Melting transition in polystyrene colloidal crystals studied by in situ ptychographic imaging

A.V. Zozulya¹, I. Besedin², J.-M. Meijer³, D. Dzhigaev¹, A. Shabalin¹, E. Sulyanova⁴, R.P. Kurta¹, I. Zaluzhnyy¹,², O. Gorobtsov¹, A.V. Petukhov³, M. Sprung¹ and I.A. Vartanyants¹,²

¹Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, D-22607 Hamburg, Germany
²National Research Nuclear University “MEPhI”, Kashirskoe shosse 31, 115409 Moscow, Russia
³Van ‘t Hoff Laboratory for Physical and Colloid Chemistry, Utrecht University, Padualaan 8, Utrecht, The Netherlands
⁴Institute of Crystallography, Russian Academy of Sciences, Leninskii prospect 59, 119333 Moscow, Russia

It has been shown that by sintering and annealing a 3D colloidal crystal at elevated temperatures it is possible to modify the photonic bandgap properties [1-3]. Furthermore, the glass transition temperature for polymers is known to be greatly influenced by free surfaces [4-5]. In a range of temperatures below the glass transition temperature of a polymer the crystal retains a long-range order and undergoes a blue shift of the optical attenuation bands. The temperature range spanning beyond this long-range ordered phase to the crystal melting is not well studied, although it has important technological aspects regarding the tolerable temperature range of a photonic device.

Various techniques can be used to monitor the structure of colloidal systems. For large colloidal particles (larger than 0.5 µm) it is possible to image directly the structure and defects in colloidal crystals using optical microscopy. For particle sizes less than 500 nm the resolution of optical microscopy comes to a limit and alternative methods have to be used. Transmission electron microscopy (TEM) provides unprecedented spatial resolution. However, TEM studies can only access thin layers of a colloidal crystal due to low penetration depth of electrons, and typically involve elaborate sample preparation. Using X-ray diffraction it is possible to circumvent the above limitations and study non-destructively crystalline and amorphous materials, especially when in situ experiments are aimed.

In this study we employed the coherent diffraction imaging (CDI), the X-ray scattering technique based on coherent illumination of the sample and measuring the oversampled scattering patterns in the far diffraction field [6]. Missing phases of scattered waves are iteratively retrieved by computational algorithm implying specific constrains. As applied to colloidal crystals, the CDI technique enables ab initio reconstruction of close-packed arrangement of colloidal particles [7-9]. The convergence of phase retrieval reconstruction can be considerably improved by collecting multiple diffraction patterns from overlapping positions during a raster scan of the probe beam over the sample. This approach is known as ptychographic imaging [10-11] and allows the extended objects to be unambiguously reconstructed at a spatial resolution down to 10 nm [11].

Our previous studies of structural evolution of colloidal crystals upon heating have revealed different phases of crystal melting [12]. At the first stage of heating the scattering patterns showed only small azimuthal tilts of the whole pattern. Apparently, these tilts indicate the presence of relaxation of domains, as induced by heating. Further temperature increase has led to a decay of higher diffraction orders. Before the crystal starts to decompose, the whole crystalline lattice undergoes a thermal shrinkage by 3-5 %.
Figure 1: Ptychographic reconstruction images (phase distributions) of the 10×10 μm² area of colloidal crystal at different temperatures during heating.

In the reported experiment we applied ptychographic imaging to directly monitor the structural evolution of colloidal crystal during melting. We performed in situ coherent X-ray ptychographic imaging experiments using microfocusing optics available at the P10 coherence beamline of PETRA III, which provides coherently focused beam of 2(ν)×3(h) μm² [9]. Prior to temperature ramping, the highly ordered crystalline domain of a colloidal crystal was selected. After the region of interest was defined, the series of ptychographic scans were performed in transmission geometry over the same sample area while raising the sample temperature in a range spanning the melting transition. In Fig. 1 the ptychographic reconstructions of polystyrene colloidal crystal film (particle size of 430 nm) undergoing melting transition are shown. On the reconstructed phase distributions (thin colloidal film represent essentially the phase object for 8 keV X-rays) one can clearly observe structural degradation of the crystal in the vicinity of melting point at T=380 K. The ongoing data analysis is aimed at decoupling of structural ordering distribution from the local film thickness phase shift influencing the reconstructed images.

References
9) A. V. Zozulya et al., Optics Express 20 (17), 18967 (2012).