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Thermal analysis, phase transitions and molecular reorientation in organic-inorganic hybrids

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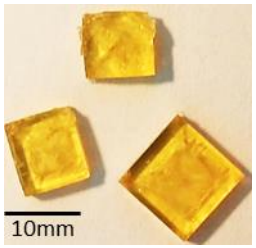
Research Project Objectives

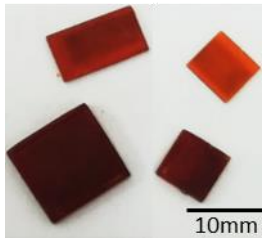
ORGANIC-INORGANIC HYBRIDS

Coordination Polymers,

CPs



DMACr



DMAFe

Alums

MAAlSe

MACrSe

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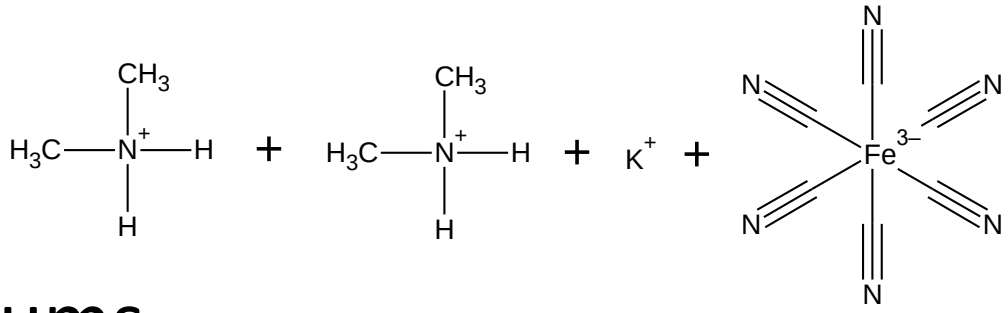
Sample preparation

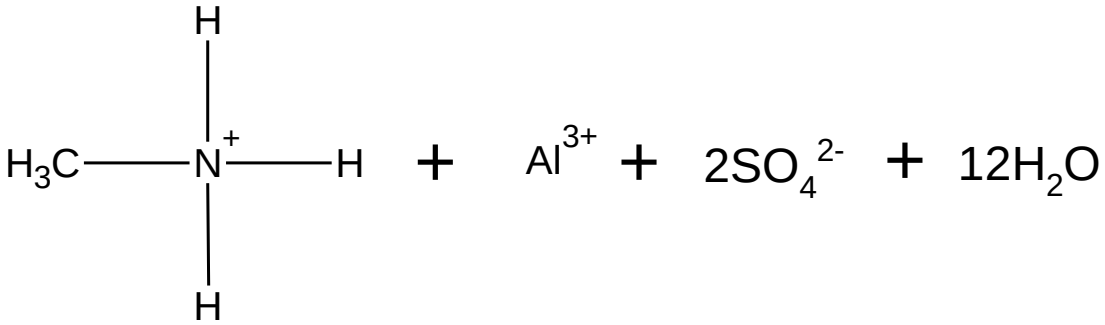
1. Coordynation polymers

$$2(CH_3)_2NH_2 \cdot HCl + K_3Cr(CN)_6 \rightarrow ((CH_3)_3NH)_2[KFe(CN)_6] + 2KCl$$



2. Alums

$$2CH_3NH_3 + Al_2(SO4)_3 + H_2SO_4 \rightarrow 2[CH_3NH_3]Al(SO_4)_2 \cdot 12H_2O$$



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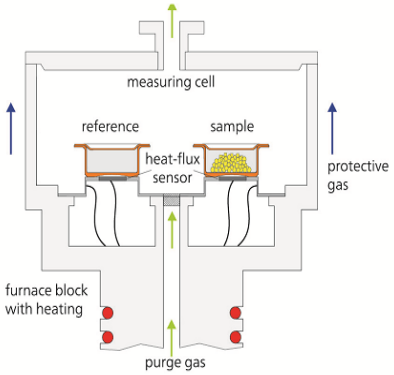
Thermal analysis DSC

