Synchrotron based XRD study on nano crystalline SnO$_2$ under pressure

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Abstract. Results of in-situ high pressure x ray diffraction measurements on 5 nm SnO$_2$ nanoparticles are reported. The ambient rutile phase remains stable up to the pressure of 18.1 GPa. However, beyond 19 GPa, the diffraction pattern shows new diffraction peaks indicating the presence of structural phase transition in the material. These new peaks could be assigned to cubic structure. The coexistence of both phases could be seen over a large pressure region indicating the sluggishness of the transition.

1. Introduction

In the last few years the scientific community has cherished the technical potential of nano sized (1-100 nm) clusters or particles of various semiconductors, elemental solids and compounds. These entities often have different physical and chemical properties than their bulk counterpart as the number of atoms or molecules on their surface can be comparable to that inside the particles. For example, a number of semiconductors prepared in nano size exhibit particle size dependence of optical and electronic properties. The studies on phase transitions in nanocrystalline materials under pressure can reveal new types of nucleation and growth dynamics and transition paths as compared to the bulk. The issue of their structural stability against pressure is of considerable interest from fundamental point of view also. There are number of research papers on the studies of phase stability of nano structured semiconductors such as CdSe [1], Si[2], CdS [3], ZnS [4], ZnO [5], PbS [6] etc. under pressure. Results of these measurements clearly show a trend that, with the decrease in the particle size the transition pressure increases in all these semiconductors, and the compressibility increases with decreasing particle size. However, there are few compounds i.e. Fe$_2$O$_3$ [7], TiO$_2$ [8], CeO$_2$ [9] where the phase transition pressure is lowered than their bulk counterpart. The reason for the decrease in the transition pressure was suggested as the large volume collapse at the transition. The thermodynamic considerations regarding the phase stability of these materials reveals that mainly three factors namely volume collapse, surface energy difference and the difference in the internal energy govern the transition pressure in nanocrystals as compared to their bulk counterpart. Tin dioxide SnO$_2$, yet another technologically important semiconductor crystallizes in the rutile-type structure. Rutile is tetragonal with space group $P4_2/mnm$ and $Z=2$. A basic building block of the structure is the SnO$_6$ octahedra; edge-linked chains of octahedral extend parallel to the $c$ axis. Each chain is linked to four
others by a corner sharing of anions. There are few reports on the high pressure investigations on nano SnO₂. The electrical resistivity and dielectric measurements under pressure shows the presence of phase transition below 3 GPa [10]. However the Raman scattering measurements did not reveal the pressure induced structural phase transition in this pressure region. The reports on the high pressure x ray diffraction on nano SnO₂ reveals the vast difference in the transition pressure [11, 12]. In this work we report the results of high quality synchrotron based angle dispersive x-ray diffraction measurements on 5nm SnO₂ to map out the transition pressure and other structural details.

2. Experimental

i Sample Preparation
Nanocrystalline SnO₂ was prepared by chemical precipitation method with different hydrolysis time. The precursor material used in this work was a 0.1 N aqueous solution of tin chloride (SnCl₂.H₂O). The particle size of 5nm was obtained with hydrolysis time of 144 hours. The prepared sample was characterized by powder x-ray diffraction (XRD) using a rotating anode generator (Rigaku-Make) with the Mo Kα (λ=0.7107 Å) radiation. The average particle size estimated using the Scherrer formula is ~ 5 nm

ii ADXRD Measurements
Angle dispersive x-ray diffraction (ADXRD) measurements were carried out at the powder x-ray diffraction beam line of ELETTRA synchrotron source, Trieste, Italy. For high-pressure experiments fine powdered samples of SnO₂ were loaded in a Mao–Bell type diamond anvil cell (DAC). Hardened stainless steel gasket with a central hole of 100 μm diameter and thickness 50 μm contained the sample. The x-ray beam was collimated by 80 μm diameter pinhole. A mixture of methanol–ethanol (4:1) was used as pressure transmitting medium. The pressure was determined in-situ by using platinum powder mixed with the sample as pressure calibrant. The wavelength of the x-ray employed and the sample to image plate distance were calibrated employing LaB₆ diffraction pattern. X-ray powder patterns at various pressures were collected employing x-rays of wavelength 0.6704 Å. Images of the powder diffraction rings were collected on a Mar345 image plate detector and read with a resolution of 100x100 pixel size. Typical exposure times of 20 to 30 minutes were employed for data collection at each pressure point. The powder rings thus obtained were integrated using the versatile FIT2D [13] software and converted to the one dimensional 2θ vs. intensity plot.

3. Results and Discussion

Figure 1(a) shows the two dimensional diffraction image of as prepared nano SnO₂ and figure 1(b) depicts the Rietveld refined one dimensional intensity vs. 2θ plot. The x ray diffraction data shows the single phase formation of the compound with rutile structure. The ambient lattice parameter obtained for as prepared sample from Rietveld refined data is a= 4.7427(6) Å; c = 3.1851(6) Å with Sn position at (0, 0, 0) and refined oxygen position at (0.3056, 0.3056, 0.3056). The average grain size estimated using the Scherrer formula gives the particle size to be 5 nm.

Pressure evolution of few selected x- ray diffraction patterns is shown in figure 2. The ambient rutile phase remains stable against pressure upto 18.1 GPa. However the pattern collected at 19.8 GPa shows a weak peak developing between (110) and (101) lines of rutile phase indicating the onset of structural phase transition in this material. The new peak position is marked by an arrow in figure 2. The intensity of this new peaks increases with further increase in pressure while that of rutile phase goes down.
The new peaks could be assigned to cubic structure as described in the literature [12]. The fitted lattice parameter for the new cubic phase is 4.9214 Å at 22 GPa. The coexistence of both phases was seen up to 30.8 GPa, the highest pressure of the present investigations indicating the sluggishness of this transition. The reported transition pressure for 3 nm particle size SnO$_2$ is 30 GPa whereas for 8 nm SnO$_2$ it is around 18 GPa. Defects and lattice strain may be responsible for difference in transition pressure. It is to be noted here that the bulk SnO$_2$ shows structural phase transition from rutile to CaCl$_2$ at 11.8 GPa and then to orthorhombic PbO$_2$ type phase. Beyond 21 GPa the structure change to cubic structure [14].

Figure 1(a) 2-D diffraction rings

Figure 1(b) One dimensional Intensity vs. 2θ plot. Solid line is the Rietveld refined data whereas the solid squares are the experimental points.

Figure 2 Pressure evolutions of x ray diffraction patterns. Appearance of new peak has been marked by an arrow. Peaks marked by an asterisk are from the gasket. Pt indicates the diffraction peaks from the pressure calibrant.
Conclusion

The high pressure x-ray diffraction measurements on 5 nm particle size of SnO$_2$ prepared by chemical precipitation method has been carried out. The data shows stability of ambient rutile phase against pressure up to 18 GPa. However beyond 19 GPa the rutile phase becomes unstable and material transforms to cubic structure.

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