

effect of particle statistics can be evaluated from the ω -scan as well as the φ -scan data in the synchrotron parallel-beam geometry.

It has been proved that the effective number of diffracting crystallites is increased by a factor of about 100, by applying continuous φ -rotation of a flat specimen during the measurement, as predicted by the theory [3]. Errors caused by particle statistics, which should be incorporated in any analysis of powder diffraction data, will also be discussed.

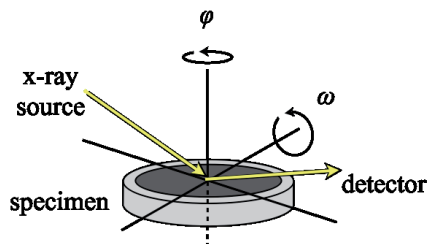


Fig. 1 Definitions of φ & ω

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Keywords: powder, particle, statistics

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A new mechanism of negative thermal expansion in an interpenetrated framework material

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Negative thermal expansion (NTE) is an unusual property that has only been recorded in a small number of materials. However, we have recently found that metal-organic framework (MOF) materials have a number of structural characteristics that promote NTE.[1]

Conventionally, porous materials tend to support transverse vibrations, as motion into the empty pores is unhindered. Hence, in frameworks in which the previously empty space is occupied either by guest molecules or an interpenetrating framework, NTE is diminished. Here, however, we show that framework interpenetration can increase the magnitude of NTE over a similar framework when the normal thermal expansion of the intermolecular contacts between the two frameworks results in a structural distortion – a phenomenon unreported in other materials.

The studied material is MOF-14, a highly porous copper-carboxylate framework which forms a singly interpenetrated network.[2] We present single-crystal and powder diffraction data demonstrating the structural change of the material over a wide temperature range, clearly showing the nature of this new mechanism for NTE.

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Keywords: negative thermal expansion, metal-organic framework, interpenetration

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Advances in guinier-type powder diffraction

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X-ray powder diffraction may be considered the main 'workhorse' in almost any field regarding solid state and materials sciences. Advances with instrumentation in recent years provided for major improvements with established methods but also induced the development of new and more specialized applications. The application of shorter wavelength (higher energy) X-rays while looking for higher resolution in the diffraction experiment is a principal contradiction calling for combinations of 'smart' solutions.

The Huber G670 Guinier system is very versatile and reliable, but at the same time simple and flexible for modifications towards more dedicated experiments. The imaging plate based detector system is well suited for any kind of typical lab-based X-ray sources ranging from Cr-K α (5.4116 keV) up to Ag-K α (22.1054 keV). However, much higher energies or synchrotron radiation may be used without any problems.

We have started to evaluate improvements and dedicated applications of the instrument on a broad basis. Concerning conditioning of the primary X-ray beam several options will be presented including 1-D and 2-D multilayer optics along with Johansson-type crystal monochromators. Such devices become very demanding in many respects when high-energy X-rays are targeted. Spot shaped beams are not commonly used with Guinier-type setups, however, a small but brilliant spot provides an excellent basis for studying small samples in general, but in particular with diamond-anvil cells or for typical samples in the fields of art and cultural heritage. Any setup discussed may be easily adapted to a broad range of X-ray sources. New ideas and developments towards improvement and modifications of the imaging plate itself but also for the entire detector system will be carefully considered.

Finally, improvements of the unit with respect to resolution but also concerning signal-to-noise ratio will be discussed with respect to the camera setup and the detector. Diffraction data of well defined samples will be presented for any particular setup evaluated. In numerous experiments we got increasingly convinced that Yttriumoxide is in many respects superior to most generally used standard materials.

Keywords: powder, guinier, optics

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Real-time behaviour of crystallizing cocoa butter. Time-resolved SAXS-WAXS study

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Almost 80% of cocoa butter (CB) in chocolate is crystalline. This is due to four different mono-unsaturated triacylglycerols (SOS, POP, POS and SOA) which are structurally closely related and crystallise together. Their crystal structures are determined from XRPD together with the structures of the two most stable polymorphs of CB itself [1], [2]. In chocolate generally the β -V polymorph is present rather than the somewhat more stable form β -VI.

We studied the crystallisation process of pure CB time-resolved

in the SAXS-WAXS instrument of the Dubble beamline BM26 at the ESRF. The length of the SAXS instrument was chosen such that the long spacing reflection of CB was detected within the SAXS signal. We followed the process at different temperatures until almost all CB was solidified.

In this abstract we concentrate on just one typical example, where the molten CB is cooled to 20° C. After 6 minutes the long spacing shows up at d-value 67.4 Å and in the next half hour this value slowly decreases to 64.75 Å where it stays. From these values we conclude that the crystallisation starts from SOA and successively SOS, POS and POP are taking part. The intensity indicates that after an hour almost all CB has been crystallised. The CB crystallites are very small; at the initial stages they are 35 nm, which doubles in an hour to 67 nm. In matured chocolate the sizes may be up to 250 nm. So even then an average crystal consists of 40 layers, or 20 times the crystallographic c-axis.

The crystallisation process is preceded by a broad WAXS signal around a 80-85 Å, which fades away when the long spacing shows up. This signal most probably corresponds to a triple layer with a very unordered oleic middle region. At present this is studied in more detail.

In the presentation other time-resolved experiments will be shown as well.

