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Crystallography of Some Double Sulfates and Chromates

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New information is given on cell parameters, density and methods of preparation of 50 compounds of the langbeinite and Tutton salt groups. The langbeinites have the general formula $(A^+)_2(B^{2+})_2(XO_4)_3$ and the Tutton salts the general formula $(A^+)_2(B^{2+})(XO_4)_2 \cdot 6H_2O$, where A is K, Rb, (NH_4), Tl or Cs; B is Mg, Ni, Cu, Co, or Zn; and X is S or Cr. A comprehensive list of references on the crystallography of the compounds is included.

Key words: Chromates; langbeinites; lattice constants; sulfates; Tutton salts.

1. Introduction

The crystallographic data on langbeinite $A_2^+B_2^{2+}(XO_4)_3$ and Tutton salt $A_2^+B^{2+}(XO_4)_2 \cdot 6H_2O$ type compounds reported here were obtained as part of a project at the National Bureau of Standards[1] in which x-ray powder patterns of pure phases are prepared to extend and improve the Powder Diffraction File (PDF).[2] Sulfates and chromates belonging to these groups of compounds, which are not represented in the PDF by good x-ray powder patterns, and which could be prepared with satisfactory purity, were studied. A literature search on other pertinent material was made and is summarized. Completely indexed x-ray patterns, optical properties, and a description of our methods are reported in the series NBS Monographs 25[3] [41, 42, 43][4] for each phase studied. Briefly, the x-ray work was done on powders using a diffractometer, with an internal standard (Ag or W) for calibration of the *d* spacing measurements.

The two groups of compounds are treated separately. In each group, the methods of preparation of the samples are outlined briefly, and tables summarizing our findings and those from the literature are given.

1.1. Langbeinite Type Compounds

a. Structure and Preparation

Langbeinite type compounds have the general formula $A_2^+B_2^{2+}(SO_4)_3$. The prototype is $K_2Mg_2(SO_4)_3$. The structure of this compound has been determined by Zemann and Zemann [64]. The basic structure is cubic with a tetramolecular unit cell and the space group $P2_1/3$ (No. 198). The SO_4 tetrahedron is regular, and the B^{2+} ions are octahedrally coordinated. The A^+ ions are of two kinds, one of which is surrounded by four oxygens at varying distances, and the other surrounded by three oxygens. Selenates or chromates of this structure have not previously been reported. The conditions for preparation of the langbeinite type compounds are given in table 1. In this study four isostructural chromates were prepared, all with $B^{2+} = Mg^{2+}$. No attempt was made to prepare selenates. Two compounds, $K_2Ca_2(SO_4)_3$ and $K_2Cd_2(SO_4)_3$, were found to have orthorhombic distortions of the langbeinite structure.

b. Results and Discussion

Table 2 gives unit cell size,[5] density, PDF card number if in the File and other relevant references. These data are given for the various langbeinite compounds from both our studies and from the literature. Two compounds were distorted from cubic and have been indexed as orthorhombic; data for these are given in table 3. It is of interest to note that Jona and Pepinsky [20] reported a transition in $(NH_4)_2Cd_2(SO_4)_3$ at about 87 K, doubtless to a distorted form. It is assumed that solid solutions will occur between most or all of these phases. The only studied solid solution here was between $K_2Mg_2(SO_4)_3$ and $K_2Ca_2(SO_4)_3$ the latter of which was orthorhombic. The compound midway between these end members was found to be cubic, confirming the findings of Morey et al. [36]. No langbeinites could be prepared with Na^+ as A and only a limited number with Cs^+. Also none were prepared with cations larger than Ca^{2+} as B^{2+}. It is of interest to note that the order of the cell size with constant A^+ is not in the one generally accepted as that of increasing radius of the B^{2+}

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[2] The Powder Diffraction File is compiled under the auspices of the Joint Committee on Powder Diffraction Standards. For information refer to the Joint Committee on Powder Diffraction Standards, 1601 Park Lane, Swarthmore, Pa. 19081.
[3] National Bureau of Standards Monograph 25, Standard X-ray Diffraction Patterns, Sec. 1–8 and Circ. 539, Sec. 1–10, have been published. They are available from the U.S. Government Printing Office, Washington, D.C. 20402.
[4] Figures in brackets indicate the literature references at the end of this paper.
[5] As is customary in crystallographic studies, the cell parameters are given in terms of Angstrom (Å) equal to 10^{-10} m.

