Time-Resolved X-ray Powder Diffraction Study of Photoinduced Phase Transition in Ti$_3$O$_5$ Nanoparticles

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Abstract: Nanoparticles of Ti$_3$O$_5$ have been reported to show a permanent photoinduced phase transition at room temperature. This suggests that light-induced phase transformations of Ti$_3$O$_5$ nanoparticles may be promising for technological applications. Here we report a photoinduced semiconductor-to-metal phase transition from $\beta$-Ti$_3$O$_5$ to $\lambda$-Ti$_3$O$_5$ nanoparticles at room temperature observed directly by time-resolved x-ray powder diffraction in a pump-probe setup. The results show a partial structural change, limited by differences between pumped and probed volumes, that persists a few microseconds after excitation. The first step in the relaxation back to the ground state can be described by a single exponential decay with time constant within microsecond time scales. Analysis of the change in lattice constants enables us to estimate an average temperature increase across the phase transition, consistent with a thermally driven process.

1 Introduction

One nearly endemic characteristic of modern technology is the ongoing demand for faster and higher density data storage devices. In the area of solid-state optical memories, so-called phase-change materials (PCM) are an important class of materials suitable for rewritable applications. Applications of PCM rely on inducing a reversible change between two different structural phases with markedly different optical properties.$^{[1,2]}$ One way to trigger the transformation between these phases is using intense light from a pulsed laser. Femtosecond pulsed lasers have been shown to initiate reversible phase transformations in several different classes of ma-
materials, including chalcogenoids, insulator-metal transitions in metal oxides, and spin-crossover transitions.\(^{[1,3,4]}\)

A complete understanding of the nature and lifetime of the photoinduced phase transformation is essential for developing applications of PCM. Here we focus on phase transitions in trititanium pentaoxide (Ti\(_3\)O\(_5\)) photoinduced at room temperature.\(^{[5]}\) Ti\(_3\)O\(_5\) is a non-stoichiometric form of titanium oxide which crystallizes in several structural forms with distinct physical properties.\(^{[6–10]}\) Titanium oxides are non-toxic and environmentally benign materials which makes them potentially attractive for widespread applications.

At ambient conditions, bulk Ti\(_3\)O\(_5\) is stable in the \(\beta\) phase with a monoclinic structure and space group \(C2/m\). The crystal structure of \(\beta\)-Ti\(_3\)O\(_5\) may be described as a network of distorted TiO\(_6\) octahedra which are joined by sharing edges and corners to form an infinite three-dimensional framework.\(^{[6]}\) The \(\beta\) phase is semiconducting with a band gap of 0.14 eV and an electrical conductivity of 3 x 10\(^{-2}\) S/cm.\(^{[5]}\) Above 460 K this material undergoes a structural phase transition to an orthorhombic structure with space group \(Cmcm\), called \(\alpha\)-Ti\(_3\)O\(_5\). This transition is marked by a thermal hysteresis, a decrease in resistivity and a sharp change in magnetic susceptibility.\(^{[10–13]}\) The \(\alpha\)-phase, stable at high temperatures \((T > 490 \text{ K})\), returns to the charge-ordered \(\beta\) phase upon cooling below 440 K. This is a first order phase transition with a thermal hysteresis of approximately 20 K.\(^{[10]}\)

Recently, Ohkoshi et al. reported observations of a new phase of Ti\(_3\)O\(_5\) in nanocrystal form with properties of a metallic conductor stable at room temperature. The new phase, dubbed \(\lambda\)-Ti\(_3\)O\(_5\), has a monoclinic structure and belongs to the space group \(C2/m\) with an electrical conductivity value of about 30 S/cm. This new phase is a metastable state at room-temperature.\(^{[5,14]}\)

