β-Technetium: An allotrope with a nonstandard volume-pressure relationship

Emily Siska [1], Dean Smith [2], Christian Childs [3], Daniel Koury [1], Paul M. Forster [1], Keith V. Lawler [1,*] and Ashkan Salamat [3,†]

[1] Department of Chemistry & Biochemistry, University of Nevada Las Vegas, Las Vegas, Nevada 89154, USA
[2] HPCAT, X-ray Science Division, Argonne National Laboratory, Illinois 60439, USA
[3] Department of Physics & Astronomy, University of Nevada Las Vegas, Las Vegas, Nevada 89154, USA

(Received 11 February 2021; revised 24 March 2021; accepted 4 May 2021; published 9 June 2021)

We report the synthesis and structure of the second allotrope of technetium, β-Tc. Transformative pathways are accessed at extreme conditions using the laser-heated diamond anvil cell and confirmed with *in situ* synchrotron x-ray diffraction and Raman spectroscopy. β-Tc is fully recoverable to ambient conditions, although counter to our DFT calculations predicting a face-centered-cubic lattice, we observe a tetragonal structure ($I4/mmm$) that exhibits further tetragonal distortion with pressure. β-Tc has an expanded volume relative to the hcp ground state phase, that when doped with nitrogen has an unexpected volume lowering. Such anomalous behavior is possibly indicative of a rare electronic phase transition in a 4d element.

DOI: 10.1103/PhysRevMaterials.5.063603

I. INTRODUCTION

Technetium's radioactivity and natural scarcity have led to limited experimental studies, especially at elevated pressures and temperatures. A more complete understanding of technetium would provide valuable insight to many other transition metals given its central position in the transition-metal block of the periodic table. Owing to the difficulty in working with technetium, its group-7 neighbor rhenium is often used as a stand-in [1]. Both technetium and rhenium have only one confirmed allotrope, an hcp metallic phase. Hcp Tc is known to be stable to the melt at ambient pressure and to 67 GPa at 300 K [2,3] while hcp Re is stable against 100 s of GPa of compression and predicted to be stable beyond the TPa regime [4,5]. In contrast, the other group-7 element manganese has five reported allotropes. Two of its polymorphs (α and β) have complicated crystal structures and α-Mn is a well-known antiferromagnet (AFM) [6–8]. Another polymorph, γ-Mn, is fcc in its 1368–1406 K stability window [9] but distorts into a bct phase below its Néel temperature due to its antiferromagntism [10,11]. When stabilized at ambient conditions, γ-Mn exhibits an expanded lattice – as much as a 10% increase in atomic volume is observed [12].

There have been reports of chemical synthesis and purification routes using either thin film grown epitaxially by ion sputtering or thermal decomposition involving Tc that have suggested a cubic (fcc) allotrope [13,14]. However, these results are treated with caution, as these studies have conflicting and unrepeatable results and their experimental procedures show that they are not within a single component composition. This is further evidenced by conflicting reports of elemental reactions between Tc and anion species, e.g., C, N, that all report similar unit cell parameters of approx. 3.98 Å—comparable to the unconfirmed reports of fcc Tc [2]. For Tc carbides, a recent publication refuted the existence of the experimentally reported high-temperature cubic phase of TcC based on evolutionary algorithm simulations [13]. It concludes that Tc_6C, the most stable carbide on the convex hull, could not be made, and that the cubic phase observed is a high-temperature cubic phase of elemental technetium which becomes thermodynamically stable above 1775 K. Such inconsistencies arise from elemental Tc not found naturally in the earth's crust and its purification being challenging.

In this paper, we unequivocally confirm the existence of the second allotrope of Tc that we designate as β-Tc. β-Tc is made at high-temperature, high-pressure conditions and is recoverable to ambient conditions without a substrate. X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM) measurements imply this is a pure allotrope of Tc with anomalous behavior not previously characterized. Room-temperature XRD reveals an expanded volume compared to the ground-state hcp phase and a tetragonal distortion while further compression reveals anomalous volume-pressure relations with a continuous deviation from an fcc motif. Density functional theory (DFT) simulations apt for a simple elemental metal are incongruent with the experimental results, indicating there is a complex underlying electronic behavior to this allotrope. We have synthesized β-Tc in two different chemical environments, Ar and N_2, and we note differences with their respective structural responses with pressure.

II. METHODS

Caution! ^{99}Tc is a weak β emitter (E_{max} = 293 KeV) with a half life of 200 000 years and no stable isotopes. Therefore, any manipulation of the material was performed in a posted radio-materials laboratory. All efforts followed locally approved handling and monitoring procedures for the specific radioisotope. Details on the containment of samples can be found in the Supplemental Material [15].

*keith.lawler@unlv.edu
†salamat@physics.unlv.edu