TABLE 1. *Preparation of langbeinite type compounds made at NBS*

Name	Method of preparation
$K_2Mg_2(SO_4)_3$	Melting K_2SO_4 and $MgSO_4$ together at about 1000 °C. The material is somewhat hygroscopic.
$K_2Ni_2(SO_4)_3$	Heating a mixture of $NiSO_4$ and K_2SO_4 at 750 °C, then regrinding and annealing at 550 °C for 1½ hr.
$K_2Co_2(SO_4)_3$	Melting a mixture of K_2SO_4 and $CoSO_4$ at about 600 °C.
$K_2Zn_2(SO_4)_3$	Melting a mixture of K_2SO_4 and $ZnSO_4$ and then grinding and annealing.
$K_2Mn_2(SO_4)_3$	Melting a mixture of K_2SO_4 and $MnSO_4$ cooling quickly and then annealing at 500 °C for 15 h.
$K_2Ca_2(SO_4)_3$	Melting a mixture of K_2SO_4 and $CaSO_4$ and annealing for 18 h at 700 °C.
$K_2Cd_2(SO_4)_3$	Melting a mixture of K_2SO_4 and $CdSO_4$ followed by annealing for 18 h at 300 °C then 3 days at 150 °C.
$K_2MgCa(SO_4)_3$	Melting a mixture of K_2SO_4, $MgSO_4$ and $CaSO_4$ followed by annealing for 20 h at 500 °C then 17 h at 400 °C.
$(NH_4)_2Mn_2(SO_4)_3$	Partial evaporation at 100 °C of a 1:2 aqueous solution of $(NH_4)_2SO_4$ and $MnSO_4$.
$(NH_4)_2Cd_2(SO_4)_3$	Partial evaporation at 90 °C of a 1:2 aqueous solution of $(NH_4)_2SO_4$ and $CdSO_4$. The crystals were then quickly washed with hot water and alcohol.
$(NH_4)_2Ca(SO_4)_3$	Heating near 100 °C a mixture of 2.7 percent $CaSO_4$, 41.1 percent $(NH_4)_2SO_4$ and 56.2 percent H_2O (by wt) for 5 h using phase study information of Hill and Yanick [15]. The slurry was filtered off rapidly.
$Tl_2Co_2(SO_4)_3$	Heating Tl_2SO_4 and $CoSO_4$ together for several hours at 500 °C.
$Tl_2Mn_2(SO_4)_3$	Slow evaporation at room temperature of a 1:2 aqueous solution of Tl_2SO_4 and $MnSO_4$.
$Tl_2Cd_2(SO_4)_3$	Heating a mixture of Tl_2SO_4 and $CdSO_4$ for 100 h at 470°; followed by regrinding and reheating.
$Rb_2Mg_2(SO_4)_3$	Melting a mixture of Rb_2SO_4 and $MgSO_4$, cooling quickly then annealing at 800 °C for 18 h.
$Rb_2Ni_2(SO_4)_3$	Heating Rb_2SO_4 and $NiSO_4$ together in N_2 for 10 min, regrinding, and reheating at 450° for 15 min.
$Rb_2Co_2(SO_4)_2$	Heating Rb_2SO_4 and $CoSO_4$ together in N_2 at 540 °C for 10 min, then grinding and reheating for 10 min at 540 °C.
$Rb_2Mn_2(SO_4)_3$	Melting a mixture of Rb_2SO_4 and $MnSO_4$.
$Rb_2Cd_2(SO_4)_3$	Melting a mixture of Rb_2SO_4 and $CdSO_4$, quenching, grinding, and annealing for 18 h at 700 °C.
$Rb_2Ca_2(SO_4)_3$	Melting a mixture of Rb_2SO_4 and $CaSO_4$, quenching, grinding and annealing at 650 °C for several days.
$Cs_2Ca_2(SO_4)_3$	Melting a mixture of Cs_2SO_4 and $CaSO_4$, quenching and annealing for 18 h at 700 °C.
$K_2Mg_2(CrO_4)_3$	Heating K_2CrO_4 and $MgCrO_4$ together for one half hour at 510 °C in N_2.
$Rb_2Mg_2(CrO_4)_3$	Heating Rb_2CrO_4 and $MgCrO_4$ together for 45 min at 500 °C in N_2.
$Tl_2Mg_2(CrO_4)_3$	Heating Tl_2CrO_4 and $MgCrO_4$ together for 1 h at 380°.
$Cs_2Mg_2(CrO_4)_3$	Heating Cr_2CrO_4 and $MgCrO_4$ together for 25 min at 440° in N_2.