Ohkoshi et al. also presented evidence of a reversible photoinduced phase transition between \(\lambda\)-Ti\(_3\)O\(_5\) and \(\beta\)-Ti\(_3\)O\(_5\) suggesting that the metal-semiconductor phase transition is a result of a transition from \(\lambda\)-Ti\(_3\)O\(_5\), a metastable phase trapped at a local configurational energy minimum, to a truly stable phase \(\beta\)-Ti\(_3\)O\(_5\), by irradiation of a pulsed laser light. The direction of the photoinduced phase transition can be controlled by adjusting the excitation fluence, or by changing the wavelength. In both cases, the fluence and the wavelength have well-defined threshold values.\(^{[5]}\) Additionally, the phase transition can be controlled by pressure, heat or electrical current.\(^{[15]}\)

The dynamics of the photoinduced phase transition using time-resolved (TR) diffuse reflectivity was observed at room-temperature in \(\beta\)-Ti\(_3\)O\(_5\) nanoparticles in a wide range of timescales.\(^{[16,17]}\) In the work of Asahara et al., a fast drop in reflectivity was observed within a few hundreds of femtoseconds, followed by a partial recovery within 1 ps. This behavior was interpreted as a non-thermal, transient phase transition from the \(\beta\) phase to the \(\lambda\) phase.\(^{[16]}\)

Ould-Homouda et al. investigated the phase transition by time-resolved reflectivity performed with a single-shot nanosecond pulse with pellets of both phases, \(\beta\) and \(\lambda\), with experimental resolution of 13 ns. Their results suggest that the phase-transition from \(\lambda\)-Ti\(_3\)O\(_5\) to
$\beta$-Ti$_3$O$_5$ is dependent on the duration of the excitation pulses and, in this timescale (ns), originates from laser induced heating and shock waves.$^{[17]}$

The results reported so far suggest that light-induced phase transformations of Ti$_3$O$_5$ nanoparticles may be promising for technological applications.$^{[5,15-17]}$ Several important questions, however, remain. One is whether the observed changes in the optical reflectance out of equilibrium correspond directly to a structural phase transition. If there is indeed such a structural component to the transition, the characteristic time scales of this transition are not yet well characterized (in either direction). Finally, the question of whether the phase transition is truly non-thermal in nature is unresolved, and in case it is non-thermal there is no clear theory for how it occurs. In this report we address predominantly the question of whether the light-induced changes have a structural component using both time-resolved x-ray powder diffraction and time-resolved optical reflectivity and we also determine some limiting time scales for the transition under the conditions of our experiment.

2 Results

2.1 Sample characterization

The X-ray powder diffraction (XRD) pattern and analysis results of the prepared sample show a complete transformation from the anatase form of TiO$_2$ to Ti$_3$O$_5$, with no evidence of other crystalline phases. The quantitative phase analysis shows the sample is composed of 83% of $\beta$-Ti$_3$O$_5$ and 17% of $\lambda$-Ti$_3$O$_5$ with estimated particle sizes of 120 nm and 90 nm, respectively. The XRD and Rietveld analysis results of the pellet showed a complete phase transition to $\beta$-Ti$_3$O$_5$, as reported elsewhere.$^{[5,15]}$

The sample lattice constants were determined by Rietveld refinement and are consistent with previous results.$^{[5,6,10,14]}$ The Rietveld results of the sample as prepared and the pellet are detailed in Supporting information.

The in-situ high temperature XRD, in Figure 1, shows an intensity decrease of the Bragg peaks from the $\beta$ phase and a simultaneous increase of the peaks of $\lambda$-Ti$_3$O$_5$ starting at 413 K, Figure 1m. A disappearance of $\beta$ peaks after 423 K indicates a clear phase transition induced by temperature, Figure 1l. On further heating, (-2 0 3) and (2 0 3) peaks of $\lambda$ phase merge into (0 2 3) peak of the $\alpha$ phase, Figure 1j, indicating a transition to the orthorhombic phase $\alpha$-Ti$_3$O$_5$. After 693 K peaks from rutile and anatase became evident, Figure 1h, indicating a transition to TiO$_2$. After the measurements the sample was cooled to RT and only peaks from anatase and rutile were present in diffractogram, Figure 1f.