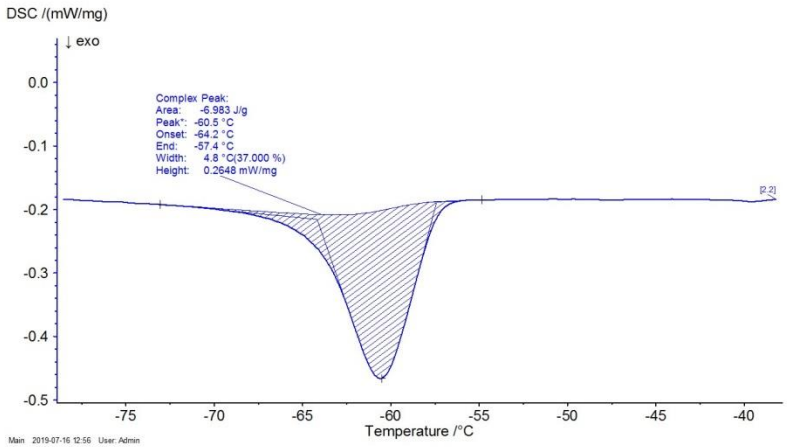
DSC - Differential Scanning Calorimetry

Technical Data

- **Temperature range:**
  -180°C to 700°C
- **Heating rates:**
  0.001 K/min to 200 K/min
- **Cooling rates:**
  max. 200 K/min
- **Automatically controlled LN_2 cooling:**
  -180°C to 700°C
- **Intracooler for the extended range:**
  -85°C to 600°C



Proteus® Software on Windows®



DSC 204 F1 Phoenix®

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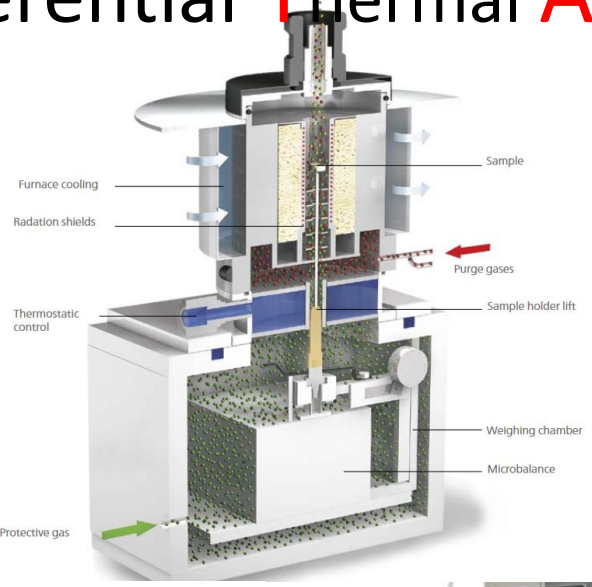
Thermal analysis TGA/DTA

TGA - Thermal Gravimetric Analysis

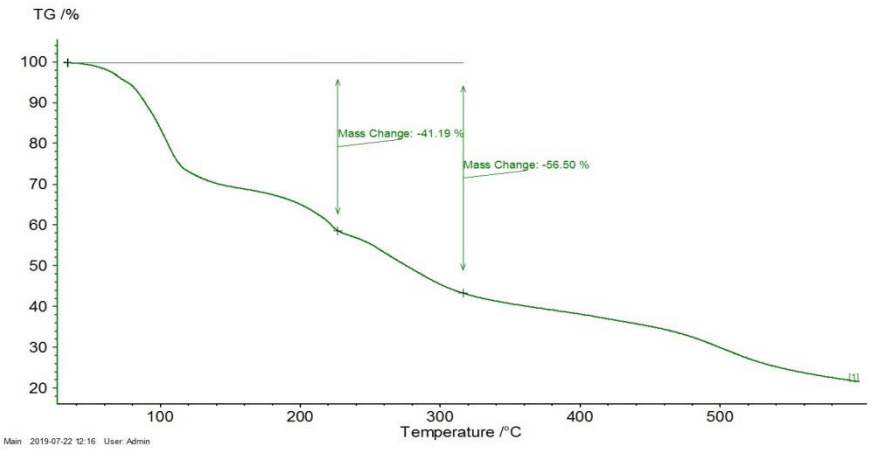
DTA – Differential Thermal Analysis

Technical Data

- **Temperature range:**
  RT to 1100°C at the sample
- **Heating and cooling rates:**
  0.001 K/min to 200 K/min



