Pulsed synchrotron X-ray as a tool for providing molecular movies at 100-picosecond temporal and sub-nanometer spatial resolution

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Abstract. Time-resolved X-ray techniques utilizing pulsed nature of synchrotron radiation are becoming general and powerful tools to explore structural dynamics in materials and biological systems. The time-resolved technique enables to produce structural movies at 100-picosecond temporal and sub-nanometer spatial resolution. It will be fascinating to apply such capabilities to capture ultrafast cooperative phenomena in strongly-correlated electron systems, photochemical catalytic reaction dynamics in liquid or on solid surface, light-induced response of photosensitive protein molecules, etc. The time-resolved X-ray studies conducted at NW14, PF-AR, KEK will be presented.

1. Introduction
Time-resolved X-ray studies using synchrotron radiation sources have been successfully applied to various dynamics studies of chemical and biological systems or condensed matters at 100-picosecond temporal and sub-nanometer spatial resolution. Such capability using synchrotron facilities provides a solid basis toward femtosecond X-ray sciences of ultrafast non-equilibrium states using next generation X-ray sources. Photon Factory Advanced Ring (PF-AR) at the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan is a storage ring dedicated for single-bunch operation, and suitable for such pulsed X-ray studies. By utilizing the full advantage of the sparse bunch structure of PF-AR, we have been developing time-resolved X-ray applications at the beam line NW14 [1]. Here we present the recent activities at the NW14.

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2. Scientific applications of the 100-ps X-ray

2.1. Shock-induced uniaxial compression revealed by nanosecond time-resolved Laue diffraction [2].

Dynamics of materials under shock compression is an essential key for understanding various impact phenomena. Atomic motion and the history of atomic rearrangement under shock-waves can be studied using time-resolved Laue diffraction with high-flux white X-rays. We have studied the laser-induced shock response of the CdS single crystal around the pressure of the phase transition using single-shot time-resolved Laue diffraction. Laser-induced shock waves propagate through the irradiation plane to the backward plane along the c-axis, and nearly parallel to the X-ray beam. The images at each delay were obtained by a snap-shot because the samples were completely broken after laser irradiation.

Figure 1. Time-resolved Laue diffraction images recorded during shock wave loading.

Figure 1 shows a series of Laue diffraction images recorded during shock wave loading. The all peaks on the Laue images initially move to higher 2θ angle then return to their original positions around 22 ns. These shifts clearly indicate the occurrence of anisotropic compression. The shock wave arrives at the backward plane after around 12 ns, and reflects towards the irradiation plane, arriving after around 22 ns. The broadening of the peaks at 22 ns shows the residual stress due to the shock loading. These results allow us to estimate the shock wave speed to be 4.2 ± 0.5 km/s, which is in good agreement with the elastic velocity. If we assume the shock compression to be purely uniaxial, the shock pressure can be estimated to be 3.92 GPa for 4.4 % compression from the elastic region. This is higher than the threshold pressure of the phase transition (~ 3 GPa), however the retention time of the shock-compressed condition using this method (~ 10 ns) is shorter than the incubation time required for the phase transition from wurtzite-to-rocksalt structures [3]. Thus, in this study, a transient CdS structure beyond the shock-induced phase transition pressure is clearly captured using single-shot time-resolved Laue diffraction. Our method will be a powerful tool for revealing the detailed ultrafast dynamics of single crystals under shock-wave loading.

2.2. Molecular structural dynamics of transition metal complexes revealed by 100-ps time-resolved X-ray absorption spectroscopy [4].

Time-resolved X-ray absorption spectroscopy (TR-XAS) elucidates electronic states and molecular structures of non-crystalline samples with 100-ps temporal resolution. TR-XAS can reveal the dynamics of the oxidation and valence states via X-ray absorption near edge structure (XANES) features and the local molecular structure via extended X-ray absorption fine structure (EXAFS) features with sub-Angstrom spatial resolution, which compliments with diffraction and scattering techniques. We have tried to observe the photo-induced spin crossover (SCO) transition of [Fe\textsuperscript{II}(phen)\textsubscript{3}]\textsuperscript{2+} in solution. This system has known to show electronic spin transition with a ~680 ps
decay time. We have successfully obtained TR-XANES and TR-EXAFS spectra of \([\text{Fe}^{II}\text{(phen)}_3]^{2+}\) in solution in picosecond time regime. The spectral features clearly indicate the SCO transition of the iron complex accompanied with the transient structural distortion in picosecond order. The detailed analysis is now underway.

2.3. Other applications.

We have been developing other applications using the 100-ps X-ray pulse as well, which are (1) photochemical reaction dynamics in solution by time-resolved X-ray liquidography (TRXL), (2) photo-induced slow dynamics of ligand migration in soft matter (protein) by time-resolved protein crystallography, (3) photo-induced insulator-to-metal transition in manganite thin film. These applications are now in progress, and will be published in the near future.

3. Summary

We have found that there are so many interesting targets for 100-ps time-resolved X-ray studies, and still we are searching for brand-new targets in physics, chemistry and biology. This exploration is fun, and we believe our scientific developments will be valuable seeds for sciences at the next generation light sources.

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