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Powder neutron diffraction of Tl_2BeF_4 at six temperatures from room temperature to 1.5 K

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The structure of thallium fluoroberyllate, Tl_2BeF_4, has been analysed by the Rietveld method on neutron diffraction patterns collected at 1.5, 50, 100, 150, 200 and 300 K, with the aim of detecting low-temperature instabilities. Atomic parameters based on the isomorphic β-K_2SO_4 crystal in the paraelectric phase were used as the starting model at room temperature; no evidence for any phase transition has been detected at lower temperature. The structure was determined in the orthorhombic space group *Pnma*. All the atoms (except one F atom) occupy sites with *m* symmetry. We have compared the structure with those of other compounds of the β-K_2SO_4 family, at room temperature, in order to gain insight into their observed instabilities. The irregular coordination of the cations may indicate stereochemical activity of the Tl^I lone pair but does not indicate a possible structural instability.

Comment

We are interested in the large family of ferroelectric compounds having the general formula A_2BX_4 with the β-K_2SO_4 structure in the paraelectric phase (space group *Pnma*, Z = 4). The most widely studied compounds are K_2SeO_4, $(NH_4)_2SO_4$ and $(NH_4)_2BeF_4$; they exhibit interesting properties, related to a low-temperature phase transition which are strikingly different. For instance, the polar axis of $(NH_4)_2BeF_4$ is the *b* axis, while that of both $(NH_4)_2SO_4$ (Hoshino *et al.*, 1958) and K_2SeO_4 is the *c* axis (Yamada *et al.*, 1984). $(NH_4)_2SO_4$ has a ferroelectric phase transition at T_c = 223.5 K (Schlemper & Hamilton, 1966), while an incommensurate phase is observed in $(NH_4)_2BeF_4$ between T_i = 182.9 K and T_c = 177.2 K (Srivastava *et al.*, 1999), and in K_2SeO_4 between T_i = 192.5 K and T_c = 93 K (Aiki & Hukuda, 1969). A review by Fábry & Pérez-Mato (1994) reported that the instability of a large number of A_2BX_4 compounds is related to the behaviour of the 11-coordinate cation rather than to the nine-coordinate cation, and especially to the bond strength of the shorter cation–anion contact parallel to the pseudo-hexagonal *a* axis. A detailed and comparative study of this type of compound is necessary. Alkali metal fluoroberyllates have been exceptional cases of A_2BX_4-type compounds in the past, and we have recently studied them by neutron powder diffraction with refinement in *Pnma* at room temperature and 1.5 K (da Silva *et al.*, 2005). Moreover, thallium oxysalts, such as Tl_2SO_4, Tl_2CrO_4 and Tl_2SeO_4, have also been studied; the last of these undergoes a phase transition at 72 K (Friese *et al.*, 2004). The different behaviour of thallium compounds with respect to other β-K_2SO_4 compounds is a result of the

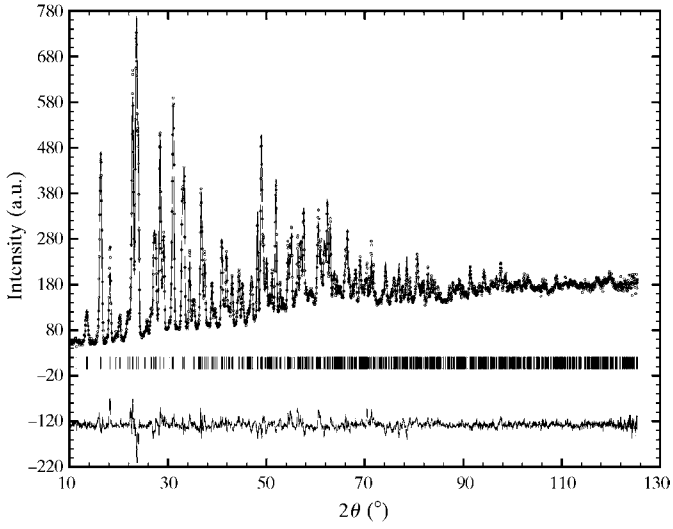

Figure 1
Plot of the Rietveld refinement result for Tl_2BeF_4 at room temperature, showing the calculated (line), observed (circle) and difference (lower) profiles.

