

was obtained. The crystals endured the high demands of the time-resolved laue experiment and several datasets, ground state and illuminated, diffracting to high resolution were collected. From this data difference maps were calculated which revealed interesting details including a tyrosin residue corresponding to tyrZ of plant photosystem II.

Keywords: time-resolved laue diffraction, membrane protein, lipidic-sponge phase

## P02.07.13

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### XAFS and XRF studies of anti-bacterial ceramics using synchrotron radiation

Chiya Numako<sup>1</sup>, Yoshihiro Kato<sup>2</sup>, Satoru Yamazaki<sup>2</sup>, Norifumi Isu<sup>2</sup>

<sup>1</sup>The University of Tokushima, Faculty of Integrated Arts and Sciences, Minami-josanjima 1-1, Tokushima, Tokushima, 770-8502, Japan, <sup>2</sup>INAX Corporation, E-mail: numako@ias.tokushima-u.ac.jp

Recently anti bacterial techniques have been spread into daily commodities with improving consciousness of health. There are several kinds of anti bacterial consumers, silver courting or silver ions are most common anti bacterial chemicals in Japan, however, the resource of silver is limited and it became so expensive to be used for daily commercial item. In addition, the anti bacterial effects on silver have been unclear because of difficulties of in-situ chemical state analyses for these systems in ordinary analytical methods. In order to elucidate the anti bacterial mechanism of silver and develop new anti-bacterial material instead of limited silver, XAFS and XRF analyses using Synchrotron Radiation were applied for the sanitary wares and anti-bacterial tiles which are the products of INAX corporation, Aichi, Japan. For the comparison, other anti-bacterial tiles containing Zn were also examined by XAFS analyses. Each specimen was cut into 1cm x 1cm blocks to be used for analyses. Crystalline materials in the sample were examined by XRD, however, no crystalline staff was detected. From elemental analyses using EPMA, a content of silver in sanitary ware was about 0.08wt% and that of zinc was about 15wt%. Then XAFS measurements of the silver in anti-bacterial stuffs were performed for K-edge at BL-01B1 in SPring-8, and for L-edge at BL9A in Photon Factory, KEK. XAFS measurements for zinc were performed at BL12C and BL9A in PF. The result of XAFS measurements, chemical state of the silver in the sanitary ware was mono-valent, and silver was coordinated with about two oxygen in 2.22Å. On the other hands, zinc in the anti-bacterial tiles was divalent and there local structure was similar to Zn<sub>2</sub>SiO<sub>4</sub> which is coordinated with four oxygen in 1.96Å

Keywords: anti-bacterial materials, synchrotron radiation, XAFS

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### Local atomic structure of iron in Fe-chitosan complexes, determined by XAFS

Marcin T Klepka, Krystyna Lawniczak-Jablonska, Iraida N Demchenko

Polish Academy of Sciences, Institute of Physics, al. Lotnikow 32/46, Warsaw, Warsaw, PL-02668, Poland, E-mail: mklepka@ifpan.edu.pl

Chitosan is natural polymer, the N-deacetylated product of chitin which is obtained from crustacean shells. It possesses attractive

for nowadays technology physical and mechanical properties: easy biodegradation, biocompatibility and bioactivity. The most important aspect is its ability to chelate metal ions, including heavy and toxic ones. In presented paper the local atomic structure of iron in the Fe-crosslinked chitosan and N-carboxylmethyl chitosan were investigated in the light of their potential biomedical applications. From the performed advanced x-ray absorption fine structure (XAFS) analysis the coordination till the third sphere was determinate. Fe atoms in the investigated samples were penta-coordinated and appeared in Fe<sup>+3</sup> ionic state. In Ch-Fe-CL in the first sphere two kinds of Fe coordination was found. Several Fe atoms are localized in the second coordination sphere. The third sphere was composed from six oxygen atoms. Knowing that amine group should come from the single chitosan monomer at least two or three monomers (or even polymers) should be bonded to each Fe atom and each of this polymer has in turn built-in Fe atom. In N-CM-Ch-Fe only one Fe neighborhood was found, three oxygen and two nitrogen atoms. Other Fe atoms were identified neither in first nor in second coordination sphere, but third coordination sphere indicates the presence of Fe atoms. In the second sphere three carbon and two oxygen atoms were identified. This provides the evidence that carboxyl group is an active one. These local atomic order were confirmed qualitatively by Mössbauer spectroscopy. This work was partially supported by national grant of Ministry of Science and High Education N202-052-32/1189 and by DESY and the EC under Contract RII3-CT-2004-506008 (IA-SFS)

