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From volatile molecular precursor to twin-free single crystals of metallic bismuth†

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A highly volatile molecular precursor, dibismuth(II) (tetra)trifluoroacetate, was successfully utilized for the gas phase growth of twin-free single crystals of metallic bismuth. This allowed for high-quality single-crystal X-ray diffraction data to be collected, providing accurate structural parameters for elemental bismuth at ambient conditions.

Two-dimensional (2D) layered polymorphs of chemical elements have been the focus of significant attention since the discovery of graphene.¹ For example, black phosphorus, which in its exfoliated 2D form resembles graphene sheets and thus become known as phosphorene, has been broadly studied and subjected to abundant applications as anode material for lithium ion batteries and hydrogen-evolving photocatalyst.^{2,3} Since the first report in 1935,⁴ the structure of black phosphorus (Fig. 1) has been re-collected several times with improved X-ray diffraction techniques in order to obtain more precise structural data.^{5,6} The heavier Group 15 congener, bismuth, also has a very long history and in recent years was proven to own excellent applications in superconductivity and carbon dioxide conversion to fuel.^{7–10} It was found that bismuth has five different polymorphs. At ambient conditions, bismuth crystallizes with a rhombohedral symmetry (Bi-I) in the 2D

layered structure that is similar to that of black phosphorus.¹¹ At room temperature, when the pressure is increased up to 2.8 GPa, the structure of bismuth transforms to a C-centered monoclinic phase (Bi-II).¹² The solid structure of this phase resembles that of Bi-I but with shorter interlayer spacing. When the pressure is between 2.8 and 7.7 GPa, the bismuth layers start to interpenetrate and form a so-called “host-guest” structure (Bi-III).¹³ If the temperature is increased to 400–500 K and the pressure is in the range of 3–5 GPa, a high-temperature phase of bismuth with an orthorhombic structure (Bi-IV) has been detected.¹⁴ If the pressure keeps increasing, bismuth finally transforms to a body-centered cubic (bcc) structure (Bi-V).¹⁵ With the exception of Bi-I, all other polymorphs were structurally characterized by X-ray powder diffraction only.

The first structural study of Bi-I can be traced back to 1921.¹⁶ However, it is the report by Cucka and Barrett¹¹ that received special recognition over the years.¹⁷ In that work, zone-leveling technique was used to grow crystals of bismuth from melt and a combination of single-crystal and powder X-ray diffraction techniques was applied to collect the data at temperatures of 298 K, 78 K, and 4.2 K. Unit cell parameters, atomic positional parameters, and Debye-Waller temperature factors along *c* axis were derived. The bond distances and angles were also calculated but only with the standard deviation for the short Bi–Bi bond distance estimated to be 6×10^{-4} (78 K) and 12×10^{-4} Å (298 K). Since 1962, the above low-precision study remained the only source of structural information for Bi-I. That can be explained by the fact that single crystals of bismuth, especially twin-free single crystals, are hard to obtain due to this element intrinsic properties.^{18,19} Traditionally, crystals of bismuth have been always prepared from a liquid phase via melting-cooling phase transitions, using zone-leveling and Bridgman methods.^{11–15} However, among all metals, bismuth is known to have the lowest thermal conductivity, which is also anisotropic. Besides, the thermal conductivity of molten bismuth is 2.5 times larger than that of its solid phase, which leads to a strong tendency of very high supercooling. Unlike most substances which have higher density in solid than in liquid phase, molten

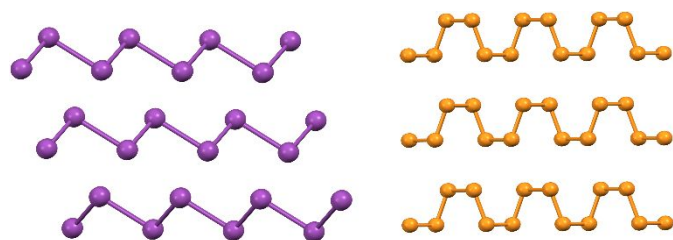


Fig. 1 The 2D layers of bismuth (left) and black phosphorus (right).

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bismuth is denser than solid. Therefore, the volume of bismuth expands by 3.32 % during melt crystallization. These factors make bismuth notorious for forming twinned crystals or so-called “hopper crystals” during crystallization processes.²⁰

Addressing the need for development of new and efficient preparation techniques to form twin-free single crystals of Bi-I, we turned to a chemical approach. In addition to physical techniques widely used to grow crystals of metals, chemical methods, such as a precursor approach, should also be considered. One of the most important classes of such precursors include metal carboxylates that have been effectively used to prepare target metal oxides or fluorides.^{21,22} However, metal carboxylates can also provide access to elemental metals under inert or reducing environments. For example, silver(I) trifluoroacetate served as a precursor to prepare pure silver in nitrogen atmosphere.²³ In addition, Shen and co-workers successfully deposited metallic bismuth films by using a mixture of two bismuth carboxylates.²⁴ Thus, metal carboxylates can function as volatile molecular precursors to prepare pure metals directly from the gas phase. Notably, in the case of bismuth, the gas-phase decomposition approach will allow to avoid the negative effect of volume expansion between metallic bismuth liquid and solid phases during crystal growth process.^{25,26}

