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The crystallographic stability and anisotropic compressibility of *C*54-type $TiSi_2$ under high pressure

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ABSTRACT

In situ synchrotron X-ray powder diffraction experiment on $TiSi_2$ has been performed using a diamond anvil cell at ambient temperature. The present experimental results showed that the structure of *C*54-type $TiSi_2$ is stable in the experimental pressure range up to around 52 GPa. The compressibility of *C*54-type $TiSi_2$ under high pressure presents anisotropic behavior. The compressibility along the *a*-, *b*- and *c*-axes has an approximate ratio of 6:5:4. And the anisotropic compressibility of the studied crystal is discussed in terms of the crystallography stacking. The *c*/*a* and *b*/*a* axial ratios both increase as the pressure increases. With pressure increasing, the *c*/*a* shows a tendency of approaching the ideal value, but the *b*/*a* deviates from the ideal value. The pressure–volume data of *C*54-type $TiSi_2$ were fitted to a Birch–Murnaghan equation of state, which yielded a bulk modulus of $B_0=155$ (2) GPa.

1. Introduction

Compounds with the general formula MSi_2, where M is an early transition metal, are of great interest in physics [1,2] and materials science [3,4]. The body-centered tetragonal $C11_b$ ($MoSi_2$), hexagonal *C*40 ($CrSi_2$, VSi_2, $NbSi_2$ and $TaSi_2$), face centered orthorhombic *C*54 ($TiSi_2$) and side centered orthorhombic *C*49 ($ZrSi_2$, $HfSi_2$) structures are commonly observed in the disilicides of group IV–VII transition metals. $TiSi_2$ is considered to be the most technologically important in microelectronic and structural materials on account of its good compatibility with standard silicon integrated circuit and low electrical resistivity [5]. Titanium disilicide ($TiSi_2$) can exist in two different crystallographic phases: *C*49 and *C*54 [6]. In the previous studies, it is assumed that the *C*54-type phase of $TiSi_2$ is the thermodynamically stable ground state phase while the *C*49-type phase is considered to be metastable. However, *C*49-type phase $TiSi_2$ is the first phase formed during the solid phase reaction between Ti and Si and then transforms to the low resistivity *C*54 phase [7]. The kinetics and mechanism of the polymorphic transformation in $TiSi_2$ thin films from *C*49-type to *C*54-type was studied by Ma and Allen [8]. The experimental results exhibited a strong correlation between transformation temperature and film thickness, and between transformation temperature and transformation velocity.

The localized epitaxial growth of *C*54 and *C*49 $TiSi_2$ on (111) Si was studied by Fung et al. [9]. The experimental results showed that the interfacial dislocations exist and the dislocation spacings were found to vary from 170 to 660 Å. Since the lattice mismatch as well as the different thermal expansion coefficients between the thin film and the substrate always leads to strain, it is important to investigate how pressure will affect the crystal structures and consequently the chemical and physical properties of these functional materials.

Besides a lot of experimental researches, $TiSi_2$ has also been extensively studied from the theoretical point of view. Meglio et al. have performed tight binding molecular dynamics calculation with reasonable accuracy to investigate the structural and electronic properties [10–12]. The elastic constants and equilibrium structural parameters of *C*54 phase of $TiSi_2$ have been investigated by means of a full potential linear muffin-tin method using the local density approximation and generalized gradient approximation [13]. In order to investigate the polymorphic structural properties of $TiSi_2$, C. Colinet et al. calculated by means of a first principle density functional theory approach the total energies of the *C*40, *C*49 and *C*54 crystal structures. And it was shown that the *C*49 structure is the most stable at $T=0$ K whereas the experimentally observed *C*54 structure was found to be less favorable [14].

Detailed experimental studies on the crystal structure properties of *C*54-type $TiSi_2$, however, have been lacking. External pressure is well known to provide a powerful method of tuning the arrangement of atoms and the consequent properties of the materials [15,16], Recently, first principle density functional theory calculation revealed that the *C*49-type phase is more stable than

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*C*54-type phase at sufficiently low temperature. And the difference in bulk free energy between the two phases, i.e., the driving force of the transition, is quite small, which has been estimated to be within 0.02–0.05 eV/atom [17,18]. Pressure is also a thermodynamic parameter, which could affect the crystal structure stability, so we are considering if the crystallographic structure is still stable of intermetallic compound $TiSi_2$ under high pressure. Therefore, the structural evolution behavior of $TiSi_2$ under high pressure was investigated by using angle dispersive X-ray diffraction (ADXRD) techniques.

2. Experimental

The sample was found to be in a single phase of face-centered orthorhombic structure with the lattice constants $a=8.2680$ (3), $b=4.8002$ (1) and $c=8.5521$ (6) Å, compared well with results of Refs. [12,19–21]. ADXRD patterns were collected using a focused synchrotron beam at the X17C beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The experiment was conducted with a monochromatic beam of 0.3651 Å. A symmetric diamond anvil cell (DAC) with a diamond culet size of 300 μm was used to apply the pressure. T301 stainless steel with a thickness of 300 μm and a pre-indentation thickness of 50 μm was served as gasket material. A hole of 120 μm diameter was drilled using laser drilling machine. The silicone oil was used as a pressure transmitting medium. The x-ray diffraction patterns at certain pressure were collected for 20 min by means of an online CCD detector. A few ruby chips were loaded at different positions of the sample for pressure determination. The experimental pressures were determined by the pressure-induced fluorescence shift of ruby [22].The two-dimensional diffraction rings were integrated into one-dimensional XRD patterns by using the FIT2D program [23]. The XRD patterns of $TiSi_2$ were analyzed with Rietveld refinement by using the GSAS program package [24] with user interface EXPGUI [25].

