B2 - Phase Transitions

B2 - O1

HIGH-RESOLUTION AND TIME-RESOLVED XRD STUDIES OF COCOA BUTTER LEAD TO BETTER CHOCOLATE

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Crystallization of cocoa butter is the critical step in making chocolate and confectioneries. Poorly crystallized chocolate may result in the formation of fat bloom, a greyish-white film at the chocolate surface. Cocoa butter has been subject to research for many years resulting in at least six different polymorphs, indicated by Greek letters , , ‘ and . In good quality chocolate predominantly the (V)-polymorph is present, but may be also the (VI)-phase.

X-ray powder diffraction (XRD) is a very useful technique to identify the fingerprint region (d = 3.0 - 6.0 Å) of the cocoa butter polymorphs, which are different for all. In fat research XRD has the advantage over DSC of giving unambiguous phase information. Time-resolved XRD (trXRD) is a very suitable tool for studying the phase transformations of the system as well as for following melting and solidification processes. It is being used extensively in our research and may be presented in movies.

Also full XRD patterns, including peaks at long d-spacing values, are being used to characterize the various cocoa-butter phases. Furthermore, the components of cocoa butter, the triacylglyceroles (TAG, see figure), are subject to structure determination studies using High-Resolution Synchrotron data. This eventually will lead to more suitable molecular models for cocoa butter to understand its crystallisation and phase transformation. Both single crystal and powder methods are being used, but, remarkably, the latter methods are more successful as it is very difficult to obtain suitable single crystals and to handle them. In order to unravel the mechanism of fat bloom, we recently took up the crystal structure solution of the (V)-polymorph of cocoabutter and we expect to be able to report on this research at the meeting.

Crystallization of cocoa butter in the phase directly from the melt under static conditions is only possible employing the memory effect of cocoa butter [1]. When -phase cocoa butter is heated below a maximum temperature and above the melting end point, it re-crystallizes in the -phase at crystallization temperatures. The influence of the maximum and crystallization temperatures on the re-crystallization behaviour has been investigated for cocoa butter from Bahia (Brazil). Re-crystallization into the (VI)-phase appears to be faster than into the (V)-phase. Structural information on the seed material initiating the re-crystallization process has been collected through Small-Angle X-ray Scattering. High-melting SOS-rich seeds in triple chain-length packing initiate the rapid-starting re-crystallization. The seed crystals initiating the slow-starting re-crystallization resulting in the (V)-phase are different from those resulting in the (VI)-phase.

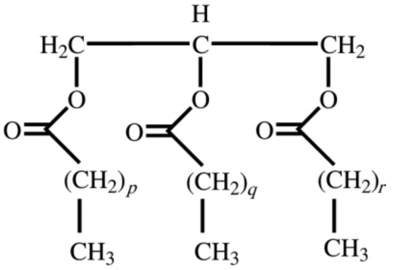

Fig. 1. Diagram of a triacylglycerole. The three fatty acid residues may have different lengths indicated by p, q, and r. Natural fats as cocoa butter are mixtures of different TAG’s in which also unsaturated fatty acid residues may be present.

As a spin-off of our basic research a new, patented, way of chocolate making [2] has been tested successfully at industrial scale. The manufacturing is based on a new and revolutionary tempering process, using seed crystals in the liquid phase and driven by a feedback system. A research machine has been developed at the mechanic laboratory of Duyvis Machine Factory [3] and produces on demand from 100 to 1000 kg of well-tempered chocolate in a continues process. A 3-ton prototype is currently being designed and first results may be reported.

