Phase Transitions of FOX-7 studied by X-ray Diffraction and Thermal Analysis

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Abstract

The phase behavior of 1,1-Diamino-2,2-dinitroethylene (FOX-7) was reinvestigated in a FOI-ICT cooperation by means of thermal analysis (DSC, TG, TMA) and X-ray diffraction. Three phases were observed, and α- and β-FOX-7 were identified by X-ray diffraction. The following transition scheme was found:

Heating:	$\alpha \rightarrow \beta \rightarrow \gamma$	at 113 °C($\alpha \rightarrow \beta$) and 173 °C($\beta \rightarrow \gamma$)
Cooling:	$\alpha(+\gamma) \leftarrow \gamma$	between 50 and 75 °C

The α/β-transition is fully reversible, and the γ/α-retransition revealed to be incomplete. A fourth phase described in literature was not found.

1. Introduction

FOX-7, 1,1-Diamino-2,2-dinitroethylene ($C_2H_4N_4O_4$) is a new high explosive. The material combines high performance and low sensitivity. FOX-7 was developed by FOI (Swedish Defense Research Agency) [1], from where the name FOX (**FO**l-e**X**plosive) is deduced. It is produced by the Swedish company EURENCO Bofors.

The molecular structure of FOX-7 is shown in Figure 1. The compound is a typical so-called push-pull ethylene. This group of compounds has donator and acceptor groups in

the same molecule. The ethylene bond distance of 1.45 Å is therefore intermediate between a single bond (1.54 Å) and a double bond (1.34 Å). Additionally, the order of the ethylene bond decreases from 2 to nearly 1.5.

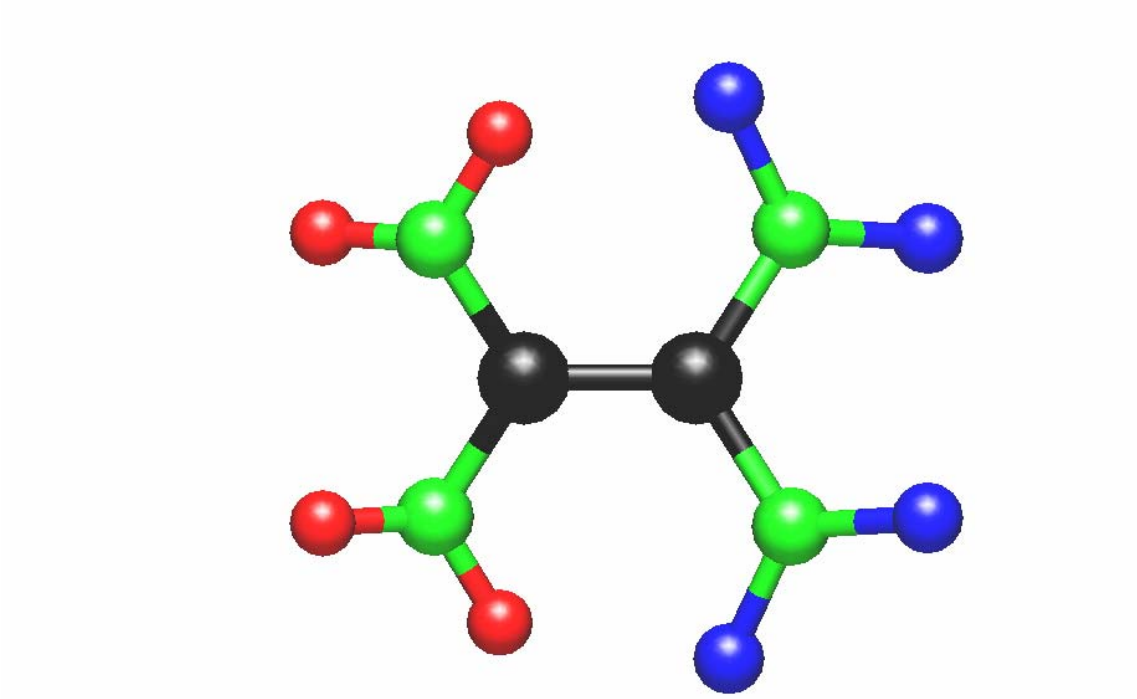

Figure 1: Molecule structure of FOX-7, calculated by the ab-initio program Gaussian98 [2].

FOX-7 is a polymorphic substance. Four phases are mentioned in literature [3]. However, the reported results obtained by X-ray diffraction and DSC are not coincident, and the transition behavior on cooling is far from being clear. Therefore reinvestigations of the phase transitions were started in a FOI-ICT cooperation by means of temperature resolved X-ray diffraction, DSC and TMA. Fox-7 was purchased from EURENCO Bofors, with deliveries to FOI and ICT from the same batch.

Thermal analysis was performed by FOI, except the TMA, and temperature resolved X-ray diffraction and the TMA by ICT.

2. Thermal Analysis

2.1. Experimental

Recrystallized FOX-7 material, lot number 2002-7033, was obtained from EURENCO Bofors (Sweden). The material has been recrystallized from wet raw FOX-7 material. A mixture of N-methylpyrrolidinone (NMP) and water 50/50 vol.-% with the raw material was heated to approximately 95°C and then cooled down slowly to room temperature.

The slurry was then filtered and the crystals washed with water.

The thermal properties of FOX-7 were analyzed at FOI with Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). A Mettler TGA 850 has been used for the thermogravimetric measurements. The analyses have been conducted in open 70 µl alumina cups and the flow of nitrogen was approximately 25 ml/min. The TG was calibrated with indium and aluminum standards. The DSC analyses were done using a Mettler DSC 30 working under a nitrogen atmosphere (50 ml/min). The samples were sealed in 40 µl aluminum pans with pierced lids. The sample weight was approximately 1,5 mg. Calibration was made with indium (Tm = 156.6°C). The DSC analyses has been performed between 30°C and 400°C using three different heating rates; 2, 5 and 10°C/min. Cyclic DSC and TG analysis has been performed between 30°C and 175°C at a rate of 5°C/min and back to 30°C at a rate of -5°C/min. The cycle has been repeated four times in the DSC and three times in the TG. Cyclic repeated DSC analysis between 30°C to 135°C and back to 30°C at the rates of 5°C/min and -5°C/min has also been performed.

The thermo-mechanical analysis was performed at ICT using a EXSTAR6000 TMA/SS (SII NanoTechnology Inc.). The sample was filled in a glass cylinder with a diameter of 5 mm and a length of 20 mm. A glass plunger with a defined mass of 5 g was put on the top of the sample. The samples were heated or cooled with defined temperature rates, and the movement of the plunger was measured mechanically, monitoring the thermal expansion behavior of the samples.