Proteus® Software on Windows®



TG 209 *F3 Libra*®

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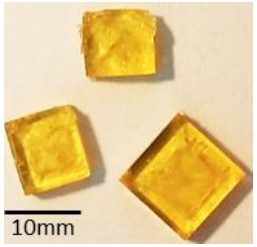
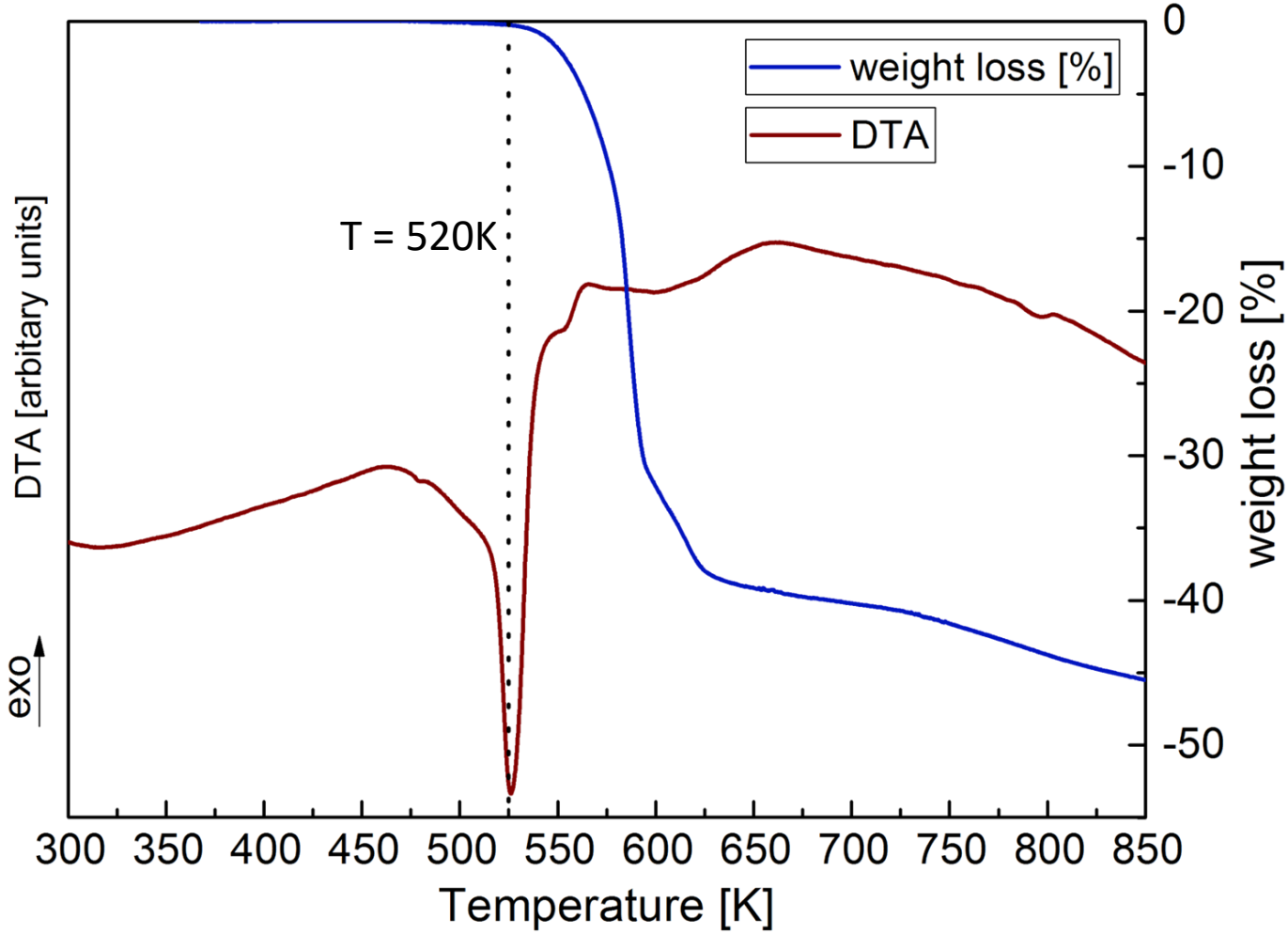
Thermal analysis TGA/DTA