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B2 - O2

TEMPERATURE EFFECTS ON THE HYDROGEN BOND PATTERNS IN SOME HYDRATED AMINOACIDS

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Cooperative effects are significant in the formation of extended patterns of hydrogen bonds in amino acids, specially when the stabilization is achieved by polarization and charge transfer effects [1,2]. On the other hand, the water molecule is unique, since it has the possibility of acting as a double donator and double acceptor of hydrogen bonds, playing an important role in biological processes such as folding and hydration of proteins [3,4]. It also helps to preserve their three-dimensional structures. If it is present in the crystal structure of small aminoacids, it can play an important role in the hydrogen-bonding patterns through cooperative effects, or reside in void spaces in the structure forming weak aminoacid-solvent interactions. In the hope of understanding the role played by the water molecules in simple biological systems, we have undertaking an investigation on the energetic and structure of hydrogen-bonding patterns of two structurally related aminoacids, 4-piperidine carboxylic acid and cis-4-aminocyclohexane carboxylic acid (Figure 1). The first has the potential to donate two hydrogen atoms for hydrogen bonding, while the second, having the animo group as a substituent of the cyclohexane ring, is able to donate three hydrogen atoms. Differential Scanning Calorimetry and Thermogravimetric Analysis were performed to investigate the dehydration process and any additional phase changes upon heating. Structural changes were followed by means of variable temperature X-ray powder diffraction experiments using beamlines BM16 and ID31, ESRF, France. Figure 2 shows a three-dimensional diagram for 4-piperidine carboxylic acid, in which three different crystalline phases are seen. In the case of cis-4-aminocyclohexane carboxylic acid only two phases were noticed. The different structures were solved by simulated annealing and refined using the Rietveld Method. In the 4-piperidine carboxylic acid, the motifs were extended chains in two crystallographic directions, while in the cis-4-aminocyclohexane carboxylic acid sandwich structures, formed by two amino acid units linked by head-to-tail hydrogen bonds, are the basic motif. These sandwich structures then form extended helicoidal chains. A detailed discussion of the hydrogen-bonding patterns of the hydrated, dehydrated and high temperature forms of the amino acids is presented, and compared with semi-empirical theoretical calculations performed in these systems. From our investigations we conclude that the water molecule has the additional role of completing the acceptor capacity of the carboxylate group of the amino acids, which is equal to four in the cases investigated here.

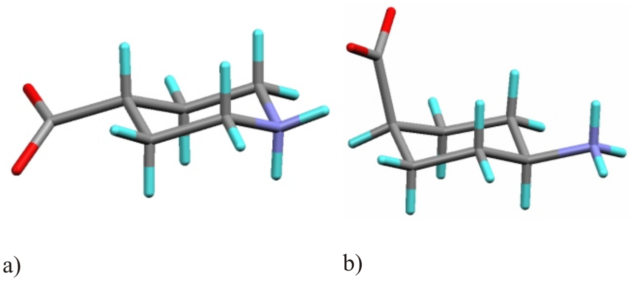
a) b)

Figure 1. (a) 4-piperidine carboxylic acid (b) cis-4- aminocyclo hexancarboxilic acid.

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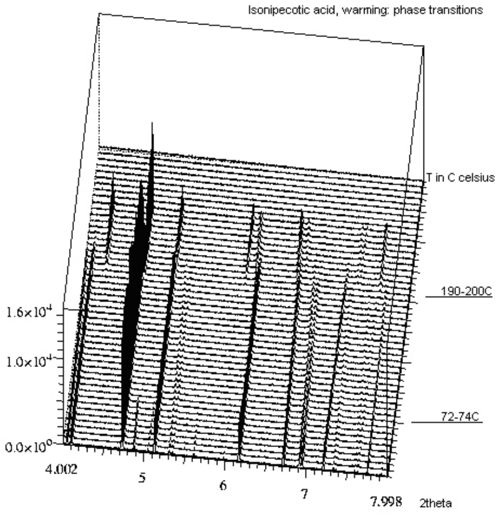

Figure 2. 3D Temperature dependent X-ray diffraction plot for 4-piperidinecarboxylic acid.

B2 - O3

EFFECT OF HYDROSTATIC PRESSURE ON THE GAMMA-POLYMORPH OF GLYCINE: A PHASE TRANSITION

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Introduction

While the majority of crystal structures of organic molecules have been determined at normal pressure conditions, there is a great demand for the observations of structural changes that occur in organic solids in response to high pressure.

Among molecular organic crystals, those of amino acids attract special attention – as biomimetics, as solid drugs, as materials for molecular electronics, as systems important for geo- and cosmochemistry.

The hot topics of the research are:

- the search of high-pressure polymorphs of amino acids,
- the studies of the anisotropy of pressure-induced structural distortion not accompanied by a phase transition.

Experimental

X-ray powder diffraction patterns were measured in transmission mode. A monochromatized synchrotron radiation source of the Swiss-Norwegian Beam Line at ESRF was used (= 0.71950 Å) for detailed studies, since glycine is a poor diffractor (having only light N, O, C and H atoms). Diffraction patterns were registered with a MAR345 image plate detector (pixel size 0.15 mm, 2300 x 2300 pixels in image, maximum resolution 1.105 Å, maximum 2 = 36.942 deg.). The frames were measured with exposing time equal to 900 - 3600 seconds, with   = 0.03 degrees. The distance crystal-detector, the beam center position, the tilt angle and the tilt plane rotation angle were refined using a Si standard put at a diamond anvil (DAC). A methanol-ethanol mixture was used as a pressure-transmitting medium [1]. It was specially dried to have no traces of water, because even traces of water are known to influence on the polymorphic transformations in glycine. The sample in the DAC was centered with respect to the beam very carefully, so that no reflections from steel gasket could be observed in the measured diffraction pattern.

Fit2D program [2] was used for processing diffraction data measured with the synchrotron source (calibration, masking, integration).

