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Tl_2CO_3 at 3.56 GPa

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The crystal structure of thallium carbonate, Tl_2CO_3 ($C2/m$, $Z = 4$), is stable at least up to 3.56 GPa, as demonstrated by hydrostatic single-crystal X-ray diffraction measurements in a diamond anvil cell at room temperature. Our results contradict earlier observations from the literature, which found a structural phase transition for this compound at about 2 GPa. Under atmospheric conditions, all atoms except for one O atom reside on the mirror plane in the high-pressure structure. The compression mainly affects the part of the structure where the nonbonded electron lone pairs on the Tl^+ cations are located.

Comment

At atmospheric pressure, thallium carbonate, Tl_2CO_3, crystallizes in the space group $C2/m$ ($Z = 4$) (Marchand *et al.*, 1975). The planar carbonate groups are parallel to [100]. Two non-equivalent Tl^+ cations are in asymmetric coordination environments, attributable to their electron lone pairs which are arranged in tunnels parallel to [010]. The coordination sphere of Tl1 includes five O atoms at distances in the range 2.67–2.82 Å and two at distances of 3.36 Å each. The coordination around the Tl2 cation includes four O atoms at distances in the range 2.67–2.69 Å, and two O atoms at distances of 3.24 and 3.60 Å. Considering only the Tl—O distances less than 3 Å, the crystal structure could be viewed as a stack of corrugated layers of cations and carbonate groups along the *a* axis (see Fig. 1). The nonbonded electron lone pairs are located between the layers.

The high-pressure behaviour of Tl_2CO_3 has already been studied using various experimental techniques by Pistorius & Clark (1969), Meisalo & Kalliomäki (1976), Adams *et al.* (1983) and Lee *et al.* (1993). Based on optical observations of the sample in a diamond anvil cell, a sequence of phase transitions to closely related crystal structures at 2, 4.2 and 6.7 GPa was postulated by Meisalo & Kalliomäki (1976). They described the X-ray powder patterns for all three polymorphs existing below 6.7 GPa as very similar. The powder pattern of the polymorph at pressures higher than 6.7 GPa was said to be 'distinctly different'. Adams *et al.* (1983) also detected phase transitions near 1.3 and 3.8 GPa using IR and Raman spectroscopies. They argued that the new polymorph occurring between 1.3 and 3.8 GPa has either a *C*- or an *I*-centred orthorhombic lattice.

Crystal structures and high-pressure behaviours of M_2CO_3 carbonates have been shown to depend on the M^+ cation (M = Li, Na, K, Rb, Cs), with the carbonate groups being rigid under extreme conditions (Grzechnik *et al.*, 2003; Cancarevic *et al.*, 2006). These compounds are of interest due to their various phase transitions (including ferroic ones) and their modulated structures (Dušek *et al.*, 2003). The structure of Tl_2CO_3 at atmospheric pressure is distinct because of the stereochemical influence of the nonbonded electron lone pair on thallium. The presence of the lone pairs could be considered a feature of covalent bonding (Marchand *et al.*, 1975; Grzechnik, 2007). The structural characterization of a new polymorph, presumably forming due to a pressure-induced phase transition at about 2 GPa (Meisalo & Kalliomäki, 1976; Adams *et al.*, 1983), thus offers an opportunity to elucidate the high-pressure behaviour of the lone pair and its participation in the increase in symmetry in Tl_2CO_3. Hence, we have performed a single-crystal X-ray diffraction study of thallium carbonate to determine its structure between 2 and 4.2 GPa.

The indexing of the single-crystal X-ray diffraction data and analysis of the reconstructed reciprocal space indicated that Tl_2CO_3 ($C2/m$, $Z = 4$) does not undergo any phase transition at about 2 GPa. Its crystal structure is stable upon compression under hydrostatic conditions at least up to 3.56 GPa at room temperature. Our observation clearly contradicts the previous reports by Meisalo & Kalliomäki (1976) and Adams *et al.* (1983). It is quite likely that these earlier studies suffered from insufficient resolution or nonhydrostatic conditions.

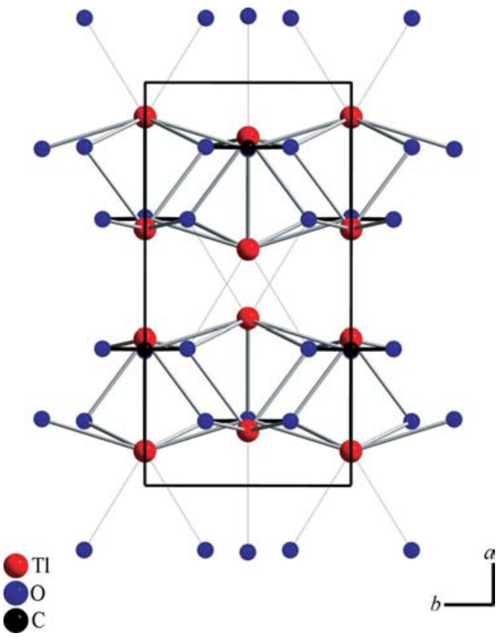

Figure 1
The crystal structure of Tl_2CO_3 at ambient pressure. The Tl—O bond distances are shown up to 3.5 Å (those less than and greater than 3 Å are drawn as thick and thin lines, respectively).

