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Experiment Report Form

	Experiment title: Impact of extreme conditions on the atomic structure of nanocrystalline titanium monoxide	**Experiment number**: MA-4840
Beamline: ID06-LVP	**Date of experiment**: from: 21.04.2021 to: 24.04.2021	**Date of report**: 14.01.2022
Shifts: 9	**Local contact(s)**: Dr. Dmitrii Druzhbin	*Received at ESRF:*

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Report:

Experimental details

During experiment 3 nanocrystalline and 2 microscrystalline TiO_y powders were studied in the temperature range from 300 to approximately 2000K, under pressures from ambient to 11 GPa. Nanocrystalline powders were of primary interest, while microcrystalline ones were studied as a reference materials for further estimation of nano-size effect on behavior of the TiO_y structure.

Multi anvil assemblies with a 10 mm Cr-doped MgO octahedral pressure medium were employed. Samples of ~5 mg mass were placed at a 2 mm outer and 1.4 inner diameter Ti capsule. As a heater, a graphite resistance furnace thermally isolated by MgO plugs and a sleeve made of the ZrO_2 was used. To estimate temperature at the sample C-type thermocouple was placed in the octahedron so that the junction was near the end of the Ti capsule. Assemblies were pressed by eight 25 mm tungsten carbide cubes with 5 mm truncated corners equipped with pyrophyllite gaskets. Along the path of the X-ray beam, cylindrical amorphous SiBCN x-ray windows and boron-epoxy were mounted into the octahedra and gaskets, respectively. Angle-dispersive x-ray diffraction was collected at monochromatic synchrotron radiation with λ = 0.233933 Å. In all experiments the high-resolution 2D detector Pilatus3X-900kW CdTe was used. Sample-detector distance and offset calibrations were carried out using LaB_6 and the collected diffraction patterns were preliminary analysed using Fit2d software. Pressure values were estimated from ex- perimental unit cell volumes of Mo [1] and Ti [2] by fitting the position and width of individual diffraction peaks. Diffraction data were typically accumulated for 1 s and every 60 s during compression and near-continuously during heating. In all runs assemblies were initially compressed to target pressure at 1 bar/min oil pressure rate and then heated typically at ~10 $^{\circ}$C/s.

First two measurements of nanocrystalline powder and first measurement of microcrystalline powder were failed due to various reasons, like sample leaving the beam because of the movement when increasing pressure, or introduction into the beam unwanted cell materials resulted in bad XRD pattern. Also in each of five measurements thermocouple failure occurred, thus “power-temperature” calibration was established based on Ti phase transitions (3) and from experimental unit cell volumes by a cross-calibration of the equation of state of both Mo (1) and Ti (2, 4, 5).

Results

Obtained during experiment XRD patterns for nano- and microcrystalline TiO_y powders are presented in Figures 1 and 2 as 2D-plots. Each of the plots is devided into 4 parts representing various steps during measurement: rise of pressure (1), rise of temperature (2), release of temperature (3) and release of pressure (4). For steps 1-3 on the left to XRD pattern the pressure and temperature dependecies are presented to match XRD pattern with sample's conditions.

Most pronounced changes take place at steps 1 and 2, both for nano and microcrystalline powders. Applying pressure results in significant decrease of lattice parameter ***a***, while applying temperature inreases it. For microcrystalline TiO_y ***a*** decreases from 4.180 to 4.103 Å when apply pressure from 0.1 MPa to 11 GPa, and then increase from 4.103 to 4.208 Å when apply temperature from 300 to ~2000 K. Further temperature increase results in TiO_y re-crystallization and, probably, melting. Existense of cubic TiO_y modification (*Fm-3m* space group) right up to temperatures about melting point is rather unexpected results. However, at T > 1600 K hexagonal TiO_y modification appears, which co-exist with cubic phase. Preliminary, behavior of nanocrystalline TiO_y is similar, but more detailed analysis of the data and structural transformations of nano TiO_y is still in progress.

For comparison, XRD patterns obtained in the beginning and the end of the experiment are presented in Figures 3 and 4 for nano- and microcrystalline TiO_y, respectively. They show that the studied systems underwent a number of irreversible structural transformations. However, on XRD patterns obtained in the end of the experiment one can see reflexes which positions are close to those corresponding to the main reflexes (at 2th ≈ 5.6° and 6.4°) of the initial TiO_y *Fm-3m* phase. Thus, it is suggested that cubic TiO_y *Fm-3m* phase partial remains after extreme conditions. Taking into account the intense re-crystallization process and high probability of melting of TiO_y at applied extreme conditions, several TiO_y *Fm-3m* phases with similar lattice parameter are expected to exist in the end.