2.2. Results

The DSC measurements between 30°C and 400°C of the recrystallized FOX-7 show two endothermic and two exothermic peaks. The second endothermic peak at ~160°C is split. The DSC thermogram obtained at a heating rate of 10°C/min from 30°C to 400°C is shown in **Figure 2**. The results of the DSC analyses at heating rates of 2 and 5°C/min follow the same pattern as for 10°C/min although the peaks show less intensity.

Cyclic repeated DSC analysis between 30°C and 135°C show one endothermic peak during heating and one exothermic peak during cooling, **Figure 3**. The peaks appear repeatedly in each heating and cooling cycle with unchanged peak areas. The endothermic peak in the first heating cycle appears at a higher temperature than in the

following cycles. The exothermic peak in the first cooling cycle is registered at a lower temperature compared to the following cycles.

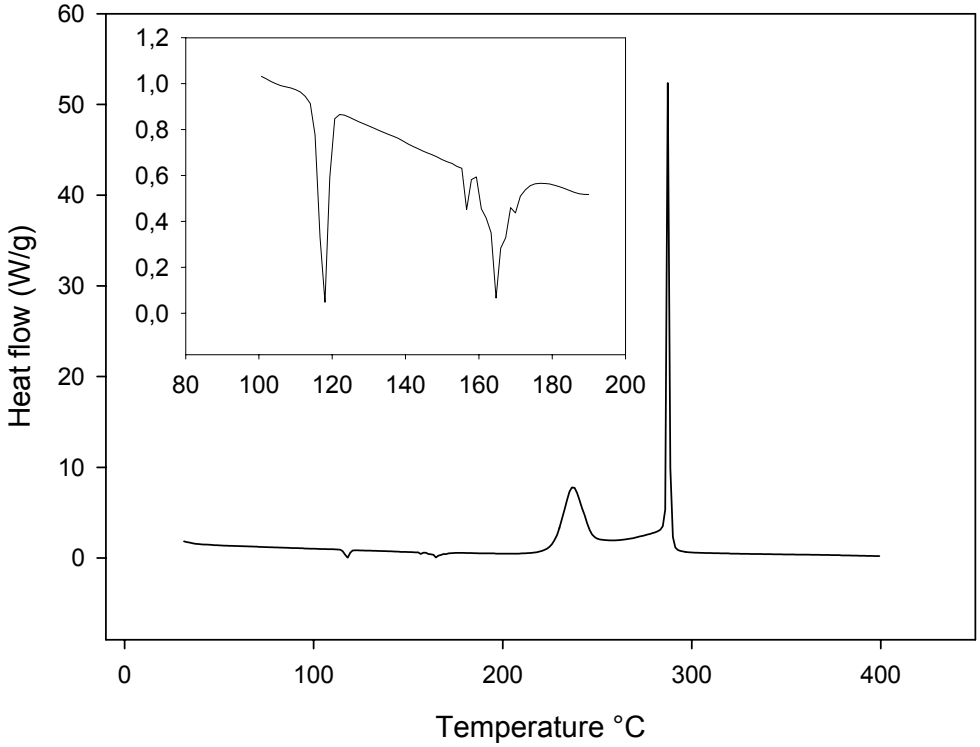

Figure 2: DSC analysis of FOX-7 between 30°C and 400°C at a heating rate of 10°C/min.

Cyclic repeated DSC analysis between 30°C and 175°C show two endothermic peaks during heating and one exothermic during cooling, **Figure 4**. The peaks appear repeatedly in each heating and cooling cycle. However, the peak areas are decreased for each new cycle. The peak at ~117°C appears repeatedly at approximately the same temperature. The shape of the peak at ~160°C changes from a split peak in the first cycle to a single peak in the following cycles. The position of the second endothermic peak shifts with the number of heating cycles. The cooling cycle shows an exothermic peak at a lower temperature than the first endothermic peak during heating.

The repeated TG analysis of FOX-7 between 30°C and 175°C show a weight loss (~2 wt-%) only in the first heating cycle, **Figure 5**. This weight loss is registered at the same temperature as the second endothermic peak in the DSC analysis.

Figure 6 shows the TMA curve of FOX-7. During the first heating cycle, two phase transitions were found at 117°C and 160°C. On cooling only one phase transition was observed at quiet low temperatures (first cooling: T=50,2°C, second cooling: T=76,2°C).

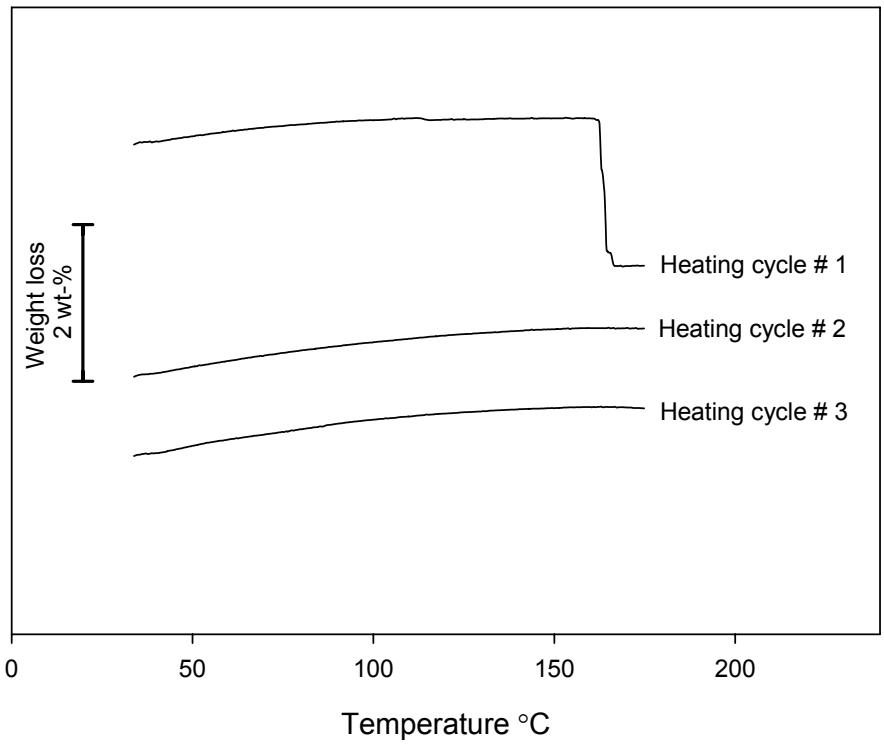

Figure 5: Cyclic repeated TG analysis of FOX-7 between 30°C and 175°C at a heating rate of 5°C/min.