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The lattice parameters at 3.56 GPa can be compared with those at ambient pressure (Marchand *et al.*, 1975). This comparison shows that the monoclinic β angle in Tl_2CO_3 increases upon compression and that the *a* lattice parameter is the most compressible one. The large compressibility of *a* can be attributed to the fact that the changes in the interlayer Tl···O and Tl···Tl distances are the largest. The compression thus mainly takes place in the region of the structure where the Tl^+ lone pairs are located.

The shortest C···C distance in Tl_2CO_3 at ambient pressure is 3.46 Å (Marchand *et al.*, 1975), comparable with values observed in other M_2CO_3 carbonates, *viz.* 3.16 Å in Li_2CO_3 (Effenberg & Zemann, 1979) or up to 4 Å for Cs_2CO_3 (Ehrhardt *et al.*, 1980). In the high-pressure form of Li_2CO_3 at 10 GPa this distance decreases to 2.57 Å (Grzechnik *et al.*, 2003; Cancarevic *et al.*, 2006). In the case of Tl_2CO_3, the contraction of the interlayer spaces also results in a decrease in the shortest C···C distance to 3.09 Å at 3.65 GPa.

Experimental

Crystals of the title compound were synthesized according to the method described by Marchand *et al.* (1975). High-pressure data were collected at 0.69, 2.37 and 3.56 GPa in an Ahsbahs-type diamond anvil cell (Ahsbahs, 1995, 2004) 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 0.12 mm. The intensities were indexed, integrated and corrected for absorption using Stoe software (Stoe & Cie, 1998). The shape of the crystal was approximated by 20 faces using the program *X-SHAPE* (Stoe & Cie, 1998). Areas of the images shaded by the diamond anvil cell were masked prior to integration. Because of their hemispherical shape, no absorption correction was necessary for the diamond anvils. The ruby luminescence method (Mao *et al.*, 1986) was used for pressure calibration, and 2-propanol, which is hydrostatic to 4.20 GPa (Angel *et al.*, 2007) and does not react with Tl_2CO_3, was used as a pressure medium.

Crystal data

Tl_2CO_3
M_r = 468.8
Monoclinic, $C2/m$
a = 12.006 (6) Å
b = 5.2173 (7) Å
c = 7.2920 (10) Å
β = 123.01 (3)°
V = 383.0 (2) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 83.87 mm^{-1}
T = 300 K
0.10 × 0.09 × 0.06 mm

Data collection

Stoe IPDS-2T diffractometer
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1998)
T_{min} = 0.004, T_{max} = 0.013
475 measured reflections
176 independent reflections
110 reflections with $I > 3\sigma(I)$
R_{int} = 0.087

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.053
S = 2.18
176 reflections
21 parameters
4 restraints
$\Delta\rho_{max}$ = 1.65 e $Å^{-3}$
$\Delta\rho_{min}$ = −2.49 e $Å^{-3}$

Data at 3.56 GPa were refined with the program *JANA2006* (Petricek *et al.*, 2006). The two Tl atoms were refined anisotropically. 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 $0.5U_{iso}(O)$. Due to the fact that the C-atom position could not be refined reliably, we had to introduce distance restraints for the carbonate group. These were C—O1 = 1.24 Å and C—O2 = 1.28 Å, 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 (Grzechnik *et al.*, 2003; Cancarevic *et al.*, 2006).

Table 1
Selected bond lengths (Å).

Tl1—O1	2.82 (6)	Tl2—O1	2.98 (13)
Tl1—$O1^i$	2.59 (11)	Tl2—$O1^v$	3.37 (16)
Tl1—O2	2.71 (9)	Tl2—$O2^{vi}$	2.68 (7)
Tl1—$O2^{ii}$	3.16 (5)	Tl2—$O2^{vii}$	2.57 (8)
Tl1—$O2^{iii}$	3.16 (5)	Tl2—$O2^{viii}$	2.57 (8)
Tl1—$O2^{iv}$	2.71 (9)	Tl2—$O2^{ix}$	2.68 (7)

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

Data collection: *X-AREA* (Stoe & Cie, 1998); cell refinement: *X-AREA*; data reduction: *JANA2006* (Petricek *et al.*, 2006); program(s) used to solve structure: starting structural model from Marchand *et al.* (1975); 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: SQ3152). Services for accessing these data are described at the back of the journal.

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