Pressure and Temperature Dependent Structure Of Zircon Type \text{ThGeO}_4

S. N. Achary$^1$, S. J. Patwe$^1$, A. K. Tyagi$^1$, P. P. Bose$^2$, R. Mittal$^2$, A. B. Shinde$^2$, P. S. R. Krishna$^2$, S. L. Chaplot$^2$, C. Narayana$^3$, G. K. Pradhan$^3$, S. Banik$^4$ and S. K. Deb$^4$

$^1$Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400085, India
$^2$Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085, India
$^3$Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, 560064, India
$^4$Indus Synchrotrons Utilization Division, Raja Ramanna Centre for Advanced Technology, Indore, 452013, India

E-mail: sachary@barc.gov.in

Abstract. Herein we report the results of high pressure diffraction studies of zircon type \text{ThGeO}_4. \text{ThGeO}_4 exhibits anisotropic compressibility with the average compressibility along $a$-axis ($20.8 \times 10^{-4}$/GPa) larger than that along $c$-axis ($9.98 \times 10^{-4}$/GPa). Fitting the pressure dependence unit cell volume to 3rd order Birch-Murnaghan equation of states, the zero pressure bulk modulus ($K_0$) and volume ($V_0$) of 166(5) GPa and 341.6(3) Å$^3$, respectively have been obtained. Preliminary studies on temperature dependent neutron and x-ray diffraction studies on \text{ThGeO}_4 revealed anisotropic expansion behaviour with larger expansion coefficient along $c$-axis compared to $a$-axis. No structural transition under temperature or pressure is observed in between ambient pressure to 10 GPa and in the temperature range of 25 to 1273K.

1. Introduction

Zircon type materials draw a significant research attention for their interesting optical properties and technological applications as solid state laser and scintillator. The zircon type materials often show low thermal expansion coefficients, significantly higher bulk modulus and high radiation stabilities, and these properties make them relevant for several important applications, like waste immobilization, host for minor actinide transmutations in nuclear energy industry [1]. The pressure dependent structural studies of the zircon type materials indicate transformations to denser scheelite and post scheelite type structures at higher pressure [2-4]. Though the nature and magnitude of the thermal expansion or compressibilities of a large number of zircon type materials have been reported in literature, the detailed analyses of the crystal structure with variations in temperature or pressure are relatively under explored in many cases.

A number of silicates of tetravalent cation crystallize in zircon type structure, however the analogous germanates preferentially crystallize in scheelite type structure [5]. Interestingly, the germanates of
thorium exhibit dimorphic behavior depending on preparation conditions [6]. High pressure studies on the scheelite type ZrGeO₄ and HfGeO₄ show no other polymorphic transformation up to 20 GPa [5]. Higher bulk moduli compared to analogous tungstates and molybdates are observed for scheelite type ZrGeO₄ (238 GPa) and HfGeO₄ (242 GPa) [5]. Recent high pressure Raman spectroscopic investigations on ZrGeO₄ indicate a possible structural phase transition around 12 GPa [7]. High pressure studies revealed a zircon-scheelite-fergusonite structural transition sequence for zircon type ThGeO₄ and scheelite-fergusonite structural transition for scheelite type ThGeO₄ [8]. Bulk moduli for both scheelite and zircon type ThGeO₄ are about 184 and 186 GPa which are significantly lower than zircon (ZrSiO₄) and scheelite type ZrGeO₄. In order to correlate the structural parameters with the thermal expansion and compressibilities detailed diffraction studies under non ambient pressure and temperature are carried out and the results are given in this manuscript.

