P1—O1	1.511 (15)	Na—O5$^{\rm vi}$	2.60 (2)
P1—O4	1.604 (9)	Na—O7$^{\rm vi}$	2.62 (2)
P2—O7	1.48 (2)		
O3$^{\rm i}$—Y—O6$^{\rm ii}$	93.8 (7)	O2$^{\rm iv}$—Y—O7$^{\rm v}$	75.4 (5)
O3$^{\rm i}$—Y—O5$^{\rm iii}$	104.3 (7)	O2—P1—O6	114.8 (8)
O6$^{\rm ii}$—Y—O5$^{\rm iii}$	76.6 (6)	O2—P1—O1	110.9 (7)
O3$^{\rm i}$—Y—O1	94.6 (5)	O6—P1—O1	111.9 (7)
O6$^{\rm ii}$—Y—O1	92.3 (5)	O2—P1—O4	106.2 (6)
O5$^{\rm iii}$—Y—O1	158.6 (5)	O6—P1—O4	106.4 (7)
O3$^{\rm i}$—Y—O2$^{\rm iv}$	169.7 (7)	O1—P1—O4	106.1 (8)
O6$^{\rm ii}$—Y—O2$^{\rm iv}$	95.5 (5)	O7—P2—O3	116.1 (12)
O5$^{\rm iii}$—Y—O2$^{\rm iv}$	82.3 (6)	O7—P2—O5	109.6 (6)
O1—Y—O2$^{\rm iv}$	80.5 (4)	O3—P2—O5	111.4 (12)
O3$^{\rm i}$—Y—O7$^{\rm v}$	97.9 (6)	O7—P2—O4	109.9 (10)
O6$^{\rm ii}$—Y—O7$^{\rm v}$	154.9 (6)	O3—P2—O4	104.5 (5)
O5$^{\rm iii}$—Y—O7$^{\rm v}$	79.0 (3)	O5—P2—O4	104.6 (10)
O1—Y—O7$^{\rm v}$	108.7 (6)	P1—O4—P2	126.5 (7)

Symmetry codes: (i) $1-x, y-\frac{1}{2}, 1-z$; (ii) $x, y-1, z$; (iii) $x-1, y-1, z$; (iv) $1-x, y-\frac{1}{2}, 2-z$; (v) $x-1, y, z$; (vi) $2-x, y-\frac{1}{2}, 2-z$.

Data were corrected for Lorentz and polarization effects. The scan width was $(0.61 + 0.79\tan\theta)^\circ$. Refinement was by full-matrix least-squares method on F^2 using all reflections with $I_{hkl} > 0$. An attempt at anisotropic refinement of all the atoms (five observations per parameter) led to negative values for the displacement coefficients of P2 and O7. This is attributed to the very small crystal size which allowed us to obtain only 399 observable reflections [$I > 2\sigma(I)$]. Only the Y atom was therefore refined anisotropically.

Data collection: *CAD*-4 *Express* (Duisenberg, 1992; Macíček & Yordanov, 1992). Cell refinement: *CAD*-4 *Express*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1993) and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1148). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2951–2954

A New Langbeinite: Dipotassium Dimanganese Tetrafluoroberyllate

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(Received 16 January 1996; accepted 2 July 1996)

Abstract

The structure of the cubic phase of a new langbeinite, $K_2Mn_2(BeF_4)_3$, has been determined at 293 K from X-ray diffraction data. Differential scanning calorimetry measurements in the temperature range 100–300 K indicated a new phase transition at 213 K, which has been confirmed by precession X-ray diffractograms, revealing a new type of structure different to those generally expected for the low-temperature phases of langbeinites.