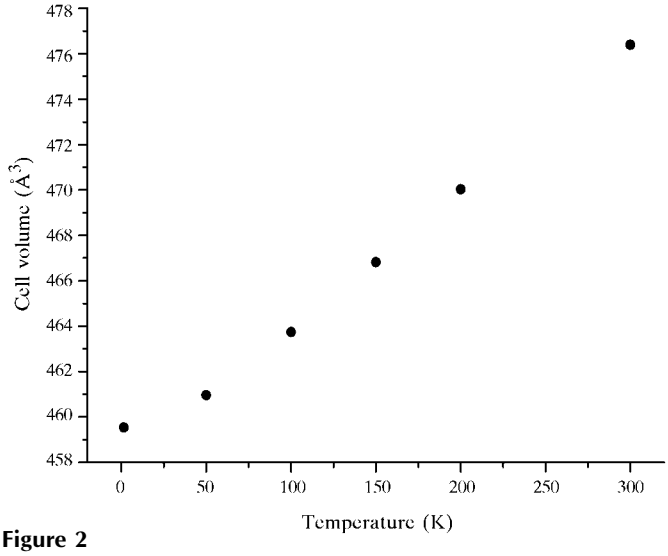

Figure 2
Variation of the unit-cell volume with temperature for Tl_2BeF_4, showing linear behaviour without anomalies.

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stereoactivity of the $6s^2$ lone pair in the Tl^I cation (Fábry & Breczewsky, 1993).

The aim of the present work is to compare the structure of Tl_2BeF_4 with the rest of this class of compounds in order to assess the role of the cations in the structural instability. The correct crystal structure of Tl_2BeF_4 has not been reported previously [only the cell parameters were reported by Arend *et al.* (1980)] and a structural phase transition has never been observed. We have measured the neutron powder diffraction patterns of Tl_2BeF_4 at room temperature and lower temperatures down to 1.5 K, and we have refined the crystal structure using the Rietveld method in space group *Pnma* for all temperatures. The fitted diffraction profile at room temperature is shown in Fig. 1 and the variation of the unit-cell volume with temperature is shown in Fig. 2. From DSC (differential scanning calorimetry) analysis and from Fig. 2, no thermal anomaly is observed. The structure of Tl_2BeF_4 consists of isolated $[BeF_4]^{2+}$ tetrahedra, with Tl^+ ions distributed between them. The cations are placed in two different cavities; one cation, within a slightly distorted bipyramidal hole, remains 11-coordinate, while the other cation, within a distorted octahedral hole, is surrounded by nine F atoms. As in other fluoroberyllates (da Silva *et al.*, 2005) and thallium selenate (Friese *et al.*, 2004), the average Be—F bond length of the fluoroberyllate anion increases at low temperature (Table 1). At variance with other compounds showing structural instability (González-Silgo *et al.*, 1997; Solans *et al.*, 1998), (i) we do not observe any significant rotation of the tetrahedra around the *b* axis, so the environment of the cations is not changed with temperature, and (ii) the bond-valence sums (Brown, 1992) at both the Tl1 and the Tl2 sites are close to 1 v.u. for the entire temperature range. Otherwise, the five F atoms nearest to Tl1 are at distances less than 3.1 Å and lie on the same side of this cation (see Fig. 3*a*), thus indicating the stereoactivity of the Tl1 lone pair, as in other thallium compounds (Fábry & Breczewsky, 1993); this situation is maintained at lower temperatures. With respect to the Tl2 environment, the stereoactivity of the lone pair is less clear, although a tendency is observed at lower temperature; at 1.5 K, the three F atoms nearest this cation are at distances that are 0.1 Å shorter than the other Tl2—F contacts and lie approximately on the same side of Tl (Fig. 3*b*).