In this work, a new gas-phase method of growing twin-free bismuth crystals has been developed. Dibismuth(II) (tetra)trifluoroacetate has been employed for the first time as a volatile molecular precursor to produce single crystals of pure metallic phase. This allowed the first single crystal X-ray diffraction study of Bi-I, using modern crystallographic techniques, to be accomplished. Accurate geometric parameters of the elemental bismuth solid state structure at two temperatures, 100 K and 298 K, are now provided.

The target crystals of Bi were synthesized by disproportionation reaction of bismuth(II) trifluoroacetate, to yield metallic bismuth and bismuth(III) trifluoroacetate by-product (Scheme 1). The starting dimetal (tetra)trifluoroacetate complex, $\text{Bi}_2(\text{TFA})_4$,^{27,28} is very volatile and can be sublimed at temperatures as low as 60 °C. In order to find optimal reaction and crystallization conditions, small-scale sublimation-deposition experiments were performed in the evacuated and sealed glass ampules placed in the temperature-gradient tube furnace under various experimental conditions (see Table S1 in ESI†). It was found that partial decomposition of $\text{Bi}_2(\text{TFA})_4$ starts at temperatures above 130 °C. To induce its complete

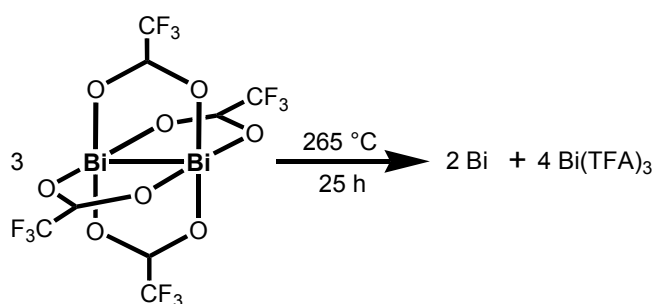
decomposition, the temperature has to be in the range of 250–265 °C. The reaction can be easily monitored by disappearance of orange dibismuth(II) (tetra)trifluoroacetate from the hot zone of the ampule accompanied by the appearance of white powdery bismuth(III) trifluoroacetate in the cold end of the ampule. Importantly, metallic bismuth crystals are formed in the middle part of the ampule and can be readily collected without the need to separate them from the by-product. The best quality bismuth crystals were grown at 265 °C in 25 hours. Note that melting temperature of bismuth is 271.5 °C, therefore a careful control of deposition temperature is critical (See ESI for more details).

Notably, the selected experimental conditions allow the formation of bismuth crystals directly from the gas phase by-passing the liquid phase. This contrasts the previously reported traditional crystallization methods that were based on melting-cooling phase transitions. In melt reactions, the volume expansion upon cooling of liquid bismuth is responsible for the formation of “stepped” and twinned crystals not suitable for accurate X-ray crystallographic analysis. In our new gas phase crystal growth method, the formation of twin crystals is avoided and well-shaped single crystals are deposited (ESI, Figs. S1, S2).

A block-shaped single crystal of bismuth, with a size of 0.12 × 0.11 × 0.06 mm, was picked up for full X-ray data collection performed at two different temperatures (100 K and 298 K, Table S2). Notably, the volume of the unit cell is slightly larger at 298 K than at 100 K, consistent with all previous studies of the thermal expansion of bismuth in the solid state.²⁹ Since bismuth is a very heavy element, it can strongly absorb the X-ray beam with an absorption coefficient as high as 124.45 mm⁻¹ (Mo K α radiation). Empirical absorption correction, such as a multi-scan method, does not work well in this case, resulting in strong artefactual electron density peaks around bismuth atoms. Therefore, numerical absorption correction was employed after indexing the crystal faces (ESI, Fig. S3).³⁰ The crystal was indexed to the same rhombohedral space group $R\bar{3}m$, as reported previously by Cucka and Barrett. A total of 3525 reflections were collected and 98.5% of those can be assigned to the same unit cell parameters setting based on CELL_NOW,³¹ indicating there is no twinning in the selected single crystal. Besides, there are no reflections with systematic absences violation or inconsistent equivalents based on refinement program SHELXTL,³² thus providing another strong evidence against twinning.

There is one symmetrically independent atomic site per unit cell in Wyckoff position 6c, plus atoms equivalent by inversion and the rhombohedral centering translations (2/3, 1/3, 1/3) and (1/3, 2/3, 2/3). Similar to black phosphorus, at ambient conditions metallic bismuth has a 2D packed layered structure. However, the 2D layers in bismuth are zig-zagged, in contrast to a gear tooth shaped layers in black phosphorus (Fig. 1). Besides, the interlayer spacing in bismuth of 4.732 Å is smaller than that in black phosphorus (5.242 Å).