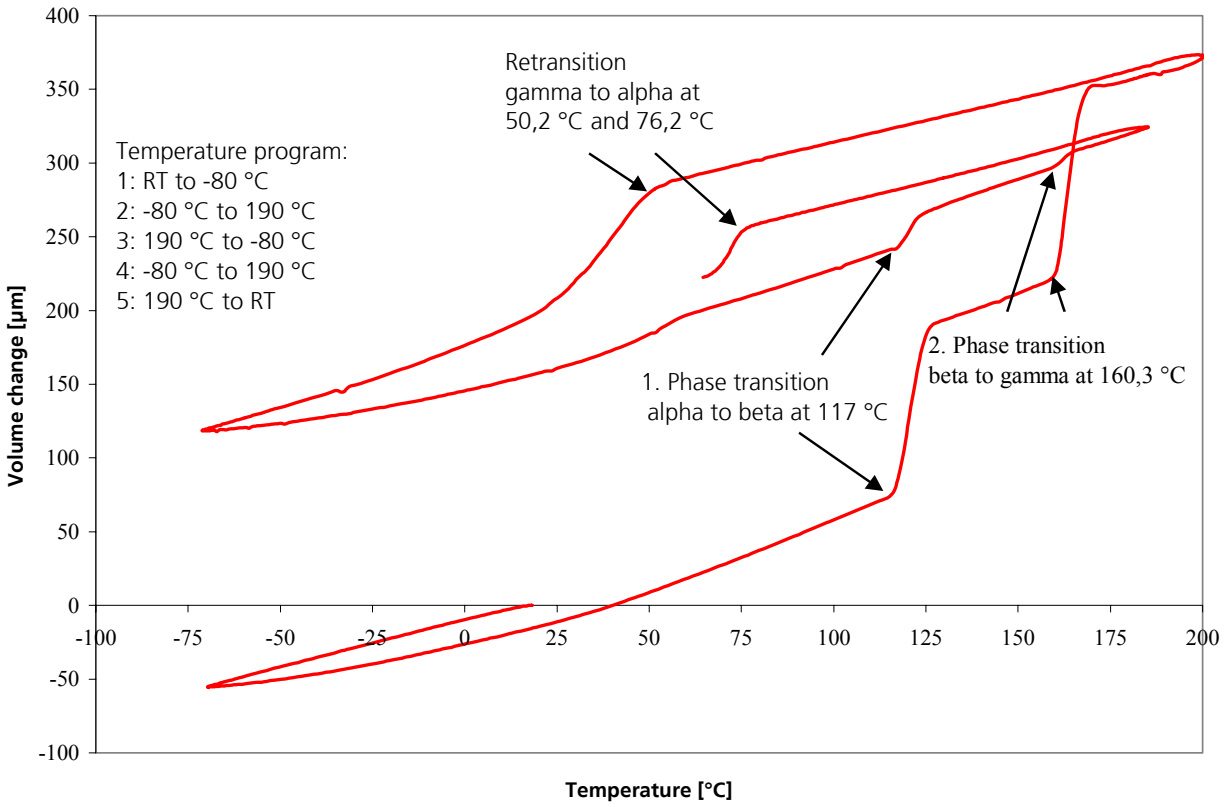

Figure 6: TMA diagram of FOX-7.

3. X-ray diffraction

3.1. Experimental

For the X-ray investigations the relatively coarse FOX-7 was ground to an average particle size of 4 µm in order to improve the orientation statistics. The measurements were performed with the diffractometer D5000 from Bruker AXS, equipped with the low temperature chamber (TTK) from Paar. The radiation used was copper with a wavelength of λ = 1.5418 Å. Samples were heated and cooled stepwise between -70 and 190 °C, and diffraction patterns were measured after each temperature step.

The measured diffraction patterns were evaluated by Rietveld analysis, identifying occurring phases on the basis of the crystal structure reported in literature. Moreover, lattice parameters and specific volume of the phases were refined and plotted versus temperature.

The structure of α-FOX-7 was described in 1998 by Bemm and Östmark [4]. The crystal structure of β-FOX-7 was solved with aid from A. Meents [5]. The structures of further phases are already unknown.

3.2. Results

The contour plot in **Figure 7** shows the changes of diffraction patterns on heating from 20 to 190 °C, representing thermal expansion and transition behavior of FOX-7. Two phase transition were found at about 115 °C and 180 °C. The initial phase at room temperature and the phase appearing after the first transition were identified as α- and β-FOX-7, respectively. As no structure data of further phases are available, the phase appearing after the second transition was assigned as γ-FOX-7. Thus the phase transition path on heating was determined as $\alpha \rightarrow \beta \rightarrow \gamma$.

Cycling of FOX-7 between -70 and 130 °C below the second transition shows a reversible phase transition $\alpha \leftrightarrow \beta$. The contour plot is shown in **Figure 8**.

This changed, when the maximum temperature of the cycles is increased above the second phase transition (**Figure 9 and 10**). Cycling between -70 and 190 °C shows two transitions on heating ($\alpha \rightarrow \beta \rightarrow \gamma$) but only one retransition on cooling, identified as $\alpha \leftarrow \gamma$. This retransition occurred between 50 and 75 °C. As it happened to be not complete, small parts of a "stabilized" γ-FOX-7 was identified beside α-FOX-7 on cooling until -70 °C and beside the transitions $\alpha \rightarrow \beta \rightarrow \gamma$ during the second heating. Increasing the maximum temperature of the cycles to 200 °C revealed the same transition path but

with a higher concentration of stabilized γ-FOX-7.