The sample morphology was investigated by scanning electron microscopy (SEM). The results, presented in Supporting information Figure S3, show that the nanoparticles are aggregated into interconnected clusters with coral-like arrangement. The typical length scale of the aggregated clusters is a few microns.
Figure 1: In-situ temperature dependence X-ray diffractograms between room-temperature and 723 K. The reference patterns are displayed on a) Anatase, b) Rutile, c) $\alpha$-Ti$_3$O$_5$, d) $\lambda$-Ti$_3$O$_5$, e) $\beta$-Ti$_3$O$_5$. The measurements were performed at f) RT after heating, g) 723 K, h) 693 K, i) 588 K, j) 445 K, k) 430 K, l) 423 K, m) 413 K and n) RT. The blue, violet, green, light blue and red tick marks represent the Bragg peak positions for anatase, rutile, $\alpha$-Ti$_3$O$_5$, $\lambda$-Ti$_3$O$_5$ and $\beta$-Ti$_3$O$_5$, respectively.
2.2 TR diffuse reflectivity

In Figure 2, the results from TR diffuse reflectivity show a fast decrease in the reflectivity after a laser pulse excitation (800 nm, 100 fs, 16, 25 and 31 mJ cm\(^{-2}\)) and a partial recovery of the intensity within 1.5 ms. The best fitting results were achieved by fitting a double exponential function of type: 

\[
f(t) = A \exp(-t/τ_{\text{slow}}) + B \exp(-t/τ_{\text{fast}}) + C\]

for delay times \(t ≥ 25 \, \mu s\), where A, B, C are amplitude constants and \(τ_{\text{slow}}\) and \(τ_{\text{fast}}\) are time constants.

Figure 2: \(\text{Ti}_3\text{O}_5\) nanoparticles transient diffuse reflectivity probed with 633 nm CW laser.

![Figure 2](image)

Table 1: Time constants fitted for reflectivity results.

<table>
<thead>
<tr>
<th>Laser fluence (mJ cm(^{-2}))</th>
<th>(τ_{\text{fast}}) ((\mu s))</th>
<th>(τ_{\text{slow}}) ((\mu s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>51 (4)</td>
<td>480 (25)</td>
</tr>
<tr>
<td>25</td>
<td>71 (2)</td>
<td>1250 (60)</td>
</tr>
<tr>
<td>31</td>
<td>98 (3)</td>
<td>1370 (70)</td>
</tr>
</tbody>
</table>

2.3 TR powder diffraction

To observe the photoinduced phase transition and the structural changes as a function of time we performed a TR x-ray powder diffraction experiment. The Figure 3 presents the experiments results with a gate width of 10 \(\mu s\) and 31 mJ cm\(^{-2}\) pump fluence. This gate width was determined due to the need for satisfactory counting statistics without compromise the time resolution of the experiment. Figure 3b shows the powder intensity profile after image reduction and integration alongside the calculated profiles for the \(\beta\) (refined parameters) and \(\lambda\) phases at room temperature and \(\alpha\) phase at 514 K.\(^{[5,10]}\) The experimental profile agrees with the calculated pattern for the \(\beta\)
phase. In the bottom part of Figure 3b is displayed the difference between the profiles after and before excitation normalized to the intensity $I_{\text{max}}$ of (110) peak at negative time delay.

We first concentrate on regions in the difference diffractogram where excitation is shown to lead to an increase in intensity at diffraction angles where no peaks are initially present. In the two theta range between 37.1° and 37.9°, shown in the inset of the Figure 3b, we can see an increase of intensity at 37.23° and 37.70° reaching a maximum change near time zero and then subsequently decreasing. Comparing this region to the calculated profile for $\lambda$ phase, we can observe two peaks close to these values, (-2 0 3) at 37.12° and (2 0 3) at 37.90°. These peaks are both present also in the $\beta$ phase, but are located at 38.62° and 39.70°, respectively. The emergence of two peaks in intensity between 37.1° and 37.9° is strong evidence that some fraction of the material is in $\lambda$ phase.

