2$ and $KCe(SO_4)_2$, both of which crystallize with $KPr(SO_4)_2$ in one structural type, as well as the double sulfates $KSm(SO_4)_2$, $KEu(SO_4)_2$, $KGd(SO_4)_2$, and $KTb(SO_4)_2$, which are isostructural with $KNd(SO_4)_2$. The parameters of the unit cells are shown in Table III.

As is seen in Table III, with an increase in the atomic number of the element and, consequently, with a decrease in the radius of the rare earth element an equivalent decrease of the unit-cell volume takes place.

In Table IV are presented the interplanar distances for the double sulfates $KEr(SO_4)_2$, $KTm(SO_4)_2$, and $KLu(SO_4)_2$, which belong to other structural types.

## TABLE IV

X-RAY DATA FOR DOUBLE SULFATES[a]

| | $KEr(SO_4)_2$ | | $KTm(SO_4)_2$ | | $KYb(SO_4)_2$ |
|---|---|---|---|---|---|
| $I/I_0$ | $d$ | $I/I_0$ | $d$ | $I/I_0$ | $d$ |
| 10 | 7.326 | 100 | 6.0177 | 100 | 8.473 |
| 10 | 6.707 | 40 | 4.3708 | 15 | 5.0634 |
| 100 | 5.3104 | 70 | 4.2588 | 60 | 4.3454 |
| 20 | 4.7210 | 100 | 3.2063 | 15 | 4.2307 |
| 30 | 4.5208 | 40 | 3.0826 | 30 | 3.8404 |
| 10 | 4.4534 | 100 | 3.0054 | 70 | 3.7761 |
| 20 | 4.3708 | 10 | 2.5601 | 40 | 3.3433 |
| 30 | 4.2148 | 10 | 2.5418 | 70 | 3.2476 |
| 90 | 3.3756 | 10 | 2.4766 | 70 | 3.0578 |
| 100 | 3.3384 | 10 | 2.3041 | 10 | 3.0253 |
| 80 | 3.2268 | 20 | 2.0942 | 90 | 2.9135 |
| 80 | 3.1185 | | | 10 | 2.5474 |
| 80 | 3.0930 | | | 10 | 2.4000 |
| 100 | 2.9780 | | | 10 | 2.2542 |
| 60 | 2.7460 | | | 10 | 2.1129 |
| 100 | 2.7168 | | | 10 | 2.0624 |
| 10 | 2.2586 | | | | |
| 15 | 2.1552 | | | | |

[a] Only lines with $I/I_0 \geq 10$ are shown.

## TABLE V

DECOMPOSITION TEMPERATURE OF DOUBLE SULFATES $KRE(SO_4)_2$

| $KRE(SO_4)_2$ | $t$ (°C) |
|---|---|
| $KPr(SO_4)_2$ | 930 |
| $KNd(SO_4)_2$ | 930 |
| $KSm(SO_4)_2$ | 830 |
| $KEu(SO_4)_2$ | 800 |
| $KGd(SO_4)_2$ | 800 |
| $KTb(SO_4)_2$ | 720 |
| $KDy(SO_4)_2$ | 700 |
| $KHo(SO_4)_2$ | 700 |
| $KEr(SO_4)_2$ | 620 |
| $KTm(SO_4)_2$ | 500 |
| $KYb(SO_4)_2$ | 500 |
| $KLu(SO_4)_2$ | 480 |
| $KY(SO_4)_2$ | 420 |

Thermographic and gravimetric analyses of the indicated compounds showed that all compounds obtained in the heating decompose in the solid phase. The character of the decomposition of the compounds was checked by X-ray analysis. The double sulfates $KPr(SO_4)_2$ and $KNd(SO_4)_2$ decompose with formation of $K_7RE_3(SO_4)_8$ and $RE_2(SO_4)_3$ phases. The compounds $KRE(SO_4)_2$ ($RE$ = Sm–Lu, Y) on decomposition in the solid phase, form a biphase mixture of $K_4RE_2(SO_4)_5$ and $RE_2(SO_4)_3$. Upon further heating, fusion of the $K_7RE_3(SO_4)_8$ and $K_4RE_2(SO_4)_5$ phases[1] and decomposition of $RE_2(SO_4)_3$ and $RE_2O_2SO_4$ takes place. The phases formed in the decomposition of $KRE(SO_4)_2$ were synthesized individually for each rare earth element and their identity was proven on the X rays.

The decomposition temperatures of the double sulfates $KRE(SO_4)_2$ are shown in Table V. They decrease with increase in the atomic number of the rare earth element.

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[1] The chemical compositions of the phases corresponding to single-phase specimens are indicated.

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