TABLE 2. *Langbeinite type sulfates—cubic, $P2_13$ (No. 198)*

Compound	Cell size		Density g/cm³	PDF[b] No.	Other Ref.
	Å	Ref.			
$K_2Mg_2(SO_4)_3$	9.9211	41	2.823	19–974	7, 10, 36, 64
$K_2Ni_2(SO_4)_3$	9.8436	41	3.369	19–984	10
$K_2Co_2(SO_4)_3$	9.9313	41	3.283	20–873	10
$K_2Zn_2(SO_4)_3$	9.9247	41	3.376	20–957	10
$K_2Fe_2(SO_4)_3$	10.007	10	3.168	18–1027	
$K_2Mn_2(SO_4)_3$	10.1143	41	3.057	20–909	3, 10
$K_2MgCa(SO_4)_3$	10.1662	42	2.723	20–866	36
$K_2Cd_2(SO_4)_3$	([a])				
$K_2Ca_2(SO_4)_3$	([a])				
$(NH_4)_2Mg_2(SO_4)_3$	9.99	22	2.248	18–110	10
$(NH_4)_2Ni_2(SO_4)_3$	9.914	22	3.011	18–120	10
$(NH_4)_2Co_2(SO_4)_3$	9.95	22	2.981	18–85	10
$(NH_4)_2Fe_2(SO_4)_3$	10.09	22	2.819	18–105	10
$(NH_4)_2Mn_2(SO_4)_3$	10.1892	42	2.726	20–96	
$(NH_4)_2Cd_2(SO_4)_3$	10.3511	42	3.288	21–791	10, 20
$(NH_4)_2Ca_2(SO_4)_3$	10.5360	43	2.297	11–241	10, 15
$Tl_2Co_2(SO_4)_3$	10.0312	43	5.361	22–1466	
$Tl_2Fe_2(SO_4)_3$	10.108	10	5.200		
$Tl_2Mn_2(SO_4)_3$	10.2236	42	5.015	20–1263	10
$Tl_2Cd_2(SO_4)_3$	10.3841	43	5.467	22–1465	10
$Rb_2Mg_2(SO_4)_3$	10.0051	42	3.367	21–1029	10
$Rb_2Ni_2(SO_4)_3$	9.9217	43	3.921	22–1284	10
$Rb_2Co_2(SO_4)_3$	10.0204	43	3.807	22–1266	10
$Rb_2Fe_2(SO_4)_3$	10.098	10	3.682		
$Rb_2Mn_2(SO_4)_3$	10.2147	42	3.546	20–1000	10
$Rb_2Cd_2(SO_4)_3$	10.3810	42	4.060	20–1022	10
$Rb_2Ca_2(SO_4)_3$	10.5687	42	3.034	20–1023	10
$Cs_2Ca_2(SO_4)_3$	10.7213	42	3.417	20–275	10

[a]Orthorhombic distorted langbeinite type—see table 3.
[b]Powder Data File issued by the Joint Committee on Powder Diffraction Standards.

TABLE 3. *Langbeinite type sulfates—orthorhombic,* $P2_12_12_1$ *(No. 19)*

Compound	Cell size			Reference	Density g/cm³	PDF [a] No.	Other reference
	a (Å)	*b* (Å)	*c* (Å)				
$K_2Cd_2(SO_4)_3$	10.212	10.280	10.171	42	3.677	20–864	10
$K_2Ca_2(SO_4)_3$	10.334	10.501	10.186	42	2.683	20–867	4, 36, 40

[a] Powder Data File issued by the Joint Committee on Powder Diffraction Standards.

ions (Mg< Ni < Co < Zn < Fe). The chromate langbeinites are reported in table 4.