3. Results and discussion

The *C*54-type $TiSi_2$ crystallizes in the face centered orthorhombic structure with space group *Fddd*. Each unit cell contains eight Ti atoms and 16 Si atoms. Si atoms locate at 8*a* Wyckoff positions and Si atoms lie in 16e positions with the atom position parameter *x*. The crystal structure and three viewing directions are shown in Fig. 1. The pressure dependence of the lattice constants *C*54-type $TiSi_2$ is shown in Fig. 2. It is observed that all the three lattice constants decrease with pressure increasing. Fig. 3 exhibited the axial compressibility as a function of pressure. Here we define axial compressibility as the lattice parameter under high pressure versus the lattice parameter measured at ambient conditions. The axial compressibility is different along different axes and the *a*-axis is more compressible compared to the *b*-axis and *c*-axis under high pressure. The relation of the compressibility values has no abnormality under high pressure. The compressibility along the *a*, *b* and *c* axes has an approximate ratio of 6:5:4 , which indicate that *C*54-type $TiSi_2$ is an anisotropic crystallographic material.

From the stacking point of view, the structure of *C*54-type $TiSi_2$ can be regarded as an alternative stacking of nearly hexagonal $TiSi_2$ layers paralleling to the (001) plane, in which a Ti atom is six-fold coordinated with Si atoms while a Si atom is coordinated with three Ti atoms and three Si atoms, topologically similar to the (110) planes in the body-centered cubic (BCC) structure. Each layer is shifted half-way along the side of the hexagon with respect to the neighboring lattice planes, yielding an *ABCDABCD* stacking sequence as shown in the inset of Fig. 3. The *B* layer is rotated

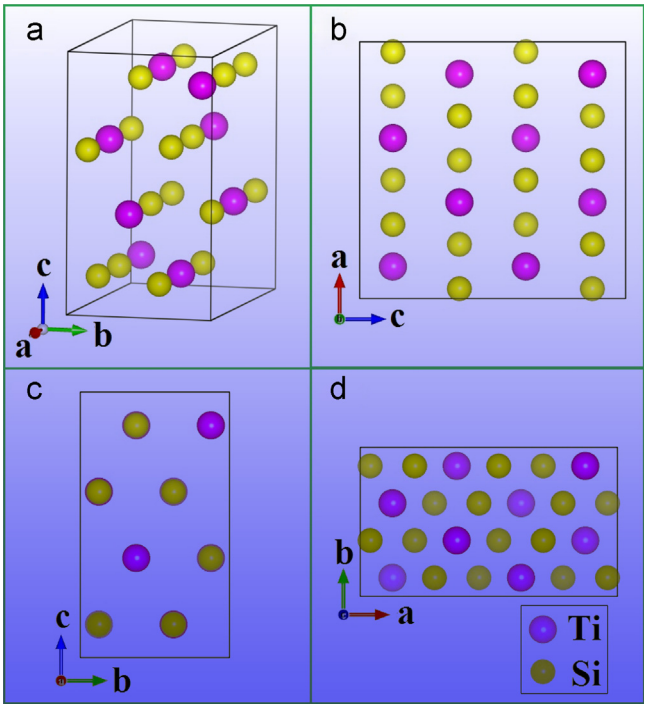

Fig. 1. (a) The schematic crystal structure of unit cell, (b)–(d): three axial direction view for *C*54-type $TiSi_2$.

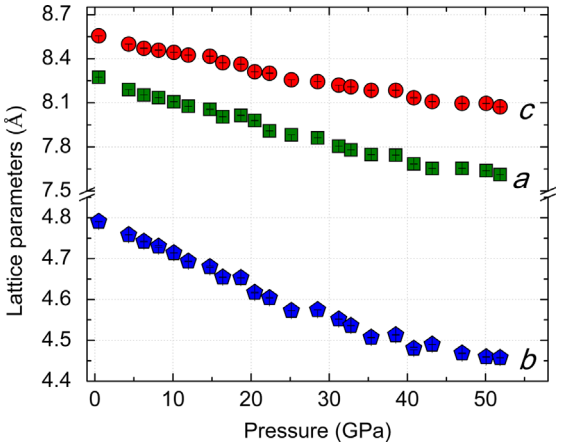

Fig. 2. Pressure dependence of the lattice parameters of *C*54-type $TiSi_2$.

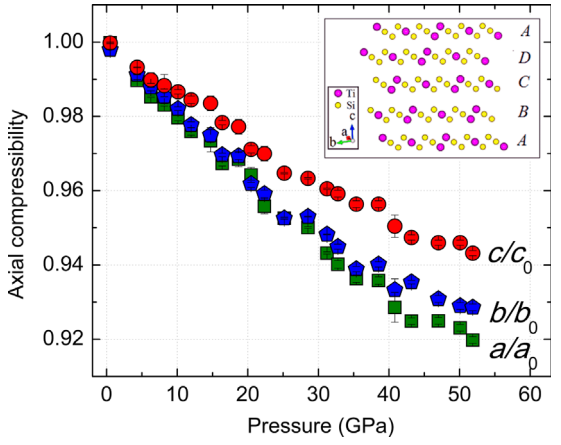

Fig. 3. The trend of axial compressibility with pressure of *C*54-type $TiSi_2$. The inset shows the layers stack of *C*54-type $TiSi_2$.