The unit cell dimensions were determined with the indexing program TREOR [3] with M_{19}= 22, F_{19} = 48 (0.009163, 44) using the first 19 peak positions. The structure was solved by the grid search procedure [4] and refined with the use of bond restraints by the MRIA program [5]. The strength of restraints was a function of interatomic separation and for intramolecular bond lengths corresponds to an r.m.s. deviation of 0.03 Å. H atoms were placed in geometrically calculated positions and allowed to refine using bond restraints with a common isotropic displacement parameter U_{iso} fixed to 0.05 $Å^2$.

PowderCell [6] was used for structure analysis and graphic representation.

Results and discussion

At 2.74 GPa the reflections of a new phase could be observed, although -polymorph was still the major component at this pressure. The new high-pressure phase was present as the main component in the pressure range 4.17 – 7.85 GPa, but even at 7.85 GPa the peaks of the low-pressure phase (-glycine) were still present in the diffraction patterns.

The structure of a new high-pressure polymorph was solved in the Pn (No 7) space group (a = 5.379(1) Å, b = 5.557(1) Å, c=4.780(1) Å,   = 118.25(1)°, V = 125.86(4) $Å^3$, Z = 4). The packing of zwitter-ions in the high-pressure polymorph turned out to be essentially different from that in the original -polymorph ($P3_1$), but similar in many respects to packing of zwitters-ions in the other two previously known polymorphs of glycine – - ($P2_1/n$) and - ($P2_1$) forms. [7]. In the -polymorph zwitter-ions are linked via hydrogen bonds in a three-dimensional network based on helical chains. In the new high-pressure polymorph the zwitter-ions are rearranged to give specific layers.

The structure of an individual layer in the high-pressure polymorph is similar in many respects to the structures of individual layers in the - and - forms, but the way how the layers are stacked is essentially different: the layers in the high-pressure polymorph are double, as in the -form, but the individual layers in the double layer are related not by inversion, as in the -form, but by a glide plane. The pressure-induced polymorphic transformation in the -polymorph can be compared to a change in the secondary structure of a polypeptide chain from a helix into a layer.

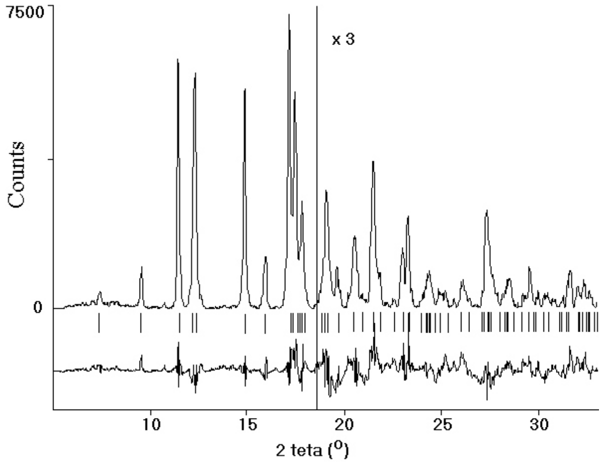

Figure 1

Table 1

atom	x	y	z	Uiso (Å^2)
O1	0.9533	0.806(2)	0.2824	0.018(1)
O2	0.308(2)	0.6525(14)	0.767(2)	0.018(1)
N1	0.780(3)	0.724(2)	0.734(2)	0.018(1)
C1	0.224(3)	0.763(3)	0.519(2)	0.018(1)
C2	0.484(3)	0.853(2)	0.496(3)	0.018(1)
H1	0.516	0.022	0.549	0.051
H2	0.433	0.825	0.294	0.051
H3	0.753	0.560	0.690	0.051
H4	0.945	0.782	0.708	0.051
H5	0.850	0.756	0.943	0.051

A high resolution, synchrotron X-ray pattern of the glycine high-pressure modification and a difference between the measured and calculated profiles are shown on Figure 1. Atomic coordinates and isotropic displacement parameters are in the Table 1.

On decompression, the high-pressure phase did not disappear completely even at ambient pressure. At 3.27 GPa the amount of the initial -polymorph increased considerably. Besides, some additional lines appeared that could not be assigned either to the new high-pressure polymorph, or to the original -form.