1.2. Tutton Salts

a. Structure

The Tutton salts have the general composition $A_2^+B^{2+}(XO_4)_2 \cdot 6H_2O$. These salts were extensively studied by the goniometric method around the turn of the century by Tutton [45–62] and proved to be an early example of a large isostructural series. The structure of one member of the series was determined by Margulis and Templeton [29] and was found to be in the space group $P2_1/a$ (No. 14) with two molecules per cell. The B^{2+} ions are octahedrally surrounded by water molecules, and the A^+ is bonded to oxygens of the sulfate tetrahedron and water oxygens. The structure reported earlier by Hofmann [16] was found incorrect [29].

Tutton found a large number of similar selenates [57–61] and three chromates were also reported in this series [62]; in all of these B^{2+} was Mg. In the present study one new chromate was made in which B^{2+} was Ni. A series of isostructural fluoberyllates has also been reported [37, 38].

b. Preparation

Most of the materials made here were prepared by slow evaporation at room temperature of 1:1 aqueous solution of A_2SO_4 and BSO_4. The phases which were prepared differently are discussed below:

$Tl_2Co(SO_4)_2 \cdot 6H_2O$, $Tl_2Cu(SO_4)_2 \cdot 6H_2O$, $Tl_2Mg(SO_4)_2 \cdot 6H_2O$ and $Tl_2Zn(SO_4)_2 \cdot 6H_2O$ were made by slow evaporation at room temperature of an 1:8 aqueous solution of Tl_2SO_4 and the relevant BSO_4. The first crystals formed were used.

$Cs_2Mg(CrO)_2 \cdot 6H_2O$, $K_2Mg(SO_4)_2 \cdot 6H_2O$, and $Rb_2Fe(SO_4)_2 \cdot 6H_2O$ were made by slow evaporation at room temperature of a 1:3 aqueous solution of the relevant A_2XO_4 and BXO_4. The first crystals formed were used.

$Tl_2Mn(SO_4)_2 \cdot 6H_2O$ was made by evaporating at about 90 °C a 1:1 aqueous solution of Tl_2SO_4 and $MnSO_4$. The crystals were filtered off while hot.

$Tl_2Fe(SO_4)_2 \cdot 6H_2O$ was made by slow evaporation at room temperature of a 1:1 solution of Tl_2SO_4 and $FeSO_4$. The first crystals formed were used.

$Rb_2Cd(SO_4)_2 \cdot 6H_2O$ and $Cs_2Cd(SO_4)_2 \cdot 6H_2O$ were too unstable to study, due to loss of water. The $(NH_4)_2Cs(SO_4)_2 \cdot 6H_2O$ and $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ tended to lose water in dry air and required special handling.

c. Results

In tables 5 and 6 are given the cell parameters from our studies [41, 42, 43] or from the indicated literature together with the cell volume and density. The PDF numbers are given when available, and references to other studies on the materials are indicated.

No Tutton salts are known with Na^+ as A^+, or with cations larger than Ca^{2+} as B^{2+}. As with the langbeinite series the volume of the cell with constant A^+ and with different B^{2+} ions is not in the accepted order of the ionic radii of the B^{2+} ions (Mg < Ni < Co < Zn < Fe).

TABLE 4. *Langbeinite type chromates, cubic* $P2_13$ *(No. 198)*

Compound	Cell size		Density g/cm³	PDF [a] No.
	Å	Reference		
$K_2Mg_2(CrO_4)_3$	10.3684	43	2.829	22–1227
$Rb_2Mg_2(CrO_4)_3$	10.4520	43	3.301	22–1281
$Cs_2Mg_2(CrO_4)_3$	10.5543	43	3.742	22–1077
$Tl_2Mg_2(CrO_4)_3$	10.4174	43	4.731	22–1471

[a] Powder Data File issued by the Joint Committee on Powder Diffraction Standards.