Keywords: XAFS, chitosan, coordination

## P02.07.15

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### 100-picosecond time-resolved X-ray absorption fine structure of Fe<sup>II</sup>(1,10-phenanthroline)<sub>3</sub>

Tokushi Sato<sup>1,3</sup>, Shunsuke Nozawa<sup>3</sup>, Kouhei Ichihyanagi<sup>3</sup>, Ayana Tomita<sup>1,3</sup>, Hirohiko Ichikawa<sup>3</sup>, Matthieu Chollet<sup>1</sup>, Hiroshi Fujii<sup>4</sup>, Shin-ichi Adachi<sup>3,5</sup>, Shin-ya Koshihara<sup>1,2,3</sup>

<sup>1</sup>Tokyo Institute of Technology, Department of Materials Science, 2-12-1 Ohokayama, Meguro-ku, Tokyo, 152-8551, Japan, <sup>2</sup>Frontier Collaborative Research Center Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo 152-8551, Japan, <sup>3</sup>Non-equilibrium Dynamics Project, ERATO, Japan Science and Technology Agency, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan, <sup>4</sup>Institute for Molecular Science, National Institutes of Natural Sciences 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan, <sup>5</sup>High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan, E-mail: sato.t.ah@m.titech.ac.jp

Studying photo-induced molecular dynamics in liquid with subnanosecond time-resolution gives a information for understanding fundamental chemistry, biology and also for developing new materials and devices. Monitoring the dynamic phenomenon requires a sensitive tools to investigate the electronic state and the structure with atomic resolution[1],[2]. Previously, we have reported the success in measuring the photodissociation of ligands in NiTPP system in solution[3]. Here, we have performed time-resolved X-ray absorption fine structure on the spin-crossover complex Fe<sup>II</sup> tris-(1,10-phenanthroline) dissolved in aqueous. In this system, excitation by femtosecond laser pulse of 400nm induces the spin state transition from low spin to high spin one as a result of the photo-induced expansion in the Fe-N bond length similar to other spin crossover systems[4]. All measurements were performed in fluorescence method at the iron K-edge on the undulator beamline NW14A at the Photon Factory Advanced Ring[3]. Obtained results clearly demonstrate the success in probing both structural and spin state changes induced by 400nm femtosecond laser pulse excitation with

100ps resolution by this method.

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Keywords: XAFS, time-resolved studies, spin

## P02.10.16

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### Indexing algorithm for powder diffraction pattern using topograph

Ryoko Oishi<sup>1</sup>, Masao Yonemura<sup>2</sup>, Akinori Hoshikawa<sup>2</sup>, Toru Ishigaki<sup>2</sup>, Kazuhiro Mori<sup>3</sup>, Shuki Torii<sup>1</sup>, Takahiro Morishima<sup>1</sup>, Takashi Kamiyama<sup>1</sup>

<sup>1</sup>HIGH ENERGY ACCELERATOR RESEARCH ORGANIZATION, 2-4, Shirane, Shirakata, Tokai, Naka, Ibaraki, 319-1195, Japan, <sup>2</sup>Ibaraki University, Hitachi, Ibaraki, Japan, <sup>3</sup>Kyoto University, Kumatori, Osaka, Japan, E-mail: roishi@post.j-parc.jp

Indexing of powder diffraction patterns is considered as the most difficult part among the procedures of *ab-initio* powder structure determination. Recently, we devised a new indexing algorithm that can search rapidly and thoroughly for the possible solutions. Topograph is a connected tree in the graph theory, which is a collection of relation formula given by  $Q(h_1+h_2) + Q(h_1-h_2) = 2 * (Q(h_1) + Q(h_2))$ . Although this formula is already known as Ito's equation and used in Ito's algorithm, it takes a more powerful role in our method as a basis of the equations among the Q-values of the peaks. Extinction rule is troublesome, but it is somehow obtained without information on the symmetry, in the process to construct the topograph. The algorithm is proved to work completely at least for lattices of dimension 2. For the case of dimension 3, some uncertain part still remains. The algorithm works without any assumption on Bravais lattice. It is efficient even if there is a false peak in the powder diffraction pattern or the material is not a single phase. The detail of the method and some results are introduced.