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B2 - O4

X-RAY POWDER DIFFRACTION USED TO EVALUATE THE KINETICS OF VARIOUS PROCESSES RELATED TO ORDERING IN Ni$_{1+}$ Sn (= 0.35, 0.50)

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The binary system Ni-Sn contains a series of non-stoichiometric phases Ni$_{1+}$ Sn with Ni$_2$In/NiAs type structures: a NiAs type sub-structure is formed by Ni(1)Sn (Sn taking the place of As) with additional Ni(2) atoms occupying partially the centres of the trigonal-bipyramids formed by five Sn atoms. In the hexagonal high-temperature (HT) phase with ca. 0.27   0.65 these Ni(2) atoms show no long-range order. Occupational ordering of Ni(2) is exhibited, however, by the three different but structurally similar orthorhombic low-temperature phases (LT, LT', LT'' [1-5]). The order-disorder phase-transition temperature is strongly composition dependent, e.g. the disordered HT-Ni$_{1.50}$Sn transforms to the ordered LT phase below 782 K, whereas for Ni$_{1.35}$Sn the LT' phase forms below 686 K. The equilibrium phase transitions occur discontinuously, i.e. by a first order transition [2]. States of (dis)order can be retained at ambient temperatures by quenching the alloys in water.

The present paper reports X-ray powder diffraction investigations on non-equilibrium states of Ni$_{1+}$ Sn obtained by various heat treatment procedures, providing insight into the mechanism of the different observed processes. For that three alloys were equilibrated at different annealing temperatures T_1 and subsequently quenched:

HT-Ni$_{1.50}$Sn quenched from T_1 = 1023 K
HT-Ni$_{1.35}$Sn quenched from T_1 = 1023 K
LT'-Ni$_{1.35}$Sn quenched from T_1 = 683 K.

These samples were afterwards annealed at various temperatures $T_2 < 600$ K for certain periods of time, quenched and then characterised by X-ray powder diffraction. The gradual changes from the equilibrium state quenched from T_1 to the new equilibrium state (often finally reached only after long times) at T_2 can be traced by measuring lattice parameters, integral reflection intensities and diffraction-line broadening as a function of the annealing time.

Annealing of HT-Ni$_{1.50}$Sn and HT-Ni$_{1.35}$Sn at T_2 generates new long-range order leading finally to the LT/LT' phases in equilibrium at T_2. This order formation occurs in a two-step fashion, which involves firstly formation of long-range order in small domains, and secondly coarsening of the ordered domains as exhibited by a narrowing of the superstructure reflections (Figure 1).

The LT'-Ni$_{1.35}$Sn sample equilibrated at and quenched from T_1 = 683 K shows long-range order with sharp superstructure reflections. However, the degree of long-range order as obtained from the intensities of the superstructure reflections is distinctly lower than for samples equilibrated at lower temperatures. In this case annealing at various temperatures T_2 now reveals simply a gradual increase of the already present long-range order (Figure 2), in contrast with the two-stage order-formation process exhibited by the samples equilibrated at T_1 = 1023 K.

The X-ray powder diffraction data were used to evaluate the kinetics of the observed processes. Particularly, the activation energies were determined. Methods for such analyses were developed. The contribution of the activation-energy values to the understanding of the transformation mechanisms is discussed.

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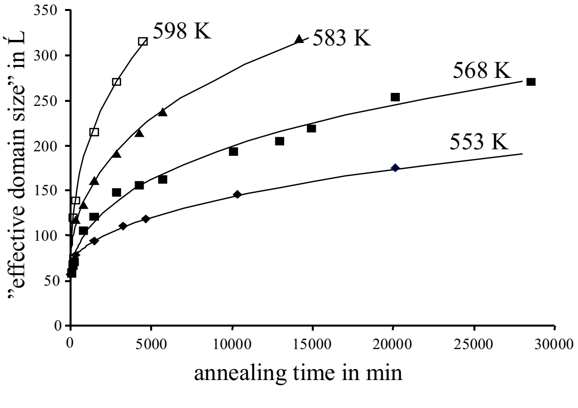

Figure 1: Coarsening of small-domain LT-Ni$_{1.50}$Sn produced by annealing HT-Ni$_{1.50}$Sn as observed by an evaluation of Scherrer-type broadening of the superstructure reflections (stage 2 of order formation).

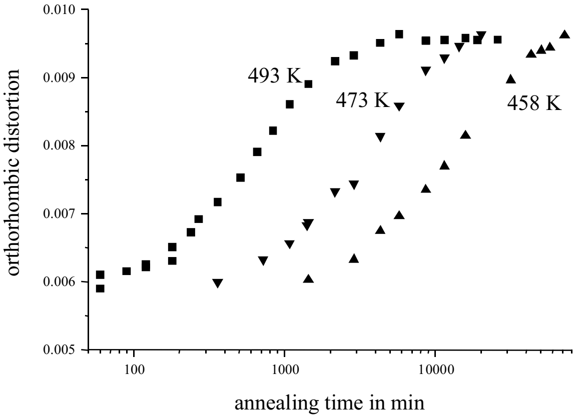

Figure 2 Evolution of the 'orthorhombic distortion' used as a measure for the degree of long-range order in LT'-Ni$_{1.35}$Sn equilibrated at T_1 = 683 K and annealed subsequently for various times at various temperatures T_2.