Figure 3: a) X-ray powder profile from Ti$_3$O$_5$ (black solid line) and calculated profiles for $\beta$-Ti$_3$O$_5$ (red dashed line), $\lambda$-Ti$_3$O$_5$ (blue dashed line) and $\alpha$-Ti$_3$O$_5$ (green dashed line). b) Intensity difference normalized to the intensity of (110) peak before excitation. The inset shows the increase in intensity between 37° and 38°.

Figure 4 shows the time evolution of the normalized integrated intensity change between 37.1° and 37.9°. After excitation there is an increase of the normalized integrated intensity reaching a maximum value at 10 $\mu$s, which is limited by the time resolution of the experiment, followed by an exponential decay. To estimate the time scale of this partial recovery to the initial state, we fit the data for delay times $t \geq 10 \mu$s to a function of the form $A \exp(-t/\tau) + C$. We obtain a value for the recovery time $\tau = 16 \pm 2 \mu$s.
Another notable feature of the data shown in Figure 3 reflects smaller shifts in the angular positions of several prominent diffraction peaks, resulting in an antisymmetric shape in the difference diffractogram. The center of mass (first moment with respect to angle) of selected peaks as a function of time is shown in Figure 5. The largest change occurs within the experimental time resolution, and then subsequently partially relaxes to a quasi-stationary level. This fast relaxation time was extracted from this set of time dependences by fitting exponential curves of the form $A_n \exp\left(-t/\tau\right) + C_n$ to the data for times $t \geq 10 \mu s$, where $n$ is an index running over all the different peaks shown. The fitted curves are shown as continuous lines in Figure 5. The time constant obtained from the global fitting has a value of $23 \pm 2 \mu s$. For the selected peaks no line width broadening was observed.
Figure 5: Center of mass as function of time, for selected peaks, and global fitting (continuous line).
3 Discussion

The static XRD results are in good agreement with previous results for \( \beta \) and \( \lambda \) phases in terms of the observed unit cell dimensions, allowed reflections and the qualitative nature of the phase transition.\(^{5,6,10,14}\) The in situ high temperature XRD shows a nearly complete transformation from \( \beta \) to \( \lambda \) at 430 K and from \( \lambda \) to \( \alpha \) at 445 K, the latter transition identified by the merging of the (-2 0 3) and (2 0 3) diffraction peaks. This falls within the relatively wide range of previously reported values of these transition temperatures, which may indicate a strong dependence on defects and particle size.\(^{14}\)

The sample morphology, seen in the SEM images presented in Supporting information Figure S3, shows the nanoparticles are aggregated into coral-like structures with heterogeneous clusters of \( \mu m \) dimensions. From the morphology we can presume some porosity in the material, which decrease the sample density relative to that calculated from the crystallographic parameters, \( \rho_\beta = 4.25 \text{ g cm}^{-3} \) and \( \rho_\lambda = 4.00 \text{ g cm}^{-3} \). With this assumption, we can estimate the heat diffusion constant from the thermal conductivities reported by Tokoro et al with values between 1.6 - 2.5 m\(^2\)s\(^{-1}\) for \( \beta\text{-Ti}_3\text{O}_5 \) and 0.8 - 1.1 m\(^2\)s\(^{-1}\) for \( \lambda\text{-Ti}_3\text{O}_5 \), considering a porosity of 0.1 - 0.4.\(^{15}\) Assuming cluster sizes between 1 \( \times \) 1 \( \mu m^2 \) and 3 \( \times \) 2 \( \mu m^2 \) we can estimate the time required for heat diffusion within a cluster as 10 - 100 \( \mu s \).