Comment

The langbeinite $K_2Mn_2(BeF_4)_3$ belongs to the family of compounds with the common chemical formula $A_2B_2(XY_4)_3$, where A is a monovalent cation such as Cs, Tl, Rb, NH_4 or K, B is a divalent cation such as Mg, Ni, Co, Zn, Fe, Mn, Cd or Ca, and XY_4 represents the divalent tetrahedral group SO_4 or BeF_4. The sulfates within this family have attracted much interest because of their ferroelastic and ferroelectric behaviour and the nature of their structural phase transitions. All of them have cubic symmetry (space group $P2_13$) in the high-temperature phase and many of them show successive phase transitions as the temperature is lowered. These transitions can be classified as two types according to the transition scheme. Crystals that exhibit a series of phase transitions from cubic ($P2_13$) to orthorhombic ($P2_12_12_1$) across two intermediate, monoclinic ($P2_1$) and triclinic ($P1$), phases belong to type I (Brezina & Glogarova, 1972; Ikeda & Yasuda, 1975; Yamada & Kawano, 1977; Hikita, Chubachi & Ikeda, 1978). Crystals of type II undergo a single phase transition from the cubic ($P2_13$) to an orthorhombic ($P2_12_12_1$) phase (Abrahams, Lissalde & Bernstein, 1978; Hikita *et al.*, 1978; Yamada, Maeda & Adachi, 1981; Speer & Salje, 1986).

In contrast to the sulfate langbeinites, the physical properties of langbeinite-type fluoroberyllates are not known. Initial work was performed by Aleonard & Le Fur (1967) and Genty, Le Fur & Aleonard (1968), who synthesized some of these compounds with K^+, Tl^+, Cs^+ and NH_4^+ as the monovalent cations and Mg^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+} and Ni^{2+} as the divalent cations. From powder X-ray diffraction they obtained values for the lattice constants and confirmed their cubic symmetry at room temperature. So far, there has been no information in the literature about possible phase transitions in this type of compound.

The structure of $K_2Mn_2(BeF_4)_3$ is similar to those of the sulfate-containing langbeinites (Zeemann & Zeemann, 1957; Abrahams *et al.*, 1978; Yamada *et al.*, 1981; Speer & Salje, 1986). It comprises BeF_4 tetrahedra and distorted coordination polyhedra around the metal positions. The coordination about K1 and K2 is ninefold. Nearest-neighbour F atoms surrounding Mn1 and Mn2 form distorted octahedra, which are generated by the application of the threefold axes on the symmetry-independent atoms F3, F4, F1 and F2. Be—F distances range from 1.500 (5) to 1.527 (6) Å, with a mean value of 1.516 (5) Å. Bond angles range from 102.5 (3) to 113.4 (3)°, with a mean value of 109.3 (4)°. This indicates a bigger distortion of the BeF_4 group as compared to that of the SO_4 group in $K_2Mn_2(SO_4)_3$ (Yamada *et al.*, 1981). The displacement parameters of the K, Mn and Be atoms are virtually isotropic, whereas the displacement ellipsoids of the F atoms are disk-shaped.

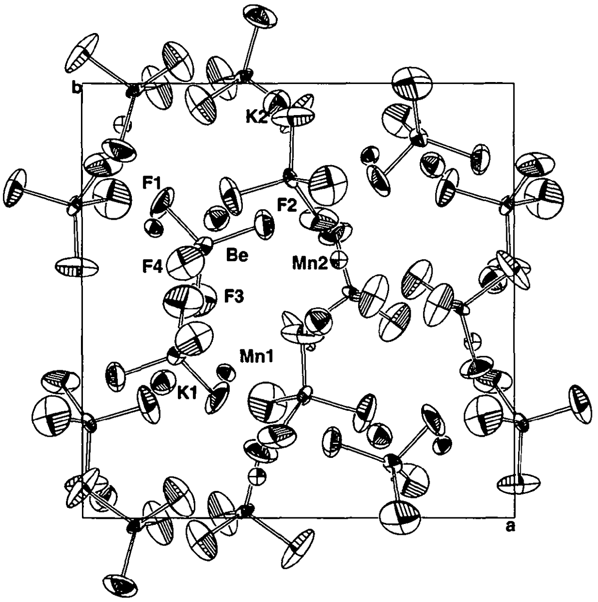

Fig. 1. Projection of the cubic structure of $K_2Mn_2(BeF_4)_3$ along the (001) direction, showing 50% probability displacement ellipsoids. Only the asymmetric unit is labelled.

