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Crystal structure and stability of Tl_2CO_3 at high pressures

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The crystal structure of dithallium carbonate, Tl_2CO_3 ($C2/m$, $Z = 4$), was investigated at pressures of up to 7.4 GPa using single-crystal X-ray diffraction in a diamond anvil cell. It is stable to at least 5.82 GPa. All atoms except for one of the O atoms lie on crystallographic mirror planes. At higher pressures, the material undergoes a phase transition that destroys the single crystal.

Comment

Pistorius & Clark (1969), Meisalo & Kalliomäki (1976), Adams *et al.* (1983), Lee *et al.* (1993) and Grzechnik & Friese (2008) reported previously on the high-pressure behaviour of Tl_2CO_3. A sequence of phase transitions at 2, 4.2 and 6.7 GPa was discovered by Meisalo & Kalliomäki (1976), in which the phases below 6.7 GPa were supposed to be structurally very similar. Adams *et al.* (1983) also observed phase transitions near 1.3 and 3.8 GPa using IR and Raman spectroscopic analyses. However, a single-crystal diffraction study demonstrated that thallium carbonate ($C2/m$, $Z = 4$) is structurally stable to at least 3.56 GPa (Grzechnik & Friese, 2008). The most likely reason for this discrepancy is that the X-ray and spectroscopic data of Meisalo & Kalliomäki (1976) and Adams *et al.* (1983), respectively, were poorly resolved and the pressures were nonhydrostatic. In this study, we continue our work on Tl_2CO_3 using single-crystal X-ray diffraction in a diamond anvil cell to characterize the postulated (Meisalo & Kalliomäki, 1976; Adams *et al.*, 1983) pressure-induced polymorphs above about 4 and 6.7 GPa.

A crystal of dithallium carbonate was compressed slowly to a pressure of 5.82 GPa. Indexing of the diffraction data, analysis of the reconstructed reciprocal space, and structure solution and refinement clearly showed that the material ($C2/m$, $Z = 4$) does not transform to a new polymorph at about 4 GPa. However, on further compression to a pressure of 7.4 GPa, no single-crystal reflections were detected. Instead, weak and very smeared incomplete Debye–Scherrer rings were visible in the diffraction diagrams on the image plate. These observations indicate that Tl_2CO_3 does undergo a pressure-induced phase transition at about 6.7 GPa (Meisalo & Kalliomäki, 1976) that also destroys the single crystal. It is thus the only transformation of those reported in the literature that we observe in our high-pressure single-crystal X-ray diffraction data under hydrostatic conditions.

As observed at ambient pressure (Marchand *et al.*, 1975) and at 3.56 GPa (Grzechnik & Friese, 2008), all atoms except for one of the O atoms lie on crystallographic mirror planes at 5.82 GPa. Two non-equivalent Tl^+ cations are in asymmetric coordination environments attributable to their electron lone pairs (E). The Tl1 cation is coordinated to seven O atoms at distances in the range 2.50 (11)–2.9 (2) Å. The coordination around the Tl2 cation includes five O atoms at distances in the range 2.42 (19)–3.4 (3) Å (Table 1). The compression mainly affects the part of the structure where the Tl^+ lone pairs are placed. A comparison with the structural data at lower pressures shows that it is the longest Tl—O distances that diminish the most, while the short distances are relatively incompressible or even increase slightly. The fact that the spread of the Tl—O distances becomes smaller on compression to 5.82 GPa indicates that the coordination environments around the Tl atoms tend to become more uniform, due to the diminished (but nevertheless still existent) stereoactivity of the electron lone pairs.

When only the Tl—O distances below 3 Å are considered, the crystal structure under ambient conditions can be viewed as a stack of corrugated layers of cations and carbonate groups along the a axis (Fig. 1). The suppression of the E pairs results in the structure losing its layered character at 5.82 GPa. This is also reflected in the fact that the Tl$\cdots$Tl distances between adjacent layers are considerably shortened with increasing pressure. Thus, the interlayer Tl1$\cdots$Tl2 and Tl2$\cdots$Tl2 distances are 3.588 (1) and 3.693 (1) Å, respectively, at ambient pressure, 3.50 (1) and 3.338 (8) Å, respectively, at 3.56 GPa, and 3.42 (2) and 3.26 (2) Å, respectively, at 5.82 GPa, indicating increasing Tl$\cdots$Tl interactions between the layers on compression. These

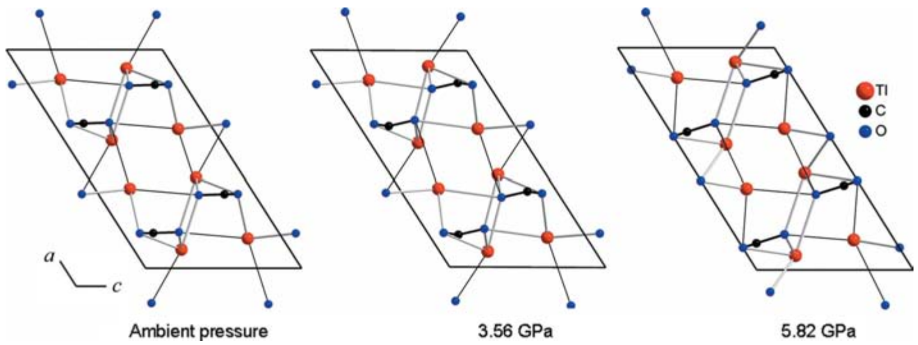

Figure 1
Crystal structures of Tl_2CO_3 at different pressures. Tl—O bond distances below 3.5 Å are shown. Distances longer than and shorter than 3 Å are drawn as thin black and thick grey lines, respectively. The C—O distances are drawn as thick black lines.

interactions might be responsible for the fact that the axial compressibility along the *a* axis (within the estimated standard deviations) changes little between 3.56 and 5.82 GPa.