The optical reflectivity relaxation was best fit with a double exponential function. The two time scales (50-100 \( \mu s \) and 0.5-1.4 ms) suggest two different relaxation processes that change somewhat with pump fluence. The fast time constant corresponds well with our estimates for the time required for heat diffusion within the micron-sized clusters of nanoparticles seen in the SEM images. The longer relaxation time scale may be associated with heat transport either among the loosely connected, porous network of clusters or with heat transfer to air. The observation that the relaxation time depends on the excitation fluence may indicate that the initial spatial distribution of the excitation depends strongly on the fluence. Because the nanoparticle size is comparable to the wavelength of the pump radiation, it is difficult to accurately model the spatial extent of the excitation. Based on the results of the time-resolved powder diffraction, it seems very likely that only a small part of the volume of the nanoparticle is converted to the \( \lambda \) phase.

Our time scale for complete recovery is significantly longer than the value of 100 \( \mu s \) as measured by Asahara et al. on 25 nm size nanoparticles with an unreported morphology.\(^{16}\) This discrepancy could possibly arise from the smaller nanoparticle size and potential differences in the micrometer-scale structure of the nanoparticle aggregates.

In Figure 3b, the intensity increase at 37.23° and 37.70° that we can associate to the peaks (-2 0 3) and (2 0 3) of \( \lambda \) phase is shifted compared to the peaks of the \( \lambda\text{-Ti}_3\text{O}_5 \) calculated pattern at room temperature, at 37.11° and 37.91°.\(^{5}\) This displacement could be correlated to a sample heating or strain, since as the temperature increases toward the transition to the \( \alpha \) phase (where
the peaks merge into one) these two peaks smoothly approach a common angle. The changes observed are in good agreement with the peaks (-2 0 3) and (2 0 3) of λ phase calculated at 430K, which are at 37.26° and 37.70°, respectively.

Also in Figure 3b, we observe a shift of β-Ti₃O₅ peaks to lower angles. By the Bragg’s law, this behaviour can be assigned to a lattice expansion as consequence of sample average heating. The displacement can be better observed in Figure 5, where the peaks shift to lower angles and subsequent relaxes to initial values. As Ti₃O₅ phase has a monoclinic structure, the peak relative change is not isotropic. The peak displacement can be used to calculate the lattice temperature over the entire probed sample volume. On this basis we estimate a change between 3 and 5 K in temperature for the five peaks presented. This very low estimate of the average temperature stands in contrast to the 430 K temperature inferred from the position of the λ phase peaks. This discrepancy suggests that indeed only a small fraction of the material that the x-rays probe strongly interacts with the excitation pulse.

In these experiments we see essentially three different time scales for a pump fluence of 31 mJ cm⁻²: (1) a ~ 20 µs relaxation of both the peak shifts and of the intensity associated with the λ phase as measured using time-resolved powder diffraction, (2) a ~ 100 µs “fast” relaxation seen in time-resolved optical diffuse reflectance at 633 nm wavelength, and (3) a long, > 1 ms “slow” relaxation component in the diffuse reflectance measurements, tentatively attributed to heat transport into deeper regions of the pellet. In addition there is also an unresolved relaxation time constant > 200 µs in the powder diffraction measurements that appears in the data as an offset at late pump-probe delays. Both processes (1) and (2) could be interpreted as diffusive heat transport, but the discrepancy in time scale suggests that there is some important difference in how such transport can be observed with the different measurement techniques. One key difference between the 633 nm and x-ray probes are volumes of the sample that interact with the light; for a planar interface to a bulk sample of Ti₃O₅ the penetration depth of the 633 nm is on the order of 34 nm, whereas the x-ray penetration depth at 2° grazing incidence is 400 nm. For a collection of nanoparticles with an average diameter of 200 nm aggregated into clusters with sizes of a few µm these numbers are not expected to be accurate, but it does indicate that the difference in cross section likely causes the x-rays to probe a wide range of differently pumped regions, including some particles or regions of particles that are hardly excited at all. This may explain why the relaxation time constant observed using x-rays is somewhat smaller, which is consistent with the systematic trend seen in the diffuse reflectance where the fast relaxation time becomes shorter as the fluence decreases.