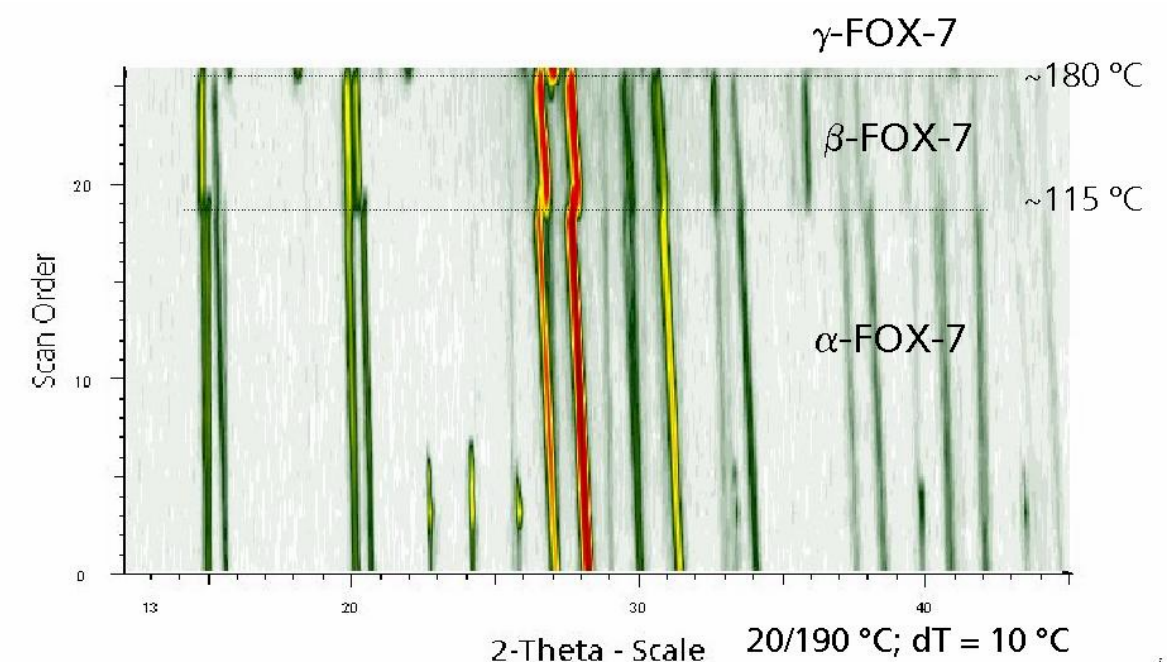

Figure 7: Temperature resolved X-ray diffraction patterns as contour plot, measured with the temperature program 20/190 °C.

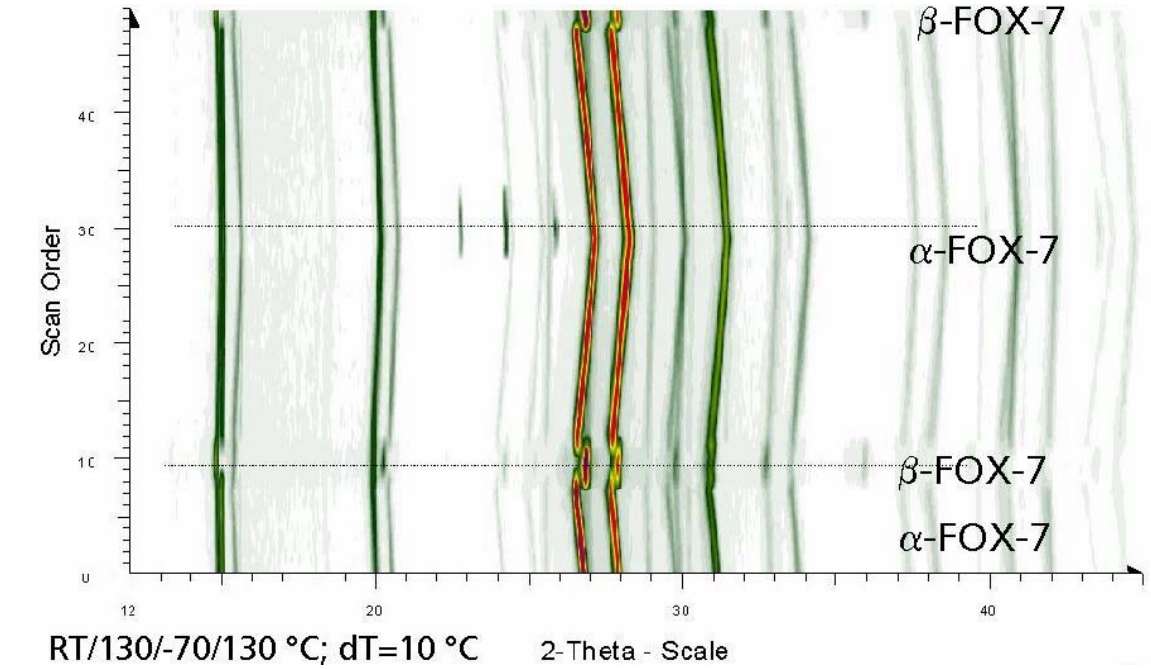

Figure 8: Temperature resolved X-ray diffraction patterns as contour plot, measured with the temperature program RT/130/-70/130 °C.

The (100) projections of α- and β-FOX-7 are shown in **Figure 11** and **12**. The crystal structures are very similar. The molecular packing of both phases consists of wave-shaped layers belong the axis c with extensive intermolecular hydrogen bonding within the layers and van der Waals interaction between the layers.

Lattice parameters and the volume of the unit cells of these phases, refined by Rietveld-Analysis, are plotted in **Figure 13** versus temperature. **Figure 14** shows e.g. the determination if thermal expansion coefficients of α-FOX-7. The relevant structural data and the linear thermal expansion coefficients are summarized in **Table 1**. The volume change of transition α→β at 113 °C amounts to 1.9 %.