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Keywords: nano-crystals in cocoa butter, time-resolved XRPD, SAXS-WAXS

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Crystal Structure of Monoclinic $\text{Sr}_{2.4}\text{Ca}_{0.6}\text{Al}_2\text{O}_6$

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Although the Portland cement related phases $\text{Sr}_x\text{Ca}_{3-x}\text{Al}_2\text{O}_6$ have been reported to crystallize in the cubic space group *Pa3* for the whole solid solution range, a monoclinic form of $\text{Sr}_{2.4}\text{Ca}_{0.6}\text{Al}_2\text{O}_6$ was prepared at 1300EC. Indexing the powder pattern was challenging; the strong split peaks could be indexing on a small orthorhombic cell, and the supercell tools in the old program NBS*LATTICE were used to identify a 32H monoclinic supercell which accounted for all of the peaks. The space group was identified as *P2₁/c* by examining possible distortions of the *Pa3* structure using ISODISTORT. $\text{Sr}_{2.4}\text{Ca}_{0.6}\text{Al}_2\text{O}_6$ crystallizes in *P2₁/c*, with $a = 15.7244(8)$, $b = 15.7361(2)$, $c = 15.7265(8)$ Å, $\beta = 90.6235(11)^\circ$, and $V = 3891.13(28)$ Å³. The lowering of the symmetry results in the presence of two independent 6-rings of corner-sharing AlO_4 tetrahedra; one 6-ring is more distorted than the other. The Sr/Ca are mostly ordered; at only one of the 20 alkaline earth sites is the occupation ~50/50. The Ca are not clustered in the unit cell. Symmetry mode analysis shows that the distortion from the cubic structure is complex, but concentrated in oxygen displacements in a few modes. The as-prepared sample contains some amorphous material, which hydrates to $\text{Sr}_3\text{Al}_2(\text{OH})_{12}$ on storage. Even in a combined synchrotron/laboratory Rietveld refinement (with extensive use of bonded and non-bonded distance restraints) it was difficult to obtain a precise structure. The final coordinates were determined by a density functional geometry optimization using the fixed experimental unit cell.

Keywords: strontium, aluminate, rietveld

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Grafting lactic acid on calcium-zinc hydroxyapatite surface

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Solid solutions of calcium-zinc hydroxyapatite [$\text{Ca}_{10-x}\text{Zn}_x(\text{PO}_4)_6(\text{OH})_2$] with $0 \leq x \leq 2$, were synthesized by a wet process in a basic medium [1]. The surface modification was carried out by dissolution of lactic acid in the organic suspension of hydroxyapatite. The hybrid organic-inorganic derivatives are characterized by means of element analysis, X-ray powder diffraction, infrared and NMR-MAS ¹³C spectroscopies. Chemical analyses indicate that the grafting process was ameliorated by the increase of the acid concentration and/or the zinc content. The X-ray powder diffraction patterns shows the conservation of apatitic structure as a unique crystalline phase with a low affectation of cristallinity which increases with increasing of acid concentration in solution. This affectation is more remarkable for phases richest in zinc. Other than characteristic bands of phosphate [ν_s (961 cm⁻¹), δ_s (474 cm⁻¹), ν_{as} (1032 cm⁻¹), δ_{as} (564 cm⁻¹)] and hydroxyl groups [ν_s (3570 cm⁻¹), ν_L (630 cm⁻¹)] of hydroxyapatite, infrared spectra display news vibration modes related to lactic acid essentially in the range from 1400 to 1600 cm⁻¹. The NMR-MAS ¹³C spectra of hydroxyapatite treated present three peaks centered around 20, 69 and 182 ppm which are attributed to the three carbons of lactic acid. The signal at 182 ppm characterizing the quaternary carbon ($\text{C}=\text{O}$) was degenerated on two or three signals respectively for hydroxyapatite containing one or two zinc atoms. This can be due to the heterogeneity of carbon environment by the presence of zinc at the apatitic surface.

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Keywords: apatite, diffraction, spectroscopy.

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Fonctionnalisation of calcium-zinc hydroxyapatite by tartaric acid

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Solid solutions of calcium-zinc hydroxyapatite [$\text{Ca}_{10-x}\text{Zn}_x(\text{PO}_4)_6(\text{OH})_2$] with $0 \leq x \leq 2$, were synthesized by a wet process in a basic medium [1]. The functionalization of their surface was carried out by dissolution of tartaric acid in organic suspension. The news hybrid inorganic-organic composites, $\text{Ca}_{10-x}\text{Zn}_x(\text{PO}_4)_6(\text{OH})_2$ -Tartaric acid obtained are characterized by means of elemental analysis, X-ray powder diffraction, FT-IR and NMR-MAS ¹³C spectroscopies. Chemical analyses approve the functionalization of hydroxyapatite and indicate that grafting process was ameliorated by the increasing of acid concentration and/or the zinc content. The X-ray powder diffraction patterns shows the conservation of apatitic structure as unique crystalline phase. The cristallinity was affected slightly as function of acid concentration increases in start solution. This affectation is more remarkable for phases richest in zinc. The relative FT-IR absorption spectra display the absorption bands characteristic of PO_4^{3-} modes [ν_s (961 cm⁻¹), δ_s (474 cm⁻¹), ν_{as} (1032 cm⁻¹), δ_{as} (564 cm⁻¹)], and the absorption bands [ν_s (3570 cm⁻¹), ν_L (630 cm⁻¹)] due to the stretching and libration modes of OH⁻ groups. In addition, news absorption bands