2. References

[1] Bakumskaya, E. L., and Bergman, A. G., Russ. J. Inorg. Chem. (Eng. Trans.) **1,** 1035 (1956).
[2] Barker, T. V., J. Chem. Soc. **99,** 1326 (1911).
[3] Bellanca, A., Accad. dei Lincei Renconti, Classe Scieza, Serces 8, **2,** 451 (1947).
[4] Bellanca, A., Periodico Mineral, (Rome) **13,** 21 (1942).
[5] Bhowmik, G., Indian J. Phys. **39,** 307 (1965).
[6] Carapezza, M., and diSansererino, C., Mineral. Petrograph Acta **13,** 321 (1967).
[7] Cipriani, C., Rend. Soc., Mineral, Italiano **14,** 3 (1958).
[8] DeWolff, P. M., Techn. Phy. Dienst., Delft, Holland, in Powder Data File.
[9] Garvanelli, C. L., Lincei Rend. Sc. Fis. Mat. i. Nat. **36,** 524 (1964).
[10] Gattow, G., and Zemann, J., Z. Anorg. Allgem. Chem. **293,** 233 (1958).
[11] Gossner, B., and Koch. J., Z. Krist. **80,** 455 (1931).
[12] Grimes, N. W., Kay, H. F., and Webb, M. W., Acta Cryst. **16,** 823 (1963).
[13] Halla, F., and Mehl, E., Z. Anorg. Allgem. Chem. **199,** 379 (1931).
[14] Hartman, P., and Woensdregt, C. F., Acta Cryst **17,** 779 (1964).

TABLE 5. *Tutton salts—sulfates, monoclinic,* $P2_1/a$ *(No. 14)*

Compound	Cell size				Vol. (Å³)	Reference	Density g/cm³	PDF [a] No.	Other references
	a (Å)	*b* (Å)	*c* (Å)	*β*					
$K_2Mg(SO_4)_2 \cdot 6H_2O$	9.096	12.254	6.128	104°47′	660.50	22	2.051	20–839	23, 48
$K_2Ni(SO_4)_2 \cdot 6H_2O$	8.991	12.184	6.130	105°	648.40	63	2.24	13–193	48
$K_2Cu(SO_4)_2 \cdot 6H_2O$	9.09	12.14	6.18	104°28′	660.35	22	2.223	17–137	23, 48
$K_2Co(SO_4)_2 \cdot 6H_2O$	9.059	12.209	6.152	104°48′	657.77	8	2.207	21–632	14, 23
$K_2Zn(SO_4)_2 \cdot 6H_2O$	9.041	12.215	6.156	104°49′	657.18	42	2.242	20–958	23, 48
$K_2Fe(SO_4)_2 \cdot 6H_2O$	9.05	12.27	6.16	104°32′	662.14	22	2.178	17–486	23, 48
$Tl_2Mg(SO_4)_2 \cdot 6H_2O$	9.273	12.472	6.214	106°23′	689.49	42	3.532	21–1243	18, 53
$Tl_2Ni(SO_4)_2 \cdot 6H_2O$	9.166	12.392	6.216	106°20′	677.55	42	3.763	20–1266	6, 56
$Tl_2Cu(SO_4)_2 \cdot 6H_2O$	9.268	12.364	6.216	105°33′.	686.22	42	3.740	21–1412	53
$Tl_2Co(SO_4)_2 \cdot 6H_2O$	9.235	12.442	6.227	106°24′	686.38	42	3.7152	21–1411	53
$Tl_2Zn(SO_4)_2 \cdot 6H_2O$	9.219	12.433	6.2317	106°18′	685.58	42	3.763	22–1244	54
$Tl_2Fe(SO_4)_2 \cdot 6H_2O$	9.264	12.499	6.236	106°9′	693.51	43	3.662	22–921	53
$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$	9.324	12.597	6.211	107°14′	696.76	22	1.718	17–135	7, 29, 30, 24, 47
$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$	9.19	12.47	6.24	106°46′	684.70	12	1.913	12–454	12, 24, 32, 50
$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$	9.206	12.38	6.299	106°12′	689.39	8	1.924	11–660	5, 14, 24, 34, 50
$(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$	9.258	12.528	6.236	107°6′	697.98	8	1.897	20–771	13, 14, 24, 50
$(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$	9.205	12.475	6.225	106°52′	684.08	22	1.950	18–138	24, 33, 47
$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	9.28	12.57	6.22	106°50′	694.47	22	1.875	17–481	9, 24, 31, 55
$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$	9.374	12.676	6.253	106°49′	711.21	43	1.827	11–134	7, 24, 30
$(NH_4)_2Cd(SO_4)_2 \cdot 6H_2O$	9.393	12.777	6.300	106°42′	724.17	43	2.058		35, 50
$Rb_2Mg(SO_4)_2 \cdot 6H_2O$	9.235	12.486	6.224	105°59′	689.85	43	2.385	21–1415	48
$Rb_2Ni(SO_4)_2 \cdot 6H_2O$	9.138	12.416	6.223	106°4′	678.47	43	2.594	21–1418	48
$Rb_2Cu(SO_4)_2 \cdot 6H_2O$	9.267	12.366	6.228	105°19′	688.35	43	2.580	21–1321	48
$Rb_2Co(SO_4)_2 \cdot 6H_2O$	9.180	12.433	6.230	106°1′	683.46	14	2.576	17–303	48
$Rb_2Zn(SO_4)_2 \cdot 6H_2O$	9.185	12.450	6.242	105°55′	686.42	42	2.596	21–1328	48
$Rb_2Fe(SO_4)_2 \cdot 6H_2O$	9.218	12.497	6.256	105°45′	693.56	43	2.523	21–1322	48
$Cs_2Mg(SO_4)_2 \cdot 6H_2O$	9.330	12.848	6.360	107°	728.97	42	2.689	20–615	48
$Cs_2Ni(SO_4)_2 \cdot 6H_2O$	9.264	12.773	6.359	106°59′	719.66	42	2.883	21–163	48
$Cs_2Cu(SO_4)_2 \cdot 6H_2O$	9.439	12.762	6.310	106°11′	729.93	42	2.864	21–846	48
$Cs_2Co(SO_4)_2 \cdot 6H_2O$	9.316	12.824	6.365	107°7′	726.74	14	2.856	17–305	48
$Cs_2Zn(SO_4)_2 \cdot 6H_2O$	9.316	12.815	6.373	106°57′	727.83	42	2.881	20–719	48
$Cs_2Fe(SO_4)_2 \cdot 6H_2O$	9.355	12.893	6.378	106°53′	736.16	42	2.805	20–402	48
$Cs_2Mn(SO_4)_2 \cdot 6H_2O$	9.425	12.970	6.389	107°10′	746.27	42	2.763	21–847	48