The relaxation time of the phase transition occurs on the same time scale of the relaxation of the center of mass. We can relate these time constants to the cooling process associated with a heat diffusion. The fitted relaxation times from the time-resolved diffuse reflectivity measurements are slower than the XRD relaxation times. This discrepancy may also be related to the different volumes of the sample probed by the two techniques.
The observation of a structural phase transition within 10 µs in our measurements might suggest a correspondence between optical and X-ray results but we cannot confirm that the optical reflectivity changes seen by Asahara et al corresponds to the structural changes we observed.[16] However, on the basis of our experiment, we could not exclude either thermal or non-thermal effects and the results are consistent with both scenarios.

4 Conclusion

In conclusion we confirmed that a transient photoinduced structural phase-transition in nanoparticles of Ti$_3$O$_5$, previously reported by time resolved optical reflectivity, has a structural component that was directly probed by time-resolved x-ray powder diffraction in microsecond time scale. After excitation by a single femtosecond laser pulse we recorded a partial phase transition from β-Ti$_3$O$_5$ to λ-Ti$_3$O$_5$, followed by a relaxation indicating sample cooling, observed from the changes in the diffracted intensity as a function of time. The changes in intensity indicate a fast change from β to λ-Ti$_3$O$_5$ in time scales faster than the 10 µs experimental time resolution and a relaxation time for the transient phase of 20 µs. Measurements of the transient diffraction peak positions give evidence of strong inhomogeneities in the temperature of the nanocrystals, but the positions of the λ phase peaks appear to be consistent with a local temperature increase that may act to drive the phase transition. In order to resolve the question of whether there is indeed a non-thermal mechanism at play higher time resolutions (< 1 ps) would be needed, which is likely possible only with a higher peak brightness x-ray source such as an x-ray free electron laser. Also, a sample consisting of smaller and better-defined nanocrystal sizes would be more uniformly excited and provide information about the importance of the particle size on the dynamics of the photoinduced phase transition.

5 Experimental Section

5.1 Sample Preparation and morphology

The sample was synthesized by sintering anatase form of TiO$_2$ nanoparticles (30 nm) under hydrogen flow of 57 dm$^3$ min$^{-1}$ at 1460 K during 75 min.[5] The time-resolved experiments were conducted using a pellet of 12 mm of diameter and 0.5 mm thickness prepared by pressing the Ti$_3$O$_5$ nanoparticles under a pressure of 1 GPa. The SEM images were acquired by a JEOL JSM-6403F microscope with 15 keV accelerating voltage. The SEM images are presented in Supporting information Figure S3.

5.2 X-ray Powder Diffraction

X-ray powder diffraction measurement has been carried out using synchrotron and conventional X-ray sources in order to characterize the samples. Measurements at room-temperature were performed using a Rigaku RINT2000 with Cu target. In addition, the in-situ high temperature
measurements were performed at the XPD beamline of the Brazilian Synchrotron LNLS, in which the sample was mounted inside a capillary coupled to a furnace able to continuously heat the sample up to 723 K.\cite{18} Analysis of the resulting diffraction patterns was performed by means of Rietveld method using the software package GSASII.\cite{19}

5.3 Time-resolved Optical Diffuse Reflectivity

For the measurements of time-resolved diffuse reflectivity, the sample was excited by 800 nm pulses of 90-100 fs full-width-half-maximum (FWHM) duration and probed with a 633 nm HeNe CW laser. The pump beam was provided by a commercial amplified 800 nm Ti:Al₂O₃ laser system with 2 kHz repetition rate. The pump pulses were focused by two lenses to an elliptical spot of 800 x 1000 µm² (FWHM) and the probe to a diameter of 135 µm (FWHM). The pump power was varied by a half-waveplate and a thin film polarizer placed in the path of the pump beam. Since the recovery time of the sample exceeded the nominal repetition time of the excitation laser (1 ms), an optical chopper synchronized to the pump laser was inserted in the pump branch to reduce the repetition rate to 33 Hz. The diffuse 633 nm light reflected by the sample was focused by a lens to a fast photodiode (Thorlabs DET36A/M) which produces an electrical output signal with an intrinsic rise time of 14 ns. The electrical signal from the photodiode was recorded by an oscilloscope (Teledyne LeCroy WR640Zi) triggered by another fast photodiode (Thorlabs DET36A/M) which detected the pump light scattered by the sample. In order to block contributions to the detected reflectivity from the small fraction of pump light scattered by the sample, a dielectric band pass filter with central wavelength in 650 nm and 40 nm bandwidth was placed in front of the photodiode. The input impedance of the oscilloscope was effectively set to 50 kΩ by placing a 50 kΩ resistor in parallel to the input, limiting the time resolution of the experiment to 5 µs. Figure 6 shows a sketch of the experimental setup.