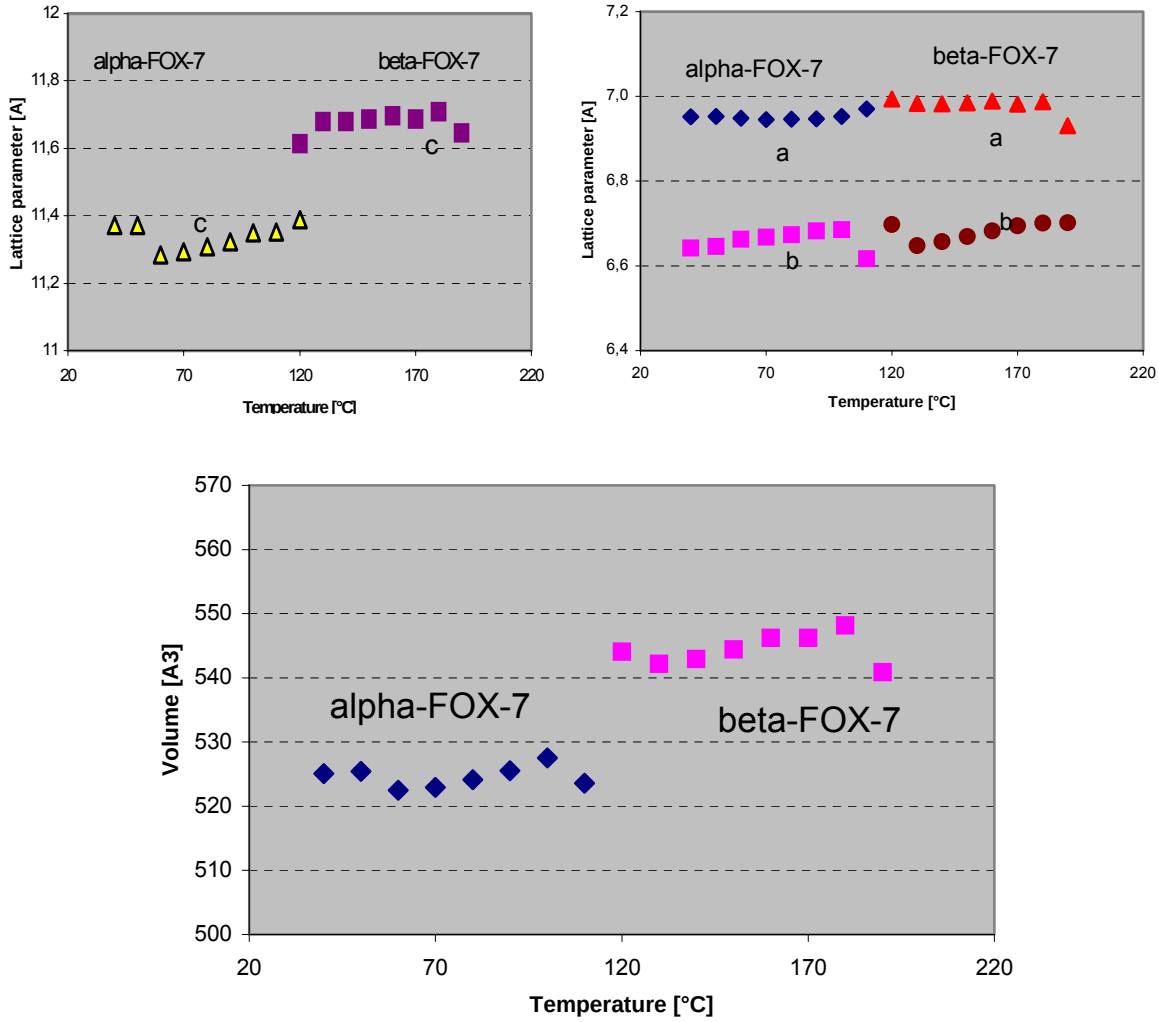

Figure 13: Lattice parameters and volume of α- and β-FOX-7 on heating.

Table 1: Lattice parameters and relative linear thermal expansions coefficient of α- and β-FOX-7

	α-FOX-7		β-FOX-7	
	20 °C [Å]; [Å^3]	Lin. Exp. [10^{-6}/°C]	130 °C [Å]; [Å^3]	Lin. Exp. [10^{-6}/°C]
a	6,939	43,4	6,978	8,7
b	6,631	124,9	6,638	147,4
c	11,349	26,6	11,660	39,5
beta	90,650	-1,1	90	
Vol.	522,2	195,3	540,1	155,3
crystal system	monoclinic		orthorhombic	
space group	$P2_1/n$		$P2_12_12_1$	

4. Discussion

The combined thermal investigations by means of DSC, TG TMA and temperature resolved X-ray diffraction yielded detailed information on the phase behavior of FOX-7.

Cyclic repeated DSC analysis between 30°C and 135°C show one endothermic peak at ~117°C during heating. A corresponding exothermal peak is also registered during the cooling cycle. The position of the peak shifts after the first cycle and remains unchanged thereafter. This can be explained by storage or thermal memory that causes a different behavior during the first heating and cooling cycle compared to the following. The peaks appear repeatedly with unchanged peak areas in each heating and cooling cycle. The peak at 117 °C indicates a fully reversible and complete phase transition.

Coincident results were found with the temperature resolved X-ray diffraction. A phase transition was found on heating at about 113 °C. The initial phase and the phase appearing above 113 °C were identified as α- and β-FOX-7 on the basis of the crystal data reported in literature. On cooling β-FOX-7 retransform completely to α-FOX-7. On further heating a third phase appears at 173 °C, denoted as γ-FOX-7. The transition is also complete. On cooling of γ-FOX-7 only one transition occurred, identified as γ→α below 75 °C. This transition is only partial. Small parts of γ-FOX-7 seem to be stable

even on cooling down to -70 °C.

The peak areas in the DSC decrease after each new heating and cooling cycle if the heating is extended above the second endothermic peak temperature, i.e. ~160 °C. With the extended heating cycles to 175°C both endothermic peaks show a decreased peak area for each new heating cycle. The split endothermic peak produced during the first heating cycle shifts to a single peak in the following heating cycles. A possible cause of this phenomenon is solvent or water inclusion in the crystals.

Repeated cyclic TG analysis supports the theory of solvent or water release. During the first heating cycle a weight loss is registered at the temperature for the appearance of the split endothermic peak in the DSC measurements. The weight loss is one explanation to the decreased endothermic peak areas in the next heating cycle. A phase change could facilitate the release of solvent or water from the crystal structure. A possible explanation to the decreased peak areas of both endothermic peaks is also that the second endothermic peak is a phase transition which, during cooling, has a slow reversion. The incomplete reversion, found by X-ray diffraction, give also an explanation for the decrease of peak areas for both endothermic peaks during the following heating cycle.

All together, the following transition scheme was found:

$\alpha \rightarrow \beta \rightarrow \gamma$ at 113 °C($\alpha \rightarrow \beta$) and 173 °C($\beta \rightarrow \gamma$)

$\alpha(+\gamma) \leftarrow \gamma$ between 50 and 75 °C

$\alpha(+\gamma) \rightarrow \beta(+\gamma) \rightarrow \gamma$

The cells of α- and β-FOX-7 are very similar, pointing to a displacive transition (small changes in atoms and lattice parameters within a similar structure). On heating, the thermal expansion of α-FOX-7 with 195 10^{-6}/°C is stronger as of β-FOX-7 with 155 10^{-6}/°C. The phase transition is combined with an increase in volume by 1.9 %. The expansion of both phases are anisotropic, dominated by the expansion of the lattice parameter *b* with 125 10^{-6}/°C in α-FOX-7 and 147 10^{-6}/°C in β-FOX-7. The anisotropy of ß-FOX-7 is stronger. The phase transition α/β is dominated by a spontaneous increasing of the parameter *c*, while *a* remains nearly constant and *b* decreases slightly. The transition into γ-FOX-7 is assumed to be reconstructive.

5. Conclusion

Three phases were observed by X-ray diffraction. The phases α- and β-FOX-7 were identified using structure data from literature. The structure of the third phase is yet unknown and needs further investigation. A fourth phase described in literature was not found.

DSC shows two endothermic peaks suggested to correspond to phase transitions of the FOX-7 crystal. The first endothermic peak is accompanied by an exothermic peak during cooling indicating a fully reversible instantaneous phase transition.

The second endothermic peak is supposed to reflect a phase transition with an incomplete or slow reversion. The latter phase transition is also suggested to be accompanied with solvent or water release in the first transition during heating.