[a] Powder Data File issued by the Joint Committee on Powder Diffraction Standards.

TABLE 6. *Tutton salts—chromates, monoclinic,* $P2_1/a$ *(No. 14)*

Compound	Cell size				Vol. (Å³)	Reference	Density g/cm³	PDF [a] No.	Other references
	a (Å)	*b* (Å)	*c* (Å)	*β*					
$(NH_4)_2Mg(CrO_4)_2 \cdot 6H_2O$	9.508	12.674	6.246	106°14′	722.64	43	1.757	21–701	
$Rb_2Mg(CrO_4)_2 \cdot 6H_2O$	9.474	12.571	6.256	104°57′	719.86	43	2.470	22–1282	2
$Cs_2Mg(CrO_4)_2 \cdot 6H_2O$	9.604	12.952	6.369	106°6′	761.23	43	2.750	21–844	2
$(NH_4)_2Ni(CrO_4)_2 \cdot 6H_2O$	9.420	12.603	6.275	105°54′	716.45	43	2.016	21–705	

[a] Powder Data File issued by the Joint Committee on Powder Diffraction Standards.

[15] Hill, A. E., and Yanick, N. S., J. Am. Chem. Soc. **57**, 645, (1935).
[16] Hofmann, W., Z. Krist. **78**, 279 (1931).
[17] Hofmann, W., Z. Krist **82**, 323 (1932).
[18] Hofmann, W., Z. Krist. **75**, 158 (1930).
[19] Hölemann, H., Z. Anorg. Allgem. Chem. **239**, 257 (1938).
[20] Jona, F., and Pepinsky, R., Phy. Rev. **103**, 1126 (1956).
[21] Kannan, K. K., and Viswamitra, M. A., Z. Krist. **122**, 161 (1965).
[22] Kohler, K., and Franke, W., Mineralogishes Mt., Freise Un., Berlin, Germany, in Powder Data File.
[23] Kohler, K., and Franke, W., Z. Anorg. Allgem. Chem. **331**, 27 (1964).
[24] Kohler, K., and Franke, W., Z. Anorg. Allgem. Chem. **331**, 17 (1964).
[25] Lepeshkov, I. N., and Noviskova, L. N., Russ. J. Inorg. Chem. (Eng. Trans.) **3**, 2395 (1958).
[26] Lindsley, L. C., and Dennis, L. M., J. Am. Chem. Soc. **47**, 377 (1925).
[27] Mallet, F. R., J. Chem. Soc. **77**, 216 (1900).
[28] Mallet, F. R., J. Chem. Soc. **81**, 1546 (1902).
[29] Margulis, T. N., and Templeton, D. H., Z. Krist. **117**, 344 (1962).
[30] Montgomery, H., Chastain, R. V., and Lingafelter, E. C., Acta Cryst. **20**, 731 (1966).
[31] Montgomery, H., Chastain, R. V., Natt, J. J., Witkowska, A. M., and Lingafelter, E. C., Acta Cryst. **22**, 775 (1967).
[32] Montgomery, H., and Lingafelter, E. C., Acta Cryst **17**, 1478 (1964).
[33] Montgomery, H., and Lingafelter, E. C., Acta Cryst. **17**, 1295 (1964).
[34] Montgomery, H., and Lingafelter, E. C., Acta Cryst. **20**, 659 (1966).
[35] Montgomery, H., and Lingafelter, E. C., Acta Cryst. **20**, 728 (1966).
