

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 unorderd oleic middle region. At present this is studied in more detail.

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

[1] J.B. van Mechelen, R. Peschar, H. Schenk, *Acta Cryst.* **2006**, B62, 1121-1130. [2] J.B. van Mechelen, R. Peschar, H. Schenk, *Acta Cryst.* **2006**, B62, 1131-1138.

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

## MS74.P13

*Acta Cryst.* (2011) A67, C675

### 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 *P2<sub>1</sub>/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 *P2<sub>1</sub>/c*, with  $a = 15.7244(8)$ ,  $b = 15.7361(2)$ ,  $c = 15.7265(8)$  Å,  $\beta = 90.6235(11)^\circ$ , and  $V = 3891.13(28)$  Å<sup>3</sup>. The lowering of the symmetry results in the presence of two independent 6-rings of corner-sharing  $\text{AlO}_4$  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

## MS74.P14

*Acta Cryst.* (2011) A67, C675

### 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 <sup>13</sup>C 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 [ $\nu_s$  (961 cm<sup>-1</sup>),  $\delta_s$  (474 cm<sup>-1</sup>),  $\nu_{as}$  (1032 cm<sup>-1</sup>),  $\delta_{as}$  (564 cm<sup>-1</sup>)] and hydroxyl groups [ $\nu_s$  (3570 cm<sup>-1</sup>),  $\nu_L$  (630 cm<sup>-1</sup>)] of hydroxyapatite, infrared spectra display news vibration modes related to lactic acid essentially in the range from 1400 to 1600 cm<sup>-1</sup>. The NMR-MAS <sup>13</sup>C 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.

[1] T. Turki, A. Aissa, H. Agougui, M. Debbabi, *Journal de la Société Chimique de Tunisie*, **2010**, 12, 161-172.

**Keywords:** apatite, diffraction, spectroscopy.

## MS74.P15

*Acta Cryst.* (2011) A67, C675-C676

### 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 <sup>13</sup>C 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  $\text{PO}_4^{3-}$  modes [ $\nu_s$  (961 cm<sup>-1</sup>),  $\delta_s$  (474 cm<sup>-1</sup>),  $\nu_{as}$  (1032 cm<sup>-1</sup>),  $\delta_{as}$  (564 cm<sup>-1</sup>)], and the absorption bands [ $\nu_s$  (3570 cm<sup>-1</sup>),  $\nu_L$  (630 cm<sup>-1</sup>)] due to the stretching and libration modes of OH<sup>-</sup> groups. In addition, news absorption bands