5.4 Time-resolved X-ray powder diffraction

The time-resolved X-ray powder diffraction experiment was carried out at X05LA beamline at the Swiss Light Source (SLS), Paul Scherrer Institut in a pump-probe scheme.\cite{20} The pellet of Ti₃O₅ nanoparticles was pumped by 800 nm pulses (115 fs FWHM, 1 kHz) delivered by a commercial Ti:Al₂O₃ based regenerative amplifier synchronized to the synchrotron storage ring. The laser beam was focused by a pair of lenses to a spot of 1000 x 700 µm² (FWHM, measured with an infrared camera) at 80° angle of incidence. The incident power on the sample was varied using a half wave-plate and a thin film polarizer in the path of the pump beam. The fluence values applied during the experiment were 16, 25 and 31 mJ cm⁻². The sample was probed with 7 keV energy X-rays at an incidence angle of 2°. The X-ray beam was vertically collimated and horizontally focused to 300 µm at the sample position by a grazing incidence toroidal mirror. Close to the sample a single elliptically bent mirror focuses vertically the beam to a size of 7 µm. The sample surface was aligned horizontally to the incident X-ray beam.
Figure 6: Sketch of the optical reflectivity setup. The pump laser was focused by a pair of lenses ($f_1$ and $f_2$) and the probe by a single focusing lens ($f_3$) on the sample. The diffuse reflectivity from the sample was focused by a lens ($f_4$) on the detector.

resulting in a spot size of 200 x 300 µm².

The X-ray diffraction patterns were recorded by a 2D detector (Pilatus 100 K). To increase the reciprocal space region covered and to reduce the air absorption, the detector was placed 11 cm from the sample. Figure 7 illustrates the experimental setup performed at X05LA beamline and Debye-Scherrer rings recorded by the detector.

To achieve time resolution for the experiment, the Pilatus detector was gated electronically with a digital signal synchronized to the laser system. During the experiment three durations of the time gates were used: 4, 10 and 25 µs. The gate times and time delay were defined in multiple numbers of cycle of the radio frequency (RF) cavity synchronized to the camshaft electron bunch. The pump pulses were furnished by the a similar laser system used for the excitation of the diffuse reflectance measurements. This is a regenerative amplifier based on Ti:Al₂O₃ designed to operate at a 1 kHz repetition rate. The laser repetition rate was reduced to 100 Hz by triggering the Pockel’s cells that control injection and extraction of seed pulses into the regenerative amplifier cavity at the reduced rate. To assist in the removal of excess heat from the sample between pump cycles, a cryogenic nitrogen blower (Oxford Instruments Cryojet) was used during the experiment and set to blow nitrogen at room temperature at flow rate of 10 l min⁻¹ on the sample.

Figure 7 shows a sample image from the Pilatus detector, showing several Debye-Scherrer rings caused by diffraction from the sample. We adopt the following procedure to converts the 2D image to a 1D diffraction pattern: the code reads the image and convert to a matrix, reads
Figure 7: Schematics of the powder diffraction setup and Debye-Scherrer rings from Ti$_3$O$_5$ recorded with Pilatus detector.

the pixel intensity, and, assuming the curves in the image are concentric arcs of circles, fits an arc along the ring intensity distribution and finds a common center for all rings. It performs a transformation from polar to Cartesian coordinates to flat lines and sums the pixel intensity along the horizontal axis.

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