[36] Morey, G. W., Rowe, J. J., and Fournier, R. O., J. Inorg. Nucl. Chem. **26**, 55 (1964).
[37] Mukherjee, P. L., Z. Krist. **91A**, 504 (1935).
[38] Mukherjee, P. L., Indian J. Phys. **18**, 148 (1944).
[39] Plyushchev, V. E., Russ. J. Inorg. Chem. (Eng. Trans.) **7**, 709 (1962).
[40] Ramsdell, L. S., Am. Mineralogist, **20**, 569 (1935).
[41] Swanson, H. E., McMurdie, H. F., Morris, M. C., and Evans, E. H., Nat. Bur. Stand. (U.S.), Monogr. 25, Sec. 6, 101 pages (1968).
[42] Swanson, H. E., McMurdie, H. F., Morris, M. C., and Evans, E. H., Nat. Bur. Stand. (U.S.), Monogr. 25, Sec. 7, 186 pages (1969).
[43] Swanson, H. E., McMurdie, H. F., Morris, M. C., and Evans, E. H., Nat. Bur. Stand. (U.S.), Monogr. 25, Sec. 8 (1970).
[44] Tret'yakov, Yu. D., Russ. J. Inorg. Chem. (Eng. Trans.) **6**, 501 (1961).
[45] Tutton, A. E. H., Z. Krist. **33**, 1 (1900).
[46] Tutton, A. E. H., Z. Krist. **27**, 113 (1897).
[47] Tutton, A. E. H., J. Chem. Soc. **87**, 1123 (1905).
[48] Tutton, A. E. H., J. Chem. Soc. **63**, 337 (1893).
[49] Tutton, A. E. H., J. Chem. Soc. **69**, 344 (1896).
[50] Tutton, A. E. H., Phil. Tran. Roy. Soc. London, Ser. A, **216**, 1 (1916).
[51] Tutton, A. E. H., Phil. Tran. Roy. Soc. London, Ser. A, **197**, 255 (1901).
[52] Tutton, A. E. H., Phil. Tran. Roy. Soc. London, Ser. A, **217**, 199 (1919).
[53] Tutton, A. E. H., Proc. Roy. Soc. (London), Ser. A, **118**, 367 (1928).
[54] Tutton, A. E. H., Proc. Roy. Soc. (London), Ser. A, **83**, 211 (1910).
[55] Tutton, A. E. H., Proc. Roy. Soc. (London), Ser. A, **88**, 361 (1913).
[56] Tutton, A. E. H., Proc. Roy. Soc. (London), Ser. A, **108**, 240 (1925).
[57] Tutton, A. E. H., Proc. Roy. Soc. (London), Ser. A, **67**, 58 (1900).
[58] Tutton, A. E. H., Proc. Roy. Soc. (London), Ser. A, **101**, 245 (1922).
[59] Tutton, A. E. H., Proc. Roy. Soc. (London), Ser. A, **101**, 225 (1922).
[60] Tutton, A. E. H., Proc. Roy. Soc. (London), Ser. A, **96**, 156 (1920).
[61] Tutton, A. E. H., Proc. Roy. Soc. (London), Ser. A, **98**, 67 (1921).
[62] Tutton, A. E. H., and Porter, M. W., Mineral. Mag. **16**, 169 (1912).
[63] Weidenborner, J. E., Tsu, I., and Godycki, L. E., Acta Cryst. **14**, 63 (1961).
[64] Zemann, A., and Zemann, J., Acta Cryst. **10**, 409 (1957).

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