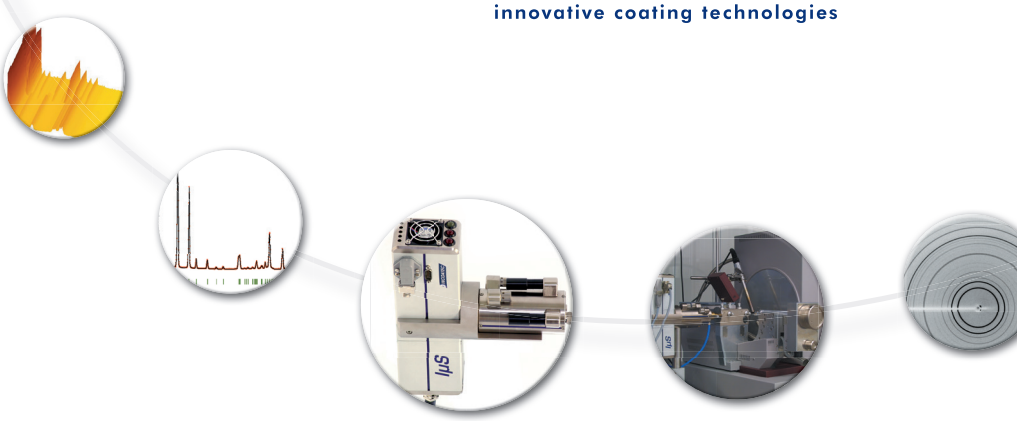
INCOATEC
innovative coating technologies



Application Note 2

Phase Transitions under non ambient Conditions

Introduction

Many organic and inorganic materials undergo a phase transition under non ambient conditions. One of the most prominent examples is the transformation from α-quartz to ß-quartz above 570 °C. In this study the organic compound copper phthalocyanine (Fig. 1) was investigated. The substance is used as an organic semiconductor and as a blue color pigment. It is transformed above 270 °C from an α-phase to a thermally stable ß-phase. There are other well-known polymorphs which also transform to the ß-phase. [1]

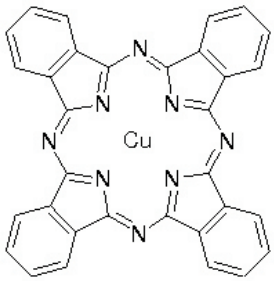


Figure 1: Structure of copper phthalocyanine

Experiment

The Incoatec Microfocus Source IμS, a 30 W air cooled microfocus source with a state-of-the-art 2dim-focusing multilayer optics, was attached to a marresearch desktop beamline with the imaging plate detector mar345. A temperature controlled hot-air blower was used for heating the sample (Fig. 2).

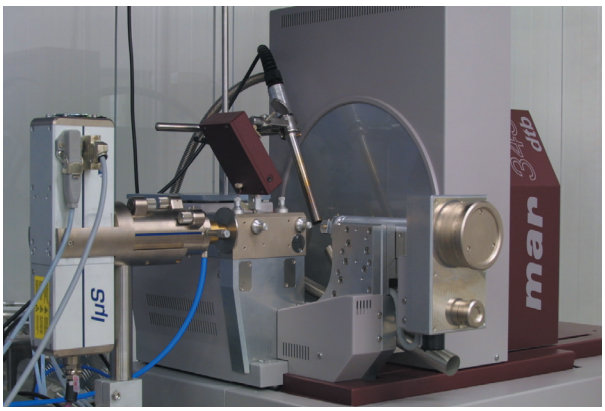


Figure 2: Incoatec Microfocus Source IμS combined with a mardtb and imaging plate detector mar345. The hot-air blower is pointed to the sample.

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A 0.3 mm capillary with a fine grained sample of copper phthalocyanine was fitted to the desktop beamline and heated at the rate of 0.75 K·min^{-1} in a temperature range from 30 °C to 350 °C. The phase transition was monitored in situ. Frames were taken with Cu radiation at an exposure time of 240 sec and a read out time of 63 sec. The frames were integrated using the program FIT2D (Hammersly, ESRF) and plotted (Fig. 3). The phase transition is clearly visible at approximately 300 °C.

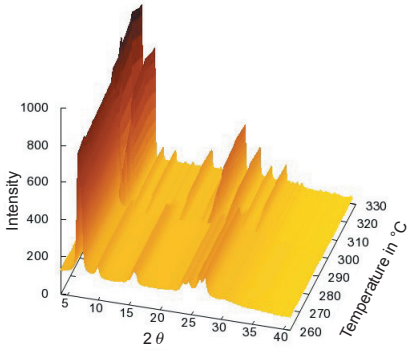

Figure 3: Diffraction pattern of copper phthalocyanine with the phase transition at approximately round 300 °C

In comparison a second data set was recorded at the synchrotron ANKA (Karlsruhe, Germany). For a quantitative evaluation of the data all patterns were Rietveld refined using TOPAS©. The fraction of ß-copper phthalocyanine was plotted versus the temperature (Fig. 4) showing the reaction temperatures at the turning point of the curve. The difference of the reaction temperature between the synchrotron data (275 °C) and the lab data (295 °C) is still under discussion.

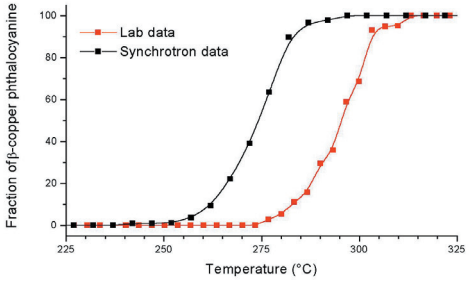

Figure 4: Plot of the fraction of ß-copper phthalocyanine versus temperature

In order to calculate the activation energy, the non-isothermal Avrami-theory [2] was used with the Avrami-parameter from an isothermal synchrotron measurement. The Arrhenius plots for both data sets are shown in Figure 5. The calculated energies from the lab data (254±15 kJ·mol^{-1}) and from the synchrotron data (245±8 kJ·mol^{-1}) correspond with each other, as well as with the activation energy calculated in an isothermal synchrotron experiment (241±3 kJ·mol^{-1}). A summary of the kinetic results is shown in Table 1.

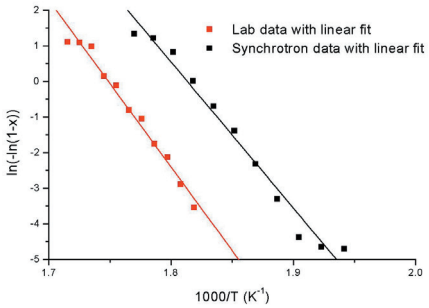

Figure 5: Arrhenius plot for lab and synchrotron data

	Lab Experiment	Synchrotron	Synchrotron isothermal
Reaction-Temperature [°C]	295	275	
Activation Energy [kJ·mol^{-1}]	254 ± 15	245 ± 8	241 ± 3

Table 1: Measurement conditions

Conclusion

The results obtained with the lab instrument on reaction temperature and activation energy of a phase transition, are comparable to results of the synchrotron data. This shows that it is possible to investigate dynamic processes with state-of-the-art lab equipment in the same way as at the synchrotron therefore saving rare and expensive beamtime.
The data used for this study of course contains much more information. Thermal expansion coefficients could be calculated from the peak shifts to name but a few.

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[1] D. Cha, J. Kor. Phys. Soc., 46 (2005) 112-116.
[2] V. Satava, Thermochim. Acta, 2 (1971) 423-428.