All together, the following transition scheme was found:

Heating:	$\alpha \rightarrow \beta \rightarrow \gamma$	at 113 °C($\alpha \rightarrow \beta$) and 173 °C($\beta \rightarrow \gamma$)
Cooling:	$\alpha(+\gamma) \leftarrow \gamma$	between 50 and 75 °C

6. Reference

[1] Latypov NV, Bergman J, Langlet A, Wellmar U, Bemm U (1998) Tetrahedron 54, 11525-11536.

[2] Frisch M.J. et al. (2001) Gaussian 98, Gaussian, Inc., Pittsburgh PA

[3] Bemm U, Eriksson L (2001) Phase Transitions in FOX-7, Proc. IM&EM Techn. Symp., Bordeaux

[4] Bemm U, Östmark H (1998) Acta Cryst. C54, 1997-1999

[5] Details will be published in Acta Cryst C

7. Acknowledgment

We thank A. Meents from Hazylab, Hamburg for the kind co-operation and investigations on the structure determination of β-FOX-7.

8. **Figures**

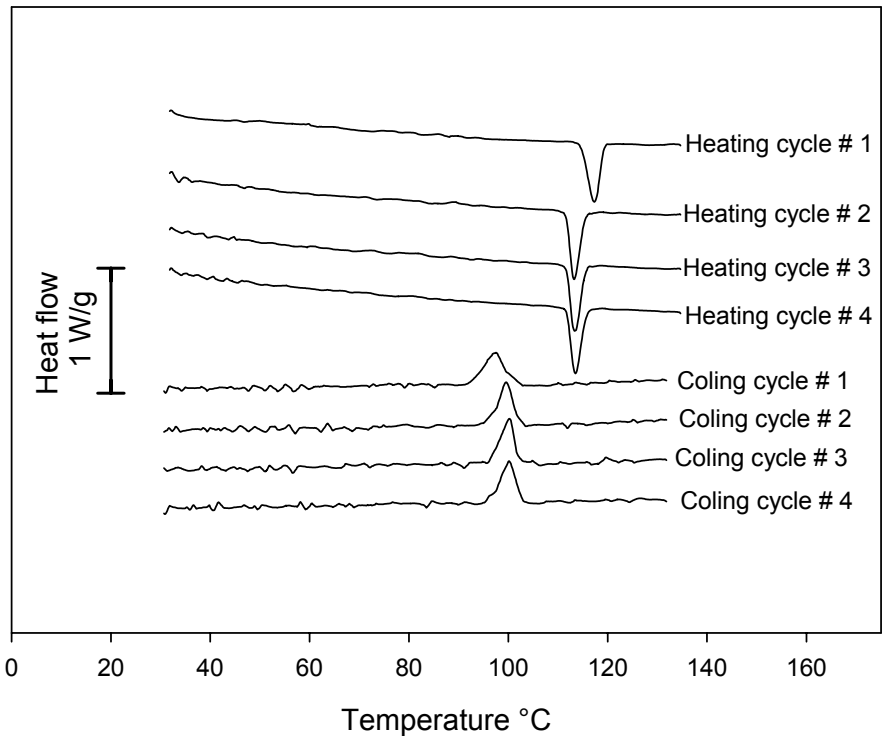

Figure 2: Cyclic repeated DSC analysis of FOX-7 between 30°C and 135°C at the rate of 5°C/min and -5°C/min.

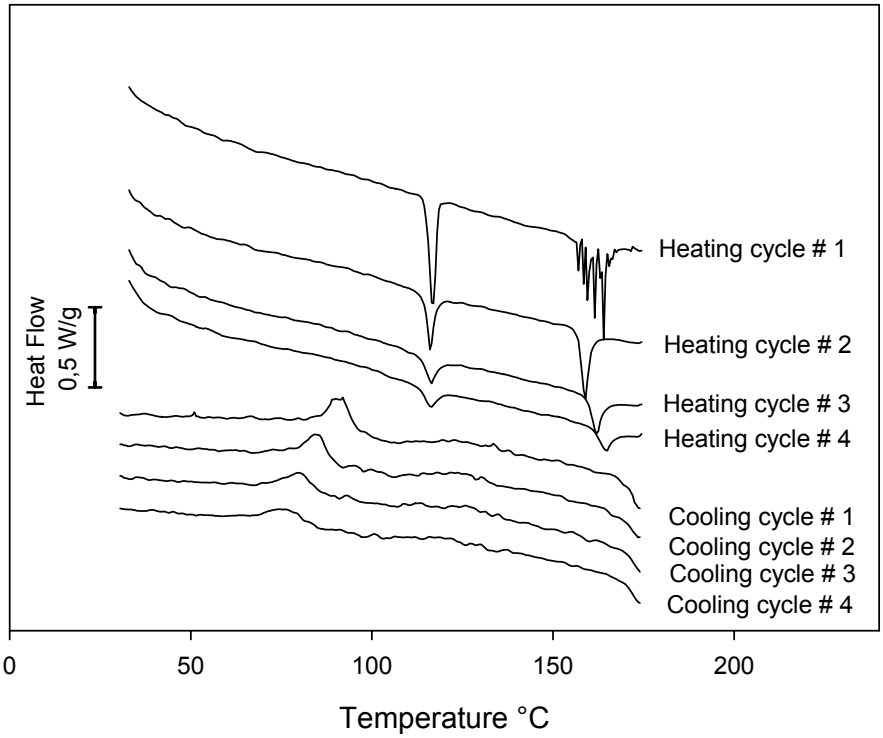

Figure 3: Cyclic repeated DSC analysis of FOX-7 between 30°C and 175°C at the rate of 5°C/min and -5°C/min.