Conclusions

One of the most important and interesting results obtained from the experiment are the following:

1. The highest obtained value of TiO_y lattice parameter ***a*** equals 4.208 Å and was obtained at the point of the simultaneous application of highest pressure (11 GPa) and temperature (~2000 K). According to literature, this value of ***a*** corresponds to complete or about complete elimination of structural vacancies in TiO_y [6, 7].
2. The cubic TiO_y *Fm-3m* phase remains present almost up to re-crystallization point at pressure of 11 GPa and temperature above 2000 K.
3. Preliminary, it is expected that TiO_y *Fm-3m* phase partially recovers after extreme conditions.

Currently, more detailed data analysis and revealing of the nano-size effect on the atomic structure and structural vacancies of TiO_y is in progress, and planning of publication is started.

References

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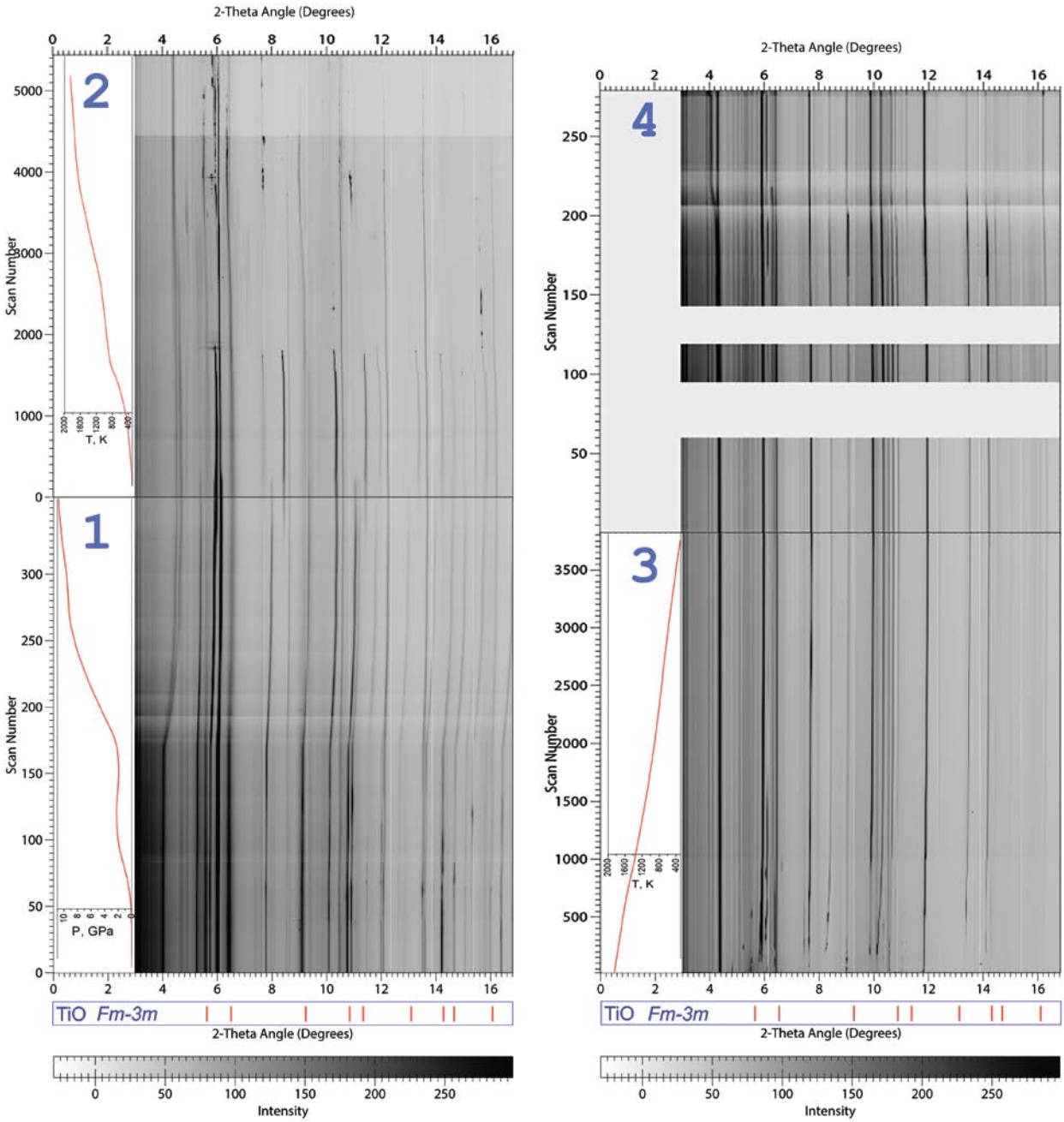