2. Experimental

The zircon type ThGeO₄ was synthesized by repeated solid state reaction of dry Th₂O₃ and GeO₂ around 900°C. The product was characterized by powder X-ray diffraction (XRD) using CuKα radiation and powder neutron diffraction (ND) using neutrons of wavelength 1.249 Å. High pressure X-ray diffraction studies were carried out using DAC (diamond anvil cell) at Elettra Synchrotron radiation source. Monochromatic X-ray wavelength of 0.688 Å was used and the diffraction data were collected using MAR 3450 image plate. Gold was used as pressure marker in the high pressure experiments. The diffraction data were converted to 2D digital data using Fit2D [9]. The observed diffraction data at different temperature or pressure were analyzed by Rietveld method using Fullprof-2K software package [10]. The temperature dependent studies above ambient temperature (in between 300 to 1273 K) were carried out by variable temperature X-ray diffraction method using Philips X-Pert Pro diffractometer coupled with Anton Parr high temperature attachment while below ambient temperature (25-300K) were carried by variable temperature neutron diffraction method, at Dhruva Research Reactors, Trombay.

3. Results and Discussions

The formation of zircon type ThGeO₄ was confirmed by Rietveld refinement of the observed XRD and ND data using the earlier reported structural data [5,8]. The refined unit cell parameters obtained from the ambient temperature powder ND data are: a = 7.2399(1), c = 6.5425(2) Å and V = 342.93(2) Å³, which are in good agreement with the earlier reported values [5,8]. Final Rietveld refinement plot and other structural parameters for ThGeO₄ are shown in figure 1. The crystal structure of zircon type ThGeO₄ is made up with the chains of alternate ThO₄ polyhedra (bisdisphenoid) and GeO₄ (tetrahedra) along c-axis. These chains are joined together by sharing other edges of the ThO₄ polyhedra along a- and b-directions. The analyses of structural parameters revealed that the ThO₄ bisdisphenoid is made up of two sets of four equivalent Th-O bonds of lengths 2.359(1) and 2.485(1) Å. Similarly, the tetrahedral GeO₄ unit has four equivalent Ge-O bonds 1.748(1) Å. High pressure XRD patterns recorded in the pressurizing conditions were analyzed for their crystal structure. The observed powder XRD patterns at some representative pressures are shown in figure 2a. The diffraction data at ambient pressure indicate characteristic reflections of the zircon type ThGeO₄ as well as reflections due to Au (used as pressure marker) and bcc-Fe (gasket). The pressure was determined from the observed unit cell parameters and equation of state (eos) of Au. The profile shape of Au indicates the pressure is hydrostatic up to about 10 GPa and beyond it becomes anhydrostatic. The prominent reflections of zircon type ThGeO₄ are observed up to 10.3 GPa. The observed XRD pattern at lowest pressure was refined using the position coordinates of the ambient temperature and pressure data. The Rietveld refinement was carried out by considering three phases, pure Au, bcc-Fe and zircon type ThGeO₄ together. Unit cell parameters and oxygen position coordinates were refined along with the overall thermal parameters. The XRD data recorded at high pressure were successively
refined using the structural parameters of the previous pressure data. The refined structural parameters for ThGeO$_4$ at different pressures are given in table 1. Rietveld refinement plot for zircon type ThGeO$_4$ at 6.4 GPa is shown in figure 2b.

![Figure 1](image1.png)

**Figure 1.** Rietveld refinement plot of powder neutron diffraction data of ThGeO$_4$ at 300K (Rp = 3.75, Rwp = 4.97, and $\chi^2 = 1.83$). Tetragonal, Space group: I4$_{1}$/amd (No. 141); Th: 4a (0,3/4,1/8); Ge: 4b (0,1/4,3/8) and O: 16h (0,y,z), $y = 0.4309(2)$, $z = 0.1981(2)$.

![Figure 2a](image2a.png)

**Figure 2a.** Evolution of XRD patterns with pressure.

![Figure 2b](image2b.png)

**Figure 2b.** Rietveld refinement plot of XRD data at 6.4 GPa.

The unit cell volume at different pressures were fitted with the 3rd order Birch-Murnaghan eos and is depicted in figure 3. The eos parameters are also included in figure 3. The zero pressure volume and bulk modulus obtained from the eos are 341.6(3) Å$^3$ and 166(5) GPa. The observed bulk modulus for zircon type ThGeO$_4$ (166(5)) GPa is smaller compared to that reported earlier [8]. The average axial compressibility between the 1.8 and 10.3 GPa are: $\beta_a = 20.8 \times 10^{-4}$/GPa and $\beta_c = 9.98 \times 10^{-4}$/GPa.