The K and Mn atoms occupy special positions along the threefold axes. The Mn1 and Mn2 cations are not at the centres of their coordination octahedra, but are shifted by 0.073 (9) Å toward the F4 triangle for Mn1 and 0.145 (9) Å toward the F2 triangle for Mn2. The values of this deformation parameter for $K_2Mn_2(SO_4)_3$ (Speer & Salje, 1986) are 0.053 and 0.095 Å for Mn2 and Mn1, respectively. Notice that the values of this parameter for $K_2Mn_2(BeF_4)_3$ are larger than those for $K_2Mn_2(SO_4)_3$, and the displacements of Mn1 are practically twice those of Mn2 for both compounds.

In order to compare the cation binding, the bond-valence sums (Brown & Altermatt, 1985) for the atoms in $K_2Mn_2(BeF_4)_3$ and $K_2Mn_2(SO_4)_3$ were calculated (Table 3). The values for K1 and K2 in $K_2Mn_2(BeF_4)_3$ indicate that these atoms are loosely bonded, which also agrees with the high values of the displacement parameters of these cations (Table 1). The bond-valence sums for the other cations and anions in this structure are approximately equal to the valences of these ions. It should be noted that the bonds in $K_2Mn_2(SO_4)_3$ are stronger than in the present structure. Anomalously low values of the bond-valence sums have also been observed for the Tl atoms in $Tl_2Cd_2(SO_4)_3$ (Guelylah, Madariaga & Breczewski, 1996), which is a type I langbeinite.

Differential scanning calorimetry studies of $K_2Mn_2(BeF_4)_3$ were carried out in the temperature range 100–300 K. A phase transition was observed at 213 K. A set of precession photographs taken at 180 K revealed the existence of a domain structure in the low-temperature phase and a doubling of the cell volume. The possible space groups compatible with the precession photographs are $P1$, $P2$, $P2_1$ (with interaxial angles approximately equal to 90°), $P222$, $P2_122$ and $P2_12_12$. All these groups must be accompanied by a duplication along one of the crystal axes (*a*, *b* or *c*) which is not parallel to the twofold screw axes in the low-temperature phase. According to the theoretical prediction of Dvorák (1974), the most probable space group is $P2_1$, with duplication of one of the cubic axes. The precession photographs taken at 180 K have confirmed the existence of a new crystal structure different from that of any other low-temperature phase reported in the literature for a langbeinite. Further structural work on the low-temperature phase of $K_2Mn_2(BeF_4)_3$ is currently in progress.

Experimental

Single crystals of $K_2Mn_2(BeF_4)_3$ were grown from saturated aqueous stoichiometric solutions by a steady-state method at 360 K. The stock reagents used for the synthesis were chemically pure KF, MnF_2 and BeF_2. The product of the synthesis was purified by recrystallization from distilled water.

The crystals obtained were 1 × 1 × 2 mm, light pink and of good optical quality. Their morphology was similar to that of crystals of $K_2Mn_2(SO_4)_3$. A sphere of radius 0.135 mm, ground in an Enraf–Nonius grinder, was mounted in a random orientation on a glass fibre for data collection.

Crystal data

$K_2Mn_2(BeF_4)_3$
$M_r = 443.11$
Cubic
$P2_13$
$a = 10.075 (2)$ Å
$V = 1022.7 (2)$ Å^3
$Z = 4$
$D_x = 2.878$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 12 reflections
$\theta = 7–13°$
$\mu = 3.43$ mm^{-1}
$T = 293$ K
Spherical
0.135 mm (radius)
Light pink

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: spherical
$T_{min} = 0.933$, $T_{max} = 0.933$
3571 measured reflections
1189 independent reflections

888 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.0319$
$\theta_{max} = 40°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = 1 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.035$
$S = 5.05$
885 reflections
58 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.029$