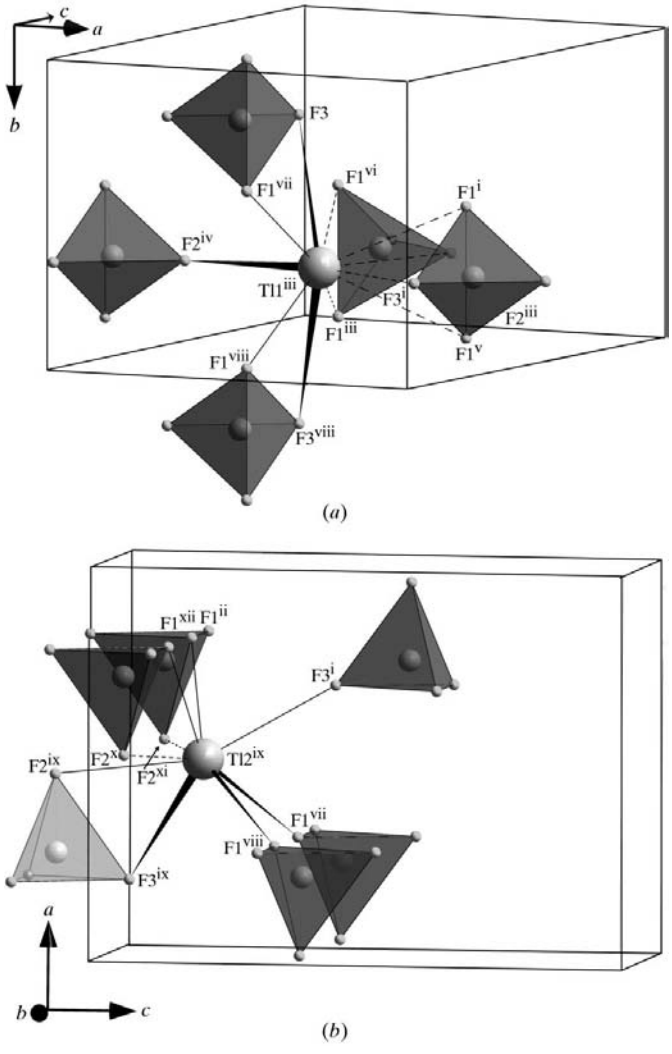

Figure 3
Arrangement of the nearest-neighbour BeF_4 tetrahedra to (*a*) 9- and (*b*) 11-coordinated Tl^+ cations, showing the shortest (thick solid lines) and longest (thin dashed lines) bonds. Intermediate bonds are drawn with thin solid lines. [Symmetry codes: (i) $1-x, \frac{1}{2}+y, 1-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (iv) $-x, \frac{1}{2}+y, 1-z$; (v) $1-x, 1-y, 1-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vii) $x, \frac{1}{2}-y, z$; (viii) $x, 1+y, z$; (ix) $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$; (x) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}-z$; (xi) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (xii) $\frac{1}{2}+x, 1+y, \frac{1}{2}-z$.]

Experimental

Tl_2BeF_4 was obtained *via* the reaction $BeF_2(s) + H_2F_2(aq) + Tl_2CO_3(s) \rightarrow Tl_2BeF_4 + CO_2 + H_2O$. BeF_2, H_2F_2 (48%) and Tl_2CO_3 were of analytical grade. After completion of the reaction at pH 7, the sample was evaporated slowly at room temperature. After a few days, a polycrystalline powder was obtained. The sample was not evaporated to dryness so as to avoid possible contamination. The polycrystalline powder was filtered off and dried. Thermal analyses were carried out on a Perkin–Elmer differential scanning calorimeter Pyris I-DSC. The sample was measured in the temperature range 98–293 K, with a warming rate of 10 K min^{-1} and a total scale sensitivity of 0.1 mW. The sample mass was 27.76 mg. This analysis showed no thermal anomaly. A helium cryostat was used in order to keep the sample at the correct temperature during the diffraction experiments. We present the data collected at 1.5, 50, 100, 150, 200 and 300 K.

Tl_2BeF_4, all temperatures

Crystal data

Tl_2BeF_4
M_r = 493.77
Orthorhombic, *Pnma*
Z = 4
Neutron radiation
Specimen shape: cylinder
50 × 10 × 10 mm
White

Data collection

Orphée reactor (Saclay, France) 3T2 line diffractometer
Specimen mounting: vanadium can
Specimen mounted in transmission mode
Scan method: step
Increment in 2θ = 0.1°

Refinement

Refinement on I_{net}
Wavelength of incident radiation: 1.2251 Å
Excluded region(s): 0 to 10°; no reflection region with a complex background shape
Profile function: pseudo-Voigt
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ = 0.01

Tl_2BeF_4 at 300 K

Crystal data

a = 7.7238 (2) Å
b = 5.90226 (17) Å
c = 10.4499 (3) Å
V = 476.39 (2) Å^3
D_x = 6.884 Mg m^{-3}
T = 300 K

Data collection

$2\theta_{min}$ = 6.3, $2\theta_{max}$ = 125.5°

Refinement

R_p = 0.036
R_{wp} = 0.048
R_{exp} = 0.076
R_B = 0.075
S = 0.63
934 reflections
35 parameters

Tl_2BeF_4 at 200 K

Crystal data

a = 7.69999 (15) Å
b = 5.86734 (11) Å
c = 10.4039 (2) Å
V = 470.03 (2) Å^3
D_x = 6.977 Mg m^{-3}
T = 200 K