Figure 1. 2D-plots of XRD patterns for nanocrystalline TiO powders

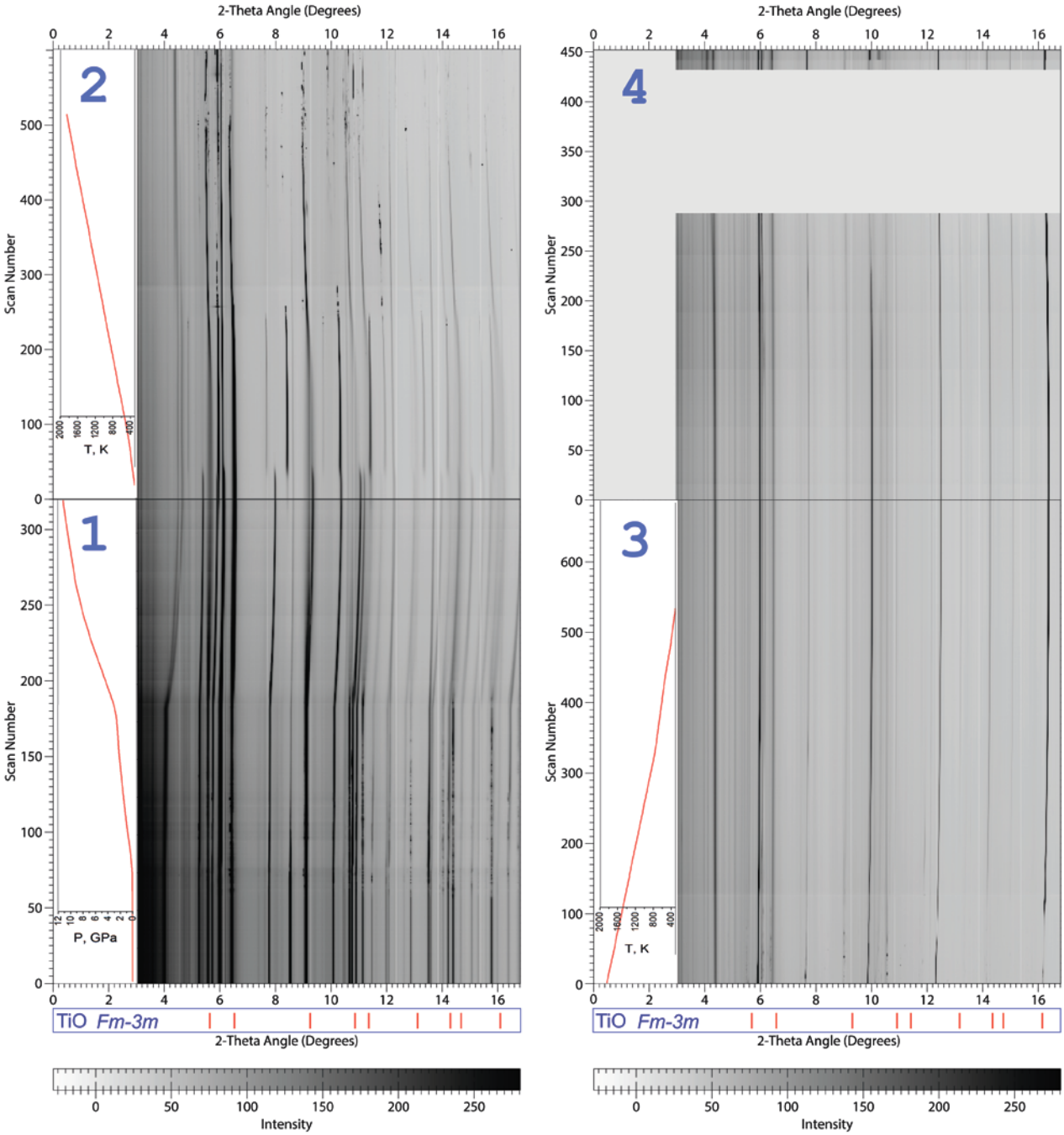

Figure 2. 2D-plots of XRD patterns for microcrystalline TiO powders

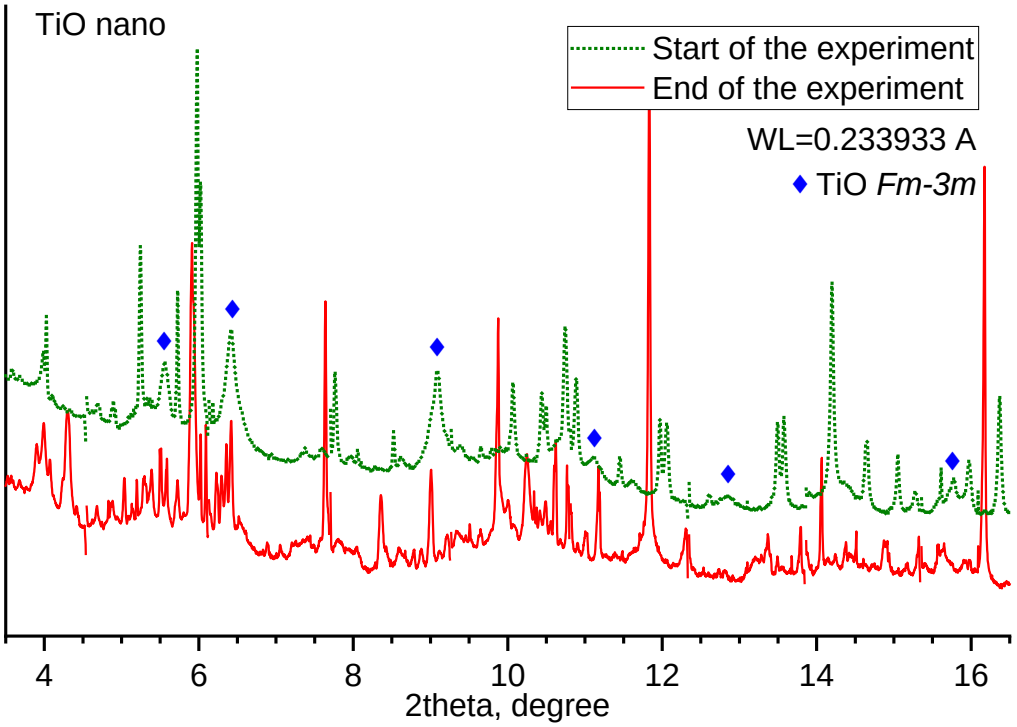