$\Delta\rho_{max} = 2.0$ e Å^{-3}
$\Delta\rho_{min} = -1.8$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
K1	0.18818 (9)	$1/2-x$	$1/2+x$	0.0359 (2)
K2	0.45198 (14)	$1/2+x$	$1-x$	0.0423 (2)
Mn1	0.33300 (5)	x	x	0.0193 (1)
Mn2	0.59513 (5)	x	x	0.0172 (1)
Be	0.2812 (5)	0.6250 (4)	0.5163 (4)	0.018 (1)
F1	0.1871 (3)	0.7243 (4)	0.4506 (5)	0.057 (1)
F2	0.4221 (3)	0.6752 (3)	0.5106 (5)	0.059 (2)
F3	0.2650 (5)	0.5017 (5)	0.4295 (5)	0.080 (2)
F4	0.2402 (5)	0.5869 (4)	0.6542 (3)	0.058 (1)

Table 2. *Selected geometric parameters (Å, °)*

K1—F1^{i}	2.950 (5)	Mn1—F4^{iii}	2.107 (3)
K1—F3^{i}	3.109 (5)	Mn2—F1^{ii}	2.093 (4)
K1—F4	2.841 (4)	Mn2—F2	2.101 (3)
K2—F1^{ii}	2.961 (4)	Be—F1	1.527 (6)
K2—F2	2.830 (4)	Be—F2	1.509 (5)
K2—F3^{ii}	3.197 (5)	Be—F3	1.527 (6)
Mn1—F3	2.075 (4)	Be—F4	1.500 (5)
F1—Be—F2	110.3 (3)	F2—Be—F3	110.6 (3)
F1—Be—F3	102.5 (3)	F2—Be—F4	112.3 (3)
F1—Be—F4	113.4 (3)	F3—Be—F4	106.9 (3)

Symmetry codes: (i) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (iii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$.

Table 3. *Bond-valence sums (v.u.) for the atoms in $K_2Mn_2(BeF_4)_3$ and $K_2Mn_2(SO_4)_3$*

$K_2Mn_2(BeF_4)_3$		$K_2Mn_2(SO_4)_3$†	
K1	0.68 (2)	K1	0.81 (9)
K2	0.65 (2)	K2	0.90 (10)
Mn1	2.08 (4)	Mn1	2.26 (15)
Mn2	2.04 (4)	Mn2	2.21 (13)
Be	2.12 (5)	S	6.2 (2)
F1	1.00 (2)	O1	2.09 (10)
F2	0.98 (2)	O2	2.05 (10)
F3	0.96 (2)	O3	2.06 (12)
F4	0.98 (2)	O4	2.07 (9)

† Cubic phase (Yamada *et al.*, 1981)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *ABSORB*, *ADDREF* and *SORTRF* in *Xtal*3.2 (Hall, Flack & Stewart, 1992). Program(s) used to refine structure: *CRYLSQ* in *Xtal*3.2. Molecular graphics: *ORTEP* (Johnson, 1965) in *Xtal*3.2. Software used to prepare material for publication: *BONDLA* in *Xtal*3.2.

This work has been carried out thanks to the financial support of the Spanish Comision Interministerial de Ciencia y Tecnologia (project No. PB91-0554). AG wishes to acknowledge the Instituto de Cooperación con el Mundo Arabe for providing him with a pre-doctoral scholarship.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AB1352). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2954-2956

Langbeinite-Type Cubic Dithallium Dicadmium Sulfate

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(Received 16 January 1996; accepted 2 July 1996)

Abstract

The structure of the cubic phase of langbeinite-type $Tl_2Cd_2(SO_4)_3$ at 295 K has been refined from X-ray diffraction data. The bond-valence sums for the monovalent cations show anomalously low values, indicating that some Tl atoms are very loosely bonded. The possible relevance of this result in the phase-transition scheme of compounds similar to $Tl_2Cd_2(SO_4)_3$ is discussed.