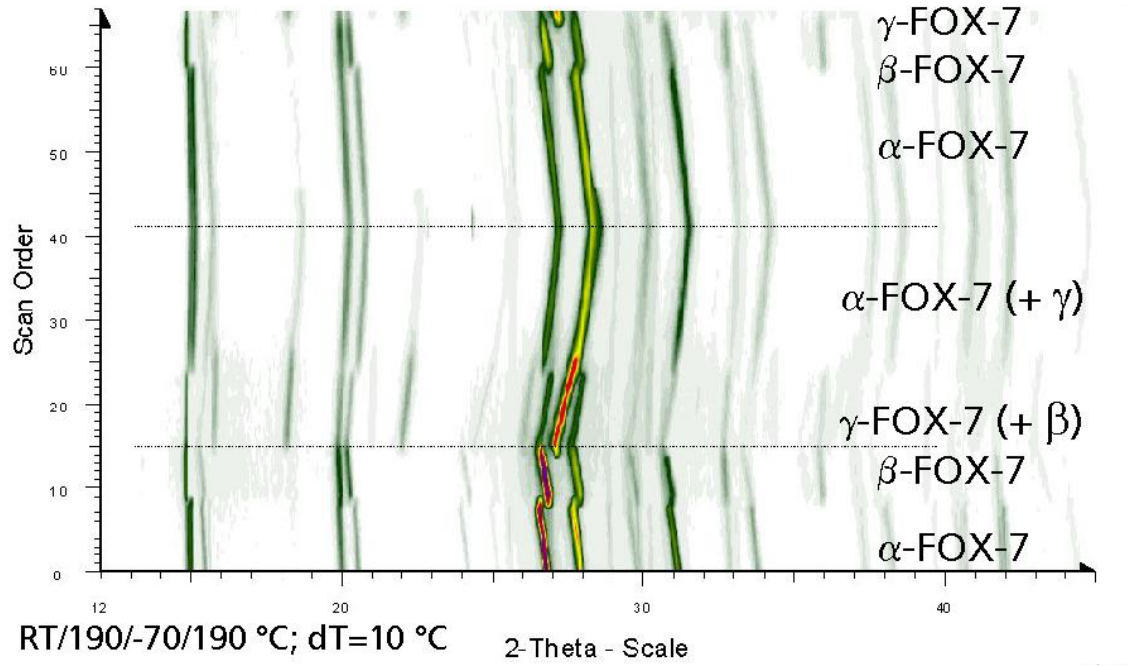

Figure 9: Temperature resolved X-ray diffraction patterns as contour plot, measured with the temperature program RT/190/-70/190 °C.

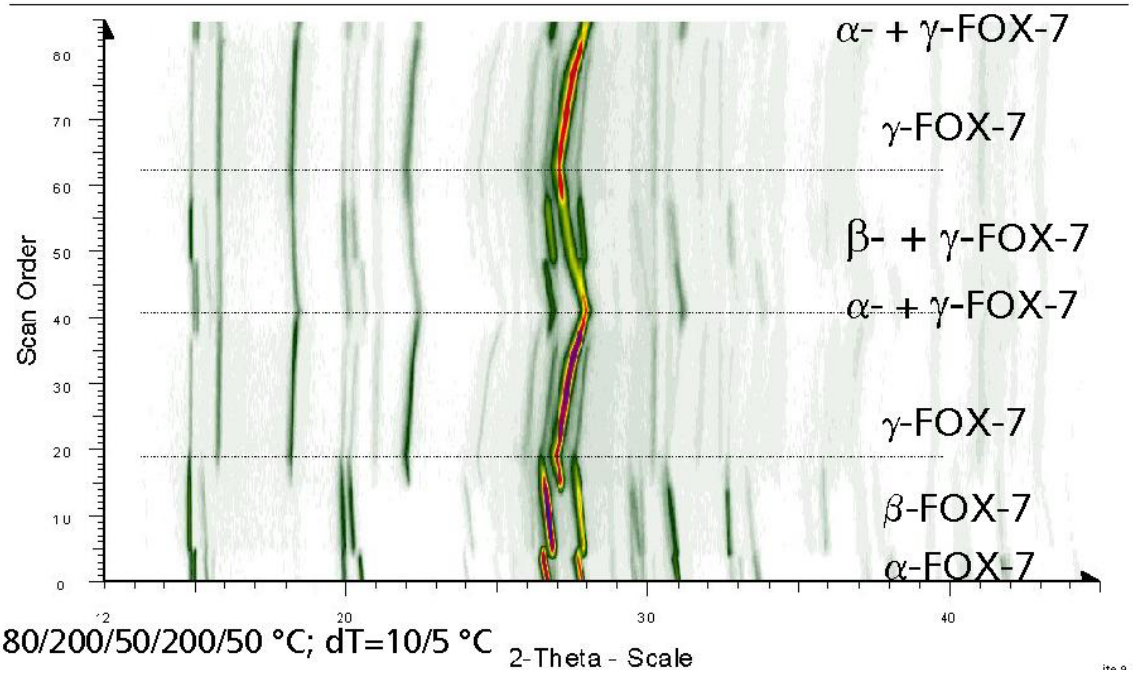

Figure 10: Temperature resolved X-ray diffraction patterns as contour plot, measured with the temperature program 80/200/50/200/50 °C.

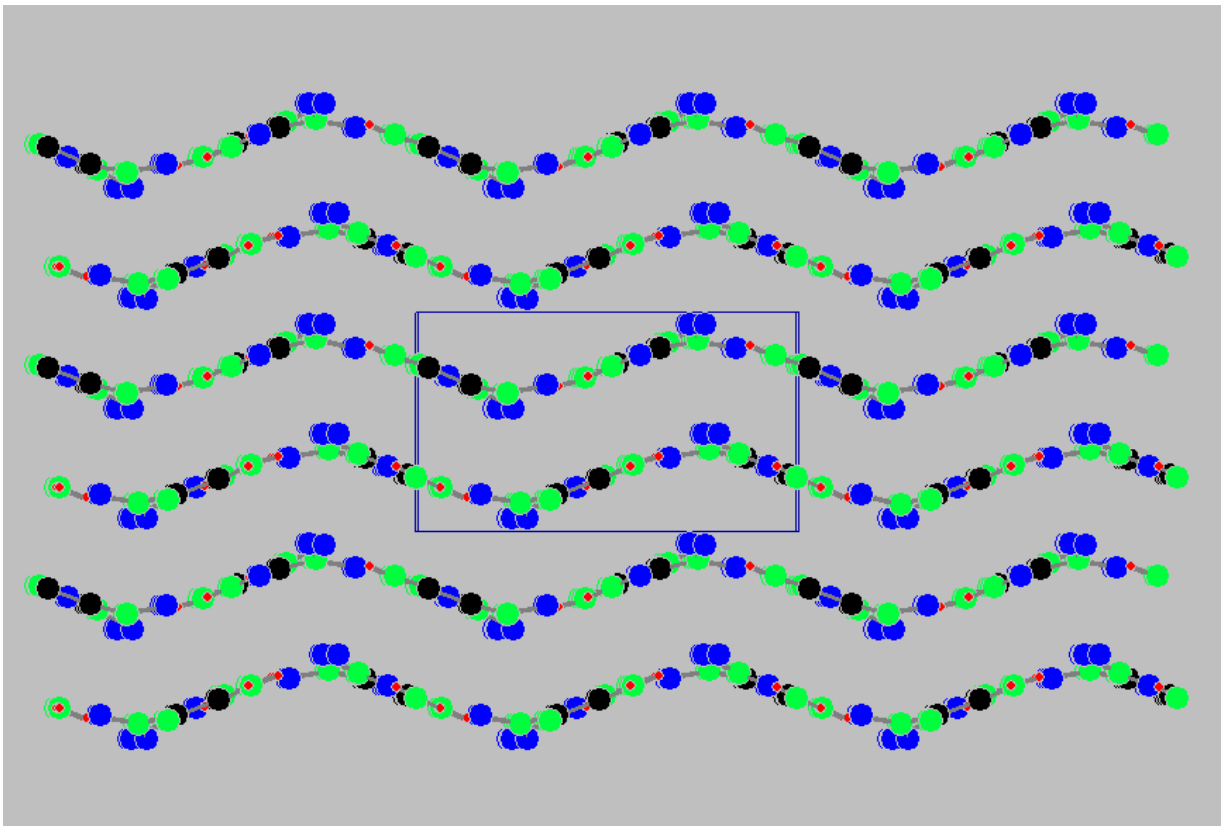

Figure 11: (100) projection of the structure of α-FOX-7.

