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Pressure and Temperature Dependent Structure Of Zircon Type ThGeO₄

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Abstract. Herein we report the results of high pressure diffraction studies of zircon type ThGeO₄. ThGeO₄ exhibits anisotropic compressibility with the average compressibility along *a*-axis (20.8×10^{-4} /GPa) larger than that along *c*-axis (9.98×10^{-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) Å³, respectively have been obtained. Preliminary studies on temperature dependent neutron and x-ray diffraction studies on ThGeO₄ 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

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thorium exhibit dimorphic behavior depending on preparation conditions [6]. High pressure studies on the scheelite type ZrGeO_4 and HfGeO_4 show no other polymorphic transformation up to 20 GPa [5]. Higher bulk moduli compared to analogous tungstates and molybdates are observed for scheelite type ZrGeO_4 (238 GPa) and HfGeO_4 (242 GPa) [5]. Recent high pressure Raman spectroscopic investigations on ZrGeO_4 indicate a possible structural phase transition around 12 GPa [7]. High pressure studies revealed a *zircon-scheelite-fergusonite* structural transition sequence for zircon type ThGeO_4 and *scheelite-fergusonite* structural transition for scheelite type ThGeO_4 [8]. Bulk moduli for both scheelite and zircon type ThGeO_4 are about 184 and 186 GPa which are significantly lower than zircon (ZrSiO_4) and scheelite type ZrGeO_4 . 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

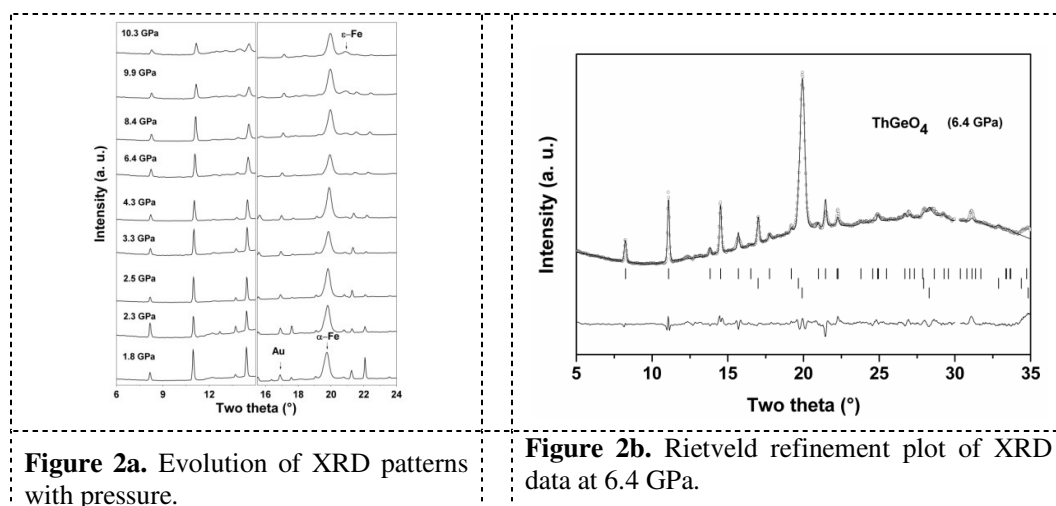
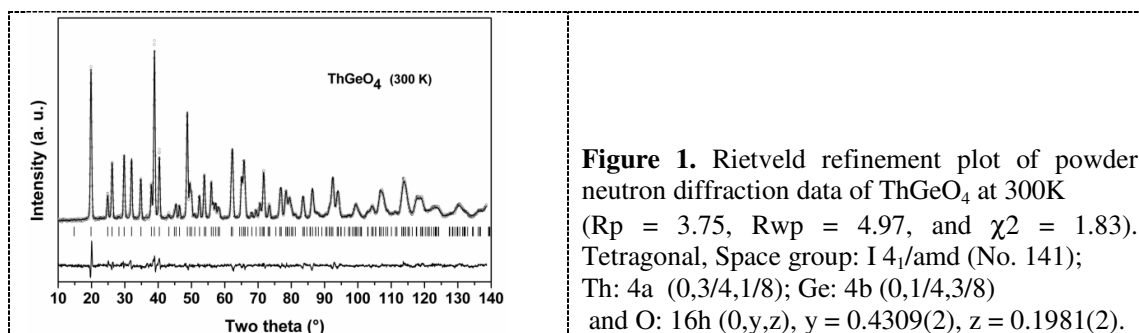
The zircon type ThGeO_4 was synthesized by repeated solid state reaction of dry ThO_2 and GeO_2 around 900°C. The product was characterized by powder X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation and powder neutron diffraction (ND) using neutrons of wavelength 1.249 Å. High pressure X-ray diffraction studies were carried out using DAC (diamond anvil cell) at *Elettra* Synchrotron radiation source. Methanol-Ethanol mixture was used as pressure transmitting medium. Monochromatic X-ray wavelength of 0.6888 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 ThGeO_4 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 ThGeO_4 are shown in figure 1. The crystal structure of zircon type ThGeO_4 is made up with the chains of alternate ThO_8 polyhedra (bisdisphenoid) and GeO_4 (tetrahedra) along c -axis. These chains are joined together by sharing other edges of the ThO_8 polyhedra along a - and b -directions. The analyses of structural parameters revealed that the ThO_8 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 GeO_4 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 ThGeO_4 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 ThGeO_4 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 ThGeO_4 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 ThGeO₄ at different pressures are given in table 1. Rietveld refinement plot for zircon type ThGeO₄ at 6.4 GPa is shown in figure 2b.



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) Å³ and 166(5) GPa. The observed bulk modulus for zircon type ThGeO₄ (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 ThGeO₄. As mentioned earlier, structure of ThGeO₄ has chains of edge shared ThO₈ and GeO₄ units along the *c*-axis. This arrangement causes larger inter-cation repulsion due to the proximity of the highly charged Th⁴⁺ and Ge⁴⁺ 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*- compared to *a*-axis causes an increase in *c/a* with both temperature as well as pressure.

Table 1. Structural parameters of zircon type ThGeO₄ at different pressure.

P (GPa)	a (Å)	c (Å)	V (Å) ³	O y	O z	B_{ov} (Å) 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)	2.0(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)	0.200(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)

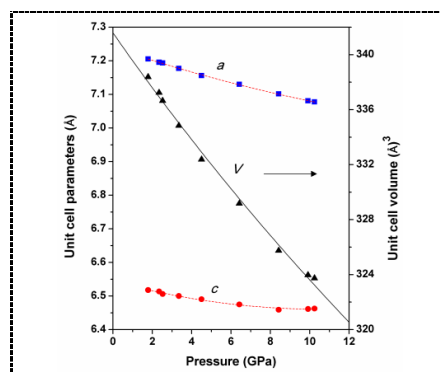


Figure 3. Unit cell parameters of ThGeO₄ at different pressure (solid lines show *eos* fit). *eos* parameters
 $V_0 = 341.6(3) \text{ \AA}^3$, $K_0 = 166(5) \text{ GPa}$, $K' = 4.0$, $K'' = -0.02342$

4. Conclusions

The variation of crystal structure of zircon type ThGeO₄ 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.

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