Keywords: powder indexing, *ab-initio* powder structure determination, computer algorithms

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### Structural characterization and developing a suitable SAXS model of diblock(DEAEMAn-DMAEMAm) polymers

Semra Ide<sup>1</sup>, U-Ser Jeng<sup>2</sup>, Yusuf Ozcan<sup>1</sup>, Vural Butun<sup>3</sup>, Ying-Huang Lai<sup>2</sup>, Chiu-Hun Su<sup>2</sup>, Pinar Batat<sup>1</sup>, Keng S. Liang<sup>2</sup>

<sup>1</sup>Hacettepe University, Faculty of Engineering, Physics Engineering, Hacettepe University, Faculty of Engineering, Physics Engineering, Beytepe, Ankara, 06800, Turkey, <sup>2</sup>National Synchrotron Radiation Research Center, Hsinch 30049 Taiwan, <sup>3</sup>Faculty of Arts and Science, Department of Chemistry, Eskisehir Osmangazi University, Campus of Meselik, 26480, Eskisehir, Turkey, E-mail: side@hacettepe.edu.tr

Small Angle X-ray Scattering (SAXS) is a powerful method to investigate nano-aggregations formed by self-assembly of block

copolymers in melt, solution or crystal state [1]. In this study, theoretical scattering models such as spherical core-shell and ellipsoidal core shell micelle models were described and discussed after the performed SAXS measurements at NSRRRC-Taiwan beside the determination of the morphologies. The studied di-block copolymers [2-(diethylamino)ethyl methacrylate (DEAEMAn)] · [2-(dimethylamino)ethyl methacrylate (DMAEMAm)] had been synthesized by Vural Bütün as a part of a serial research on pH dependent-water soluble block copolymers [2-3]. Our previous studies have been showed that micellar aggregations are expected due to hydrophobic and polyelectrolyte ends of polymeric units [4]. Two samples which have 23576 and 12177 g/mol molecular weights were prepared for SAXS measurements. Model-independent approximations with Guinier, Porod and Kratky plots together with the results of static and dynamic light scattering (SLS and DLS) are used to extract morphology characteristics, on which basis, a suitable model shape is chosen to fit the SAXS profiles. Beside of these investigations, a semi-empirical calculation method (PM3 [5]) was also used to examine crosslink effect of free polymeric units. So, electron densities in the layered thicknesses were also predicted before construction of the models. At the end of the study, the details related with mathematical and physical explanation for the models are also described in this presentation.

Keywords: DEA, DMA, Core-shell, SAXS, DLS, SLS, PM3, Nano structures

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### High-pressure phase transformations in aragonite, strontianite and witherite

Sergiu Arapan<sup>1</sup>, Ahuja Rajeev<sup>1,2</sup>

<sup>1</sup>Uppsala University, Department of Physics and Materials Science, Box 530, Uppsala, Sweden, 75121, Sweden, <sup>2</sup>Applied Materials Physics, Department of Materials and Engineering, Royal Institute of Technology, 10044 Sockholm, Sweden, E-mail: sergiu.arapan@fysik.uu.se

We have studied structural phase transformation in aragonite CaCO<sub>3</sub> and related isostructural compounds strontianite SrCO<sub>3</sub> and witherite BaCO<sub>3</sub> at high pressure by performing first principle calculations. The following phase transition sequence *Pmmn* - *Pmcn* - *C222<sub>1</sub>* have been found for all three compounds. Furthermore, CaCO<sub>3</sub> and SrCO<sub>3</sub> undergo a phase transition from *C222<sub>1</sub>* to *Pmmn* modified-aragonite phase at very high pressure as a result of carbon sp<sup>2</sup> to sp<sup>3</sup> transition. Thus the structural trends of these compounds are determined by both the cation size and the chemistry of CO<sub>3</sub> group. The formation of sp<sup>3</sup> hybridized bonds is driven by the intrinsic property of the carbon atom to form tetrahedrally covalent bonds at high pressure and explains the stability of MgCO<sub>3</sub> and CaCO<sub>3</sub> at the Earth's lower mantle pressure conditions. The presence of sp<sup>3</sup> hybridized carbon may serve as a criterion for new possible high-pressure phases of carbon bearing minerals.

Keywords: *ab-initio* calculations, high-pressure phase transformations, carbonates

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### Crystal structures of moderately complex organic molecules are predictable

Marcus A. Neumann