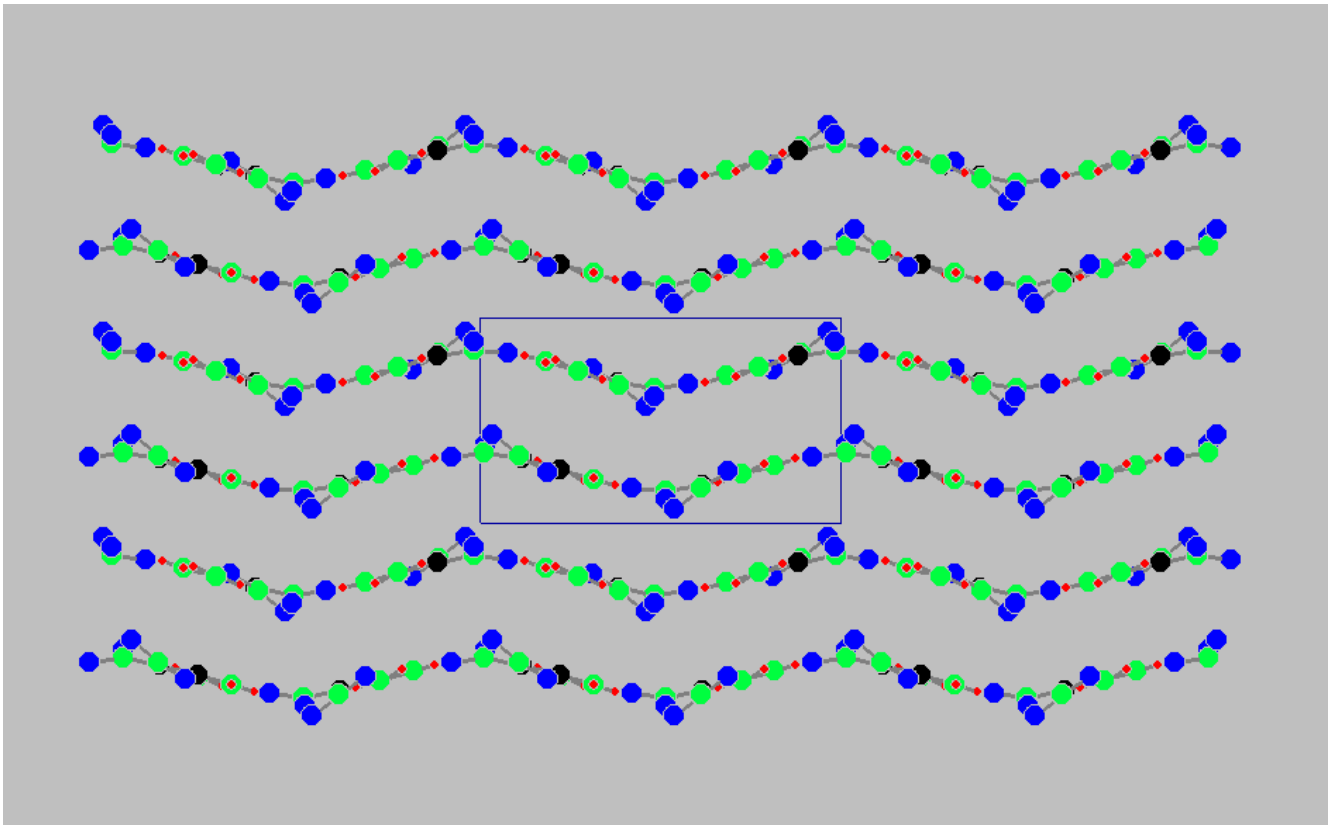

Figure 11: (100) projection of the structure of β-FOX-7.

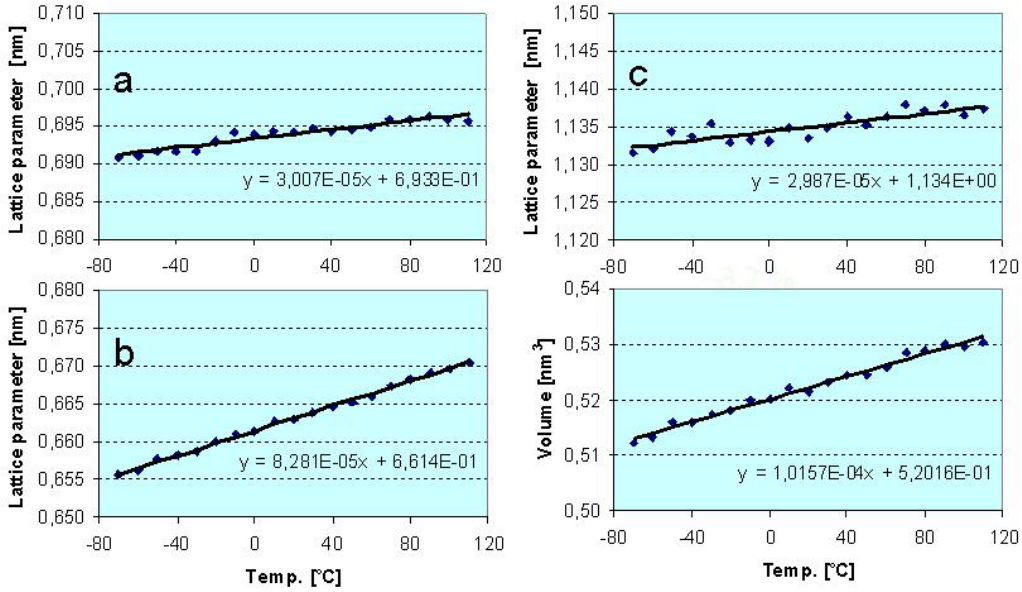

Figure 14: Linear thermal expansion of lattice parameters and volume of α-FOX-7.