Within a corrugated layer, each bismuth atom has three short Bi–Bi contacts with the same bond distance of 3.0674(3) Å (100 K) and 3.0723(4) (298 K) (Table 1). This leads to the formation of six-membered rings that resemble the classic chair



Scheme 1 Synthesis of metallic bismuth via disproportionation of $\text{Bi}_2(\text{TFA})_4$.

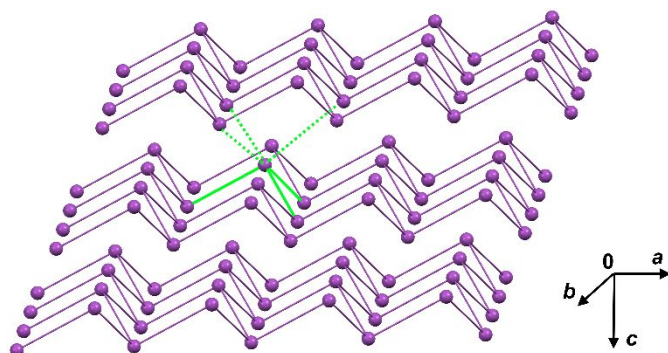


Fig. 2 Solid-state packing of bismuth along *c*-axis. Three short and three long interactions of Bi atom are shown with solid and dashed green lines, respectively.

conformation of cyclohexane (ESI, Fig. S5). Between the layers, each bismuth atom has three additional long Bi–Bi contacts (3.5207(4) Å at 100 K and 3.5294(4) Å at 298 K) with three bismuth atoms in the neighbouring layer. Altogether each bismuth atom has six metal-metal interactions, thus adopting a distorted trigonal prismatic geometry (Fig. 2). The distortion is caused by the stereoactivity of the $6s^2$ bismuth lone pair, which points its orbital lobe between the bismuth layers along the *c*-axis.

Since for the highly-absorbing crystals the unit cell parameters tend to be underestimated due to a virtual shift of reflections to lower 2θ angles, the Nelson-Riley analysis³³ was performed for metallic Bi (see ESI, Figures S6–S9 and Tables S4–S7 for more details and results). The values of corrected unit cell parameters and the Bi–Bi distances are presented in Table 1.

In summary, twin-free single crystals of metallic bismuth

Table 1 Unit cell parameters and main bond distances for the structure of metallic bismuth.

<i>T</i> (K)	100 K		298 K	
	original	N.-R. corrected	original	N.-R. corrected
<i>a</i> (Å)	4.5392(4)	4.5567(4)	4.5481(5)	4.5768(5)
<i>c</i> (Å)	11.8347(11)	11.8480(11)	11.8600(12)	11.8870(12)
<i>V</i> (Å ³)	211.18(4)	213.05(4)	212.46(5)	215.64(5)
Bi–Bi (Å)	3.0674(3)	3.0770(3)	3.0723(4)	3.0884(4)

have been grown via gas phase disproportionation reaction using volatile and easy-to-decompose molecular precursor, namely dibismuth(II) (tetra)carboxylate. This gas phase technique allowed to exclude twinning problems associated with melt-based crystallization processes used over the past decades. The high-quality single crystal of Bi-I has been structurally characterized by X-ray crystallography at room (298 K) and low (100 K) temperatures. The comprehensive and precise structural data of the metallic bismuth ambient phase, which were not available prior to this work, should provide the

new standard for reference and comparison of Bi–Bi bonding interactions in various low-valent inorganic and organometallic compounds of bismuth. Furthermore, the developed relatively simple crystal growth method of metallic bismuth from the gas phase should expand investigations of semiconducting, superconducting and thermoelectric properties of crystalline bismuth as well as facilitate the search for novel applications of bismuthene.

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Conflicts of interest

The authors declare no conflict of interest.

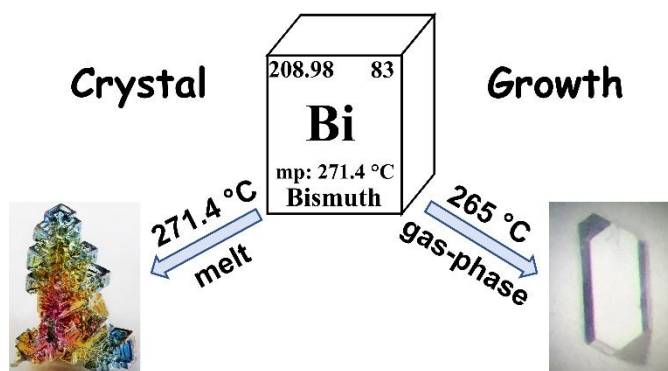
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A new gas-phase method employing volatile metal carboxylate precursor to grow twin-free bismuth single crystals is reported.