Figure 3. XRD patterns for nanocrystalline TiO powders corresponding to the beginning and the end of the experiment

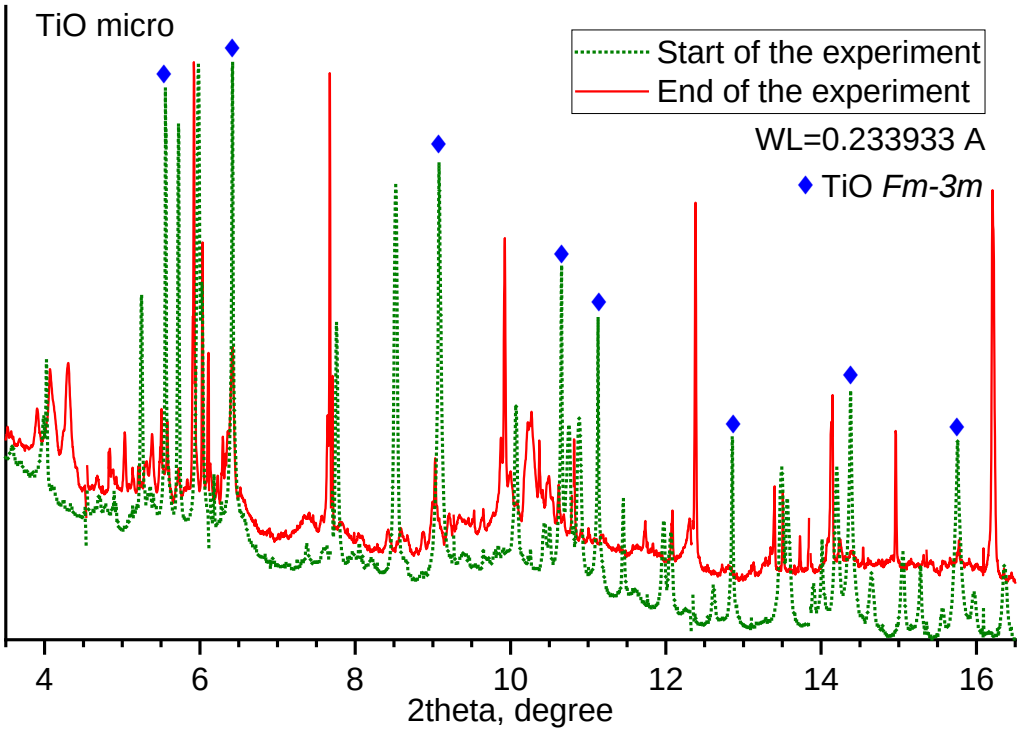

Figure 4. XRD patterns for microcrystalline TiO powders corresponding to the beginning and the end of the experiment