The other striking aspect of the high-pressure behaviour of Tl_2CO_3 is the rotation of the carbonate groups to accommodate the electron lone pairs (Fig. 1). The pressure-induced lattice contraction and changes in the orientation of the carbonate group in Tl_2CO_3 cause a decrease of the shortest C···C distance from 3.46 Å under ambient conditions (Marchand *et al.*, 1975) to 2.4 (3) Å at 5.82 GPa. At the intermediate pressure of 3.56 GPa, this distance is 3.09 (16) Å (Grzechnik & Friese, 2008). Since experimental data for the shortest C···C distances in X_2CO_3 (X = Li, Na, K, Rb, Cs or Tl) at higher pressures are not available, the result of this study can only be compared with the theoretical work by Cancarevic *et al.* (2006), in which the C···C distances in high-pressure phases of Li_2CO_3 are expected to be below 2.5 Å.

Experimental

Crystals of Tl_2CO_3 were synthesized according to the method described by Marchand *et al.* (1975). High-pressure data were collected at 5.82 and 7.40 GPa in a Boehler–Almax-type diamond anvil cell (Boehler, 2006) at room temperature using a Stoe IPDS 2T diffractometer with Mo $K\alpha$ radiation. A 0.25 mm hole was drilled into a stainless steel gasket preindented to a thickness of about 0.08 mm. The intensities were indexed, integrated and corrected for absorption using Stoe software (*X-AREA* and *X-RED32*; Stoe & Cie, 2006). Areas of the images shaded by the diamond anvil cell were masked prior to integration. Corrections for the effect of absorption by the diamond anvil and the crystal were made using the program *ABSORB* (Angel, 2004). The ruby luminescence method (Mao *et al.*, 1986) was used for pressure calibration and a 1:1 mixture of pentane and isopentane was used as pressure medium. The hydrostatic pressure limit is 7.4 GPa (Piermarini *et al.*, 1973), higher than that of propan-2-ol, which is 4.2 GPa (Angel *et al.*, 2007), used in the previous work on this compound (Grzechnik & Friese, 2008).

Crystal data

Tl_2CO_3
M_r = 468.8
Monoclinic, $C2/m$
a = 12.02 (2) Å
b = 5.150 (2) Å
c = 7.198 (4) Å
β = 122.08 (10)°
V = 377.6 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 85.08 mm^{-1}
T = 300 K
0.10 × 0.07 × 0.05 mm

Data collection

Stoe IPDS 2T diffractometer
931 measured reflections
142 independent reflections
81 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.114

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.091
$wR(F^2)$ = 0.088
S = 2.99
142 reflections
15 parameters
6 restraints
$\Delta\rho_{\rm max}$ = 4.31 e Å^{-3}
$\Delta\rho_{\rm min}$ = −4.44 e Å^{-3}

Data at 5.82 GPa were refined with the program *JANA2006* (Petříček *et al.*, 2006). All atoms were refined isotropically. Isotropic displacement parameters of the two O atoms were restrained to be equal and the isotropic displacement parameter of the C atom was set at $0.5U_{\rm iso}$(O). Because the C-atom position could not be refined reliably, we had to introduce distance and angle restraints for the carbonate group, as in our previous study of Tl_2CO_3 (Grzechnik & Friese, 2008). The distance restraints in the carbonate group were C—O = 1.3 (2) Å with the corresponding angles restrained to values of 120 (1)°, in accordance with the ambient-pressure data published by Marchand *et al.* (1975). This restriction is justified as the carbonate groups in other M_2CO_3 compounds are rigid at high pressures (Cancarevic *et al.*, 2006).

Table 1
Selected geometric parameters (Å, °).

Tl1—O2	2.82 (18)	Tl2—O2$^{\rm v}$	2.42 (19)
Tl1—O2$^{\rm ii}$	2.50 (11)	Tl2—O1$^{\rm vii}$	3.4 (3)
Tl1—O1	2.81 (14)	Tl2—O1$^{\rm iii}$	3.2 (3)
Tl1—O1$^{\rm iii}$	2.9 (2)	C1—O2	1.31 (11)
Tl2—O2	3.07 (18)	C1—O1	1.4 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2006); cell refinement: *X-AREA*; data reduction: *JANA2006* (Petříček *et al.*, 2006); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2006*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *JANA2006*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3213). Services for accessing these data are described at the back of the journal.

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