Preliminary temperature dependent studies revealed an anisotropic expansion with higher coefficient of expansion along c-axis compared to a-axis. The observed unit cell parameters at 1273 K are: $a = 7.2602(1)$, $c = 6.5808(2)$ Å and at 25K are: $a = 7.2394(2)$, $c = 6.5393(2)$ Å. The close behavior of expansion and compressibility behavior are reflected from the increase axial ratio ($c/a$) with temperature or pressure. The $c/a$ increases from 0.903 to 0.906 as the temperature increase from 25 K to 1273 K, while the $c/a$ increases from 0.905 to 0.913 as the pressure increases from 1.8 to 10.3 GPa. The origin of the anisotropy in expansion or compression is related to the crystal structure of ThGeO$_4$. As mentioned earlier, structure of ThGeO$_4$ has chains of edge shared ThO$_6$ and GeO$_4$ units along the c-axis. This arrangement causes larger inter-cation repulsion due to the proximity of the highly charged Th$^{4+}$ and Ge$^{4+}$ ions along the c-axis. This is reflected in the higher expansion and lower compressibility of c-axis compared to a-axis. The higher expansion and lower compressibility of c-axis compared to a-axis causes an increase in c/a with both temperature as well as pressure.
Table 1. Structural parameters of zircon type ThGeO$_4$ at different pressure.

| $P$ (GPa) | $a$ (Å)   | $c$ (Å)   | $V$ ($\AA^3$) | $Oyz$ | $Oz$ | $B_m$ ($\AA^3$) |
|-----------|-----------|-----------|----------------|-------|------|-----------------|
| 1.79      | 7.205(1)  | 6.518(2)  | 338.4(1)       | 0.437(2) | 0.205(2) | 2.8(5)          |
| 2.34      | 7.195(2)  | 6.514(3)  | 337.2(2)       | 0.432(2) | 0.198(2) | 3.0(9)          |
| 2.53      | 7.193(2)  | 6.506(2)  | 336.6(2)       | 0.435(2) | 0.203(2) | 2.6(5)          |
| 3.35      | 7.177(2)  | 6.500(3)  | 334.8(2)       | 0.433(2) | 0.199(2) | 2.2(6)          |
| 4.50      | 7.156(2)  | 6.491(3)  | 332.4(2)       | 0.435(2) | 0.202(2) | 1.3(5)          |
| 6.42      | 7.130(3)  | 6.475(4)  | 329.2(3)       | 0.437(3) | 0.201(4) | 3.7(1.0)        |
| 8.42      | 7.102(2)  | 6.459(3)  | 325.7(2)       | 0.436(2) | 0.199(3) | 4.4(8)          |
| 9.91      | 7.081(4)  | 6.462(6)  | 324.0(4)       | 0.435(4) | 0.197(4) | 6.0(1.4)        |
| 10.27     | 7.078(8)  | 6.463(12) | 323.7(8)       | 0.435(4) | 0.197(5) | 8.02(3.0)       |

Figure 3. Unit cell parameters of ThGeO$_4$ at different pressure (solid lines show eos fit). eos parameters $V_o = 341.6(3) \AA^3$, $K_o = 166(5)$ GPa, $K' = 4.0$, $K'' = -0.02342$

4. Conclusions
The variation of crystal structure of zircon type ThGeO$_4$ with pressure and equation of state have been investigated by in situ high pressure X-ray diffraction. Anisotropic compressibility and expansion behavior is concluded from the HPXRD and variable temperature structural studies.

5. References
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