Comment

Langbeinite-type crystals have the general formula $A_2B_2(SO_4)_3$, where A = K, Tl, Cs, Rb or NH_4, and B = Mg, Zn, Fe, Ni, Cd, Co, Ca or Mn, and take their names from the natural mineral langbeinite, $K_2Mg_2(SO_4)_3$. The structure of $K_2Mg_2(SO_4)_3$ was solved at room temperature by Zeemann & Zeemann (1957), and the chemical stability of other isostructural double sulfates has been investigated by Gatow & Zeemann (1958).

Langbeinites have a common high-temperature cubic phase (space group $P2_13$), and many of them exhibit phase transitions to ferroelectric or ferroelastic phases as the temperature is lowered. Up to now, two different sequences of phase transitions have been observed among langbeinites. Compounds classified as type I [*e.g.* $(NH_4)_2Cd_2(SO_4)_3$, $Tl_2Cd_2(SO_4)_3$ and $Rb_2Cd_2(SO_4)_3$] undergo a series of phase transformations from cubic to orthorhombic ($P2_12_12_1$) through two phases; one monoclinic ($P2_1$) and one triclinic ($P1$) (Brezina & Glogarova, 1972; Glogarova & Fousek, 1973; Yamada & Kawano, 1977). The so-called type II compounds [*e.g.* $K_2Mn_2(SO_4)_3$ and $K_2Cd_2(SO_4)_3$] show only a single phase transition to an orthorhombic structure ($P2_12_12_1$) as temperature is lowered (Abrahams, Lissalde & Bernstein, 1978; Hikita, Chubachi & Ikeda, 1978; Yamada, Maeda & Adachi, 1981). Based on group theoretical analysis, Dvorák (1972) has shown that a spatially homogeneous phase transition could result only from a phonon instability at the points M and Γ of the cubic Brillouin zone. An instability at the M point would lead to an improper ferroelectric phase ($P2_1$) with a doubled unit-cell volume (type I compounds), while an instability at the Γ point leads to a potentially ferroelastic phase ($P2_12_12_1$) with no change in the unit-cell volume (type II compounds).

There are several reports of type I compounds, which are of interest because of the ferroelectric character of the low-temperature phases. In particular, crystals of $Tl_2Cd_2(SO_4)_3$ (hereinafter TCdS) were first studied by Brezina & Glogarova (1972), who discovered three phase transitions at about 98, 127 and 130 K by dielectric and optical measurements. Based on the work of Dvorák (1972), they suggested that the space groups of the low-temperature phases of TCdS are those cited above for type I compounds. A few years later, Ikeda & Yasuda (1975) confirmed the assignment of the space groups by X-ray diffraction and spontaneous polarization measurements; $Tl_2Cd_2(SO_4)_3$ was considered to be a typical langbeinite of type I. Recently, Cao, Dalley & Boerio-Goates (1993) determined the structure of TCdS at room temperature by X-ray diffraction. However, an incomplete correction for absorption prevented an accurate structure solution (R = 8.6%) and hindered observation of such details as the anisotropy of the atomic displacements. Here, we report a more reliable structure determination for TCdS. The calculated bond-valence sums (Brown & Altermatt, 1985) show anomalies when compared with those of typical langbeinites of type II, which could indicate a possible mechanism responsible for the two different sequences of phase transitions shown by langbeinites.

The structure of TCdS is similar to that of the sulfates belonging to the langbeinite family (Speer & Salje, 1986; Abrahams *et al.*, 1978, Yamada *et al.*, 1981; Zeemann & Zeemann, 1957), and comprises SO_4 tetrahedra and distorted coordination polyhedra around the metal cations. The metal cations occupy special positions along the threefold axes. Each Tl atom is surrounded by nine O atoms that form a complicated polyhedron. Cd1 and Cd2 are each coordinated by six O atoms, forming distorted octahedra, which are generated by the application of the threefold axes on the symmetry independent atoms O3, O4, O1 and O2. Cd1 and Cd2 are not at the midpoints of the octahedra, but are shifted by 0.03 (3) Å toward the O4 triplet for Cd1 and 0.13 (3) Å toward the O2 triplet for Cd2.

The SO_4 group is a distorted tetrahedron with S—O distances ranging from 1.41 (2) to 1.49 (2) Å