Data collection

$2\theta_{min}$ = 6.3, $2\theta_{max}$ = 125.5°

Refinement

R_p = 0.042
R_{wp} = 0.055
R_{exp} = 0.076
R_B = 0.072
S = 0.73
924 reflections
35 parameters

Tl_2BeF_4 at 150 K

Crystal data

a = 7.69020 (13) Å
b = 5.84889 (9) Å
c = 10.37848 (17) Å
V = 466.82 (1) Å^3
D_x = 7.025 Mg m^{-3}
T = 150 K

Data collection

$2\theta_{min}$ = 6.3, $2\theta_{max}$ = 125.5°

Refinement

R_p = 0.047
R_{wp} = 0.063
R_{exp} = 0.076
R_B = 0.075
S = 0.83
918 reflections
35 parameters

Table 1
Average Be—F and Tl—F distances (Å) and F—Be—F angles (°) for Tl_2BeF_4 at each temperature.

Temperature (K)	Be—F	Tl—F	F—Be—F
300	1.534 (8)	3.040 (8)	109.5 (3)
200	1.537 (6)	3.022 (6)	109.47 (20)
150	1.539 (5)	3.014 (5)	109.47 (18)
100	1.546 (4)	3.004 (4)	109.47 (14)
50	1.548 (4)	2.997 (5)	109.46 (13)
1.5	1.560 (4)	2.996 (5)	109.46 (14)

Tl_2BeF_4 at 100 K

Crystal data

a = 7.68265 (11) Å
b = 5.83059 (8) Å
c = 10.35278 (15) Å
V = 463.75 (1) Å^3
D_x = 7.072 Mg m^{-3}
T = 100 K

Data collection

$2\theta_{min}$ = 6.3, $2\theta_{max}$ = 125.5°

Refinement

R_p = 0.048
R_{wp} = 0.062
R_{exp} = 0.076
R_B = 0.063
S = 0.82
913 reflections
35 parameters
$(\Delta/\sigma)_{max}$ = 0.01

Tl_2BeF_4 at 50 K

Crystal data

a = 7.67874 (9) Å
b = 5.81248 (7) Å
c = 10.32788 (12) Å
V = 460.96 (1) Å^3
D_x = 7.115 Mg m^{-3}
T = 50 K

Data collection

$2\theta_{min}$ = 6.3, $2\theta_{max}$ = 125.5°

Refinement

R_p = 0.053
R_{wp} = 0.068
R_{exp} = 0.076
R_B = 0.061
S = 0.90
905 reflections
35 parameters

Tl_2BeF_4 at 1.5 K

Crystal data

a = 7.67735 (10) Å
b = 5.80377 (8) Å
c = 10.31316 (13) Å
V = 459.53 (1) Å^3
D_x = 7.137 Mg m^{-3}
T = 1.5 K

Data collection

$2\theta_{min}$ = 7.3, $2\theta_{max}$ = 125.5°

Refinement

R_p = 0.067
R_{wp} = 0.085
R_{exp} = 0.093
R_B = 0.069
S = 0.91
901 reflections
35 parameters

Rietveld refinement of the six powder diffraction patterns was carried out with the program *FULLPROF* (Rodríguez-Carvajal, 2005) and visualization of the results was performed using the program *WINPLOTR* (Roisnel & Rodríguez-Carvajal, 2005). The experimental profiles were all modelled using a pseudo-Voigt profile shape function, with five adjustable parameters (U, V, W, η and X); initial values were obtained from the instrumental resolution parameters. After preliminary refinements to establish the scale factor, zero-point displacement, cell parameters and profile parameters, several cycles were performed to refine the atomic positions and isotropic displacement parameters. The starting values for the atomic positions were those of the β-K_2SO_4 structure, in space group *Pnma*. Space group $Pn2_1a$ was also examined, without any improvement. Owing to the poor values obtained for the agreement factors and the modulated residuals that remained after the refinements, it was necessary to apply a Fourier filtering treatment in order to model the background and to improve the results. This can be justified because from the modulated residues it has been possible to calculate the

radial distribution function of other fluoroberyllates, because of the co-existence of an amorphous phase with the crystalline material (da Silva *et al.*, 2005).

For all temperature determinations, cell refinement: *FULLPROF* (Rodríguez-Carvajal, 2005); program(s) used to refine structure: *FULLPROF*; molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *FULLPROF*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1150). Services for accessing these data are described at the back of the journal.

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