DMACr



Mass loss valuted on TG curve of the DMACr sample together with DTA measured in the temperature range from 300 to 850 K

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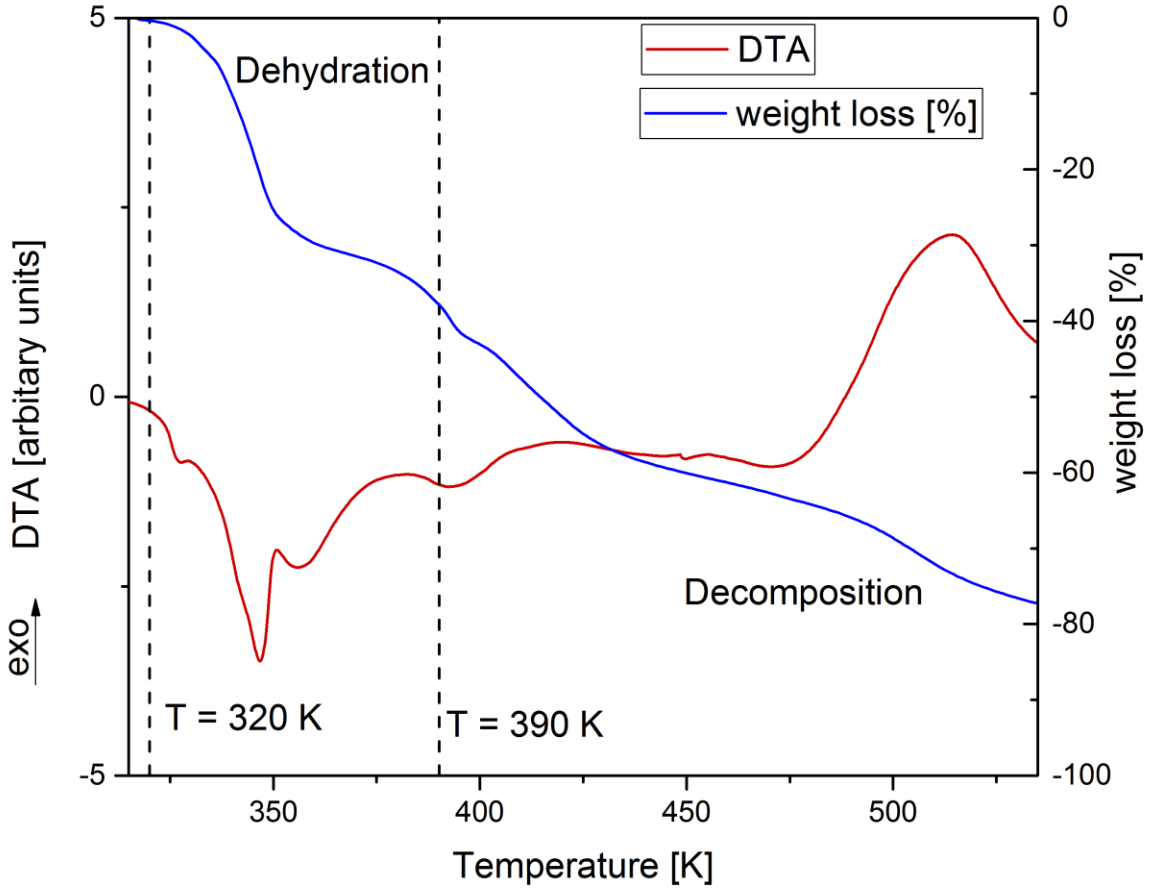
Thermal analysis TGA/DTA



MAAlSe

Mass loss valuted on TG curve of the MAAlSe sample together with DTA measured in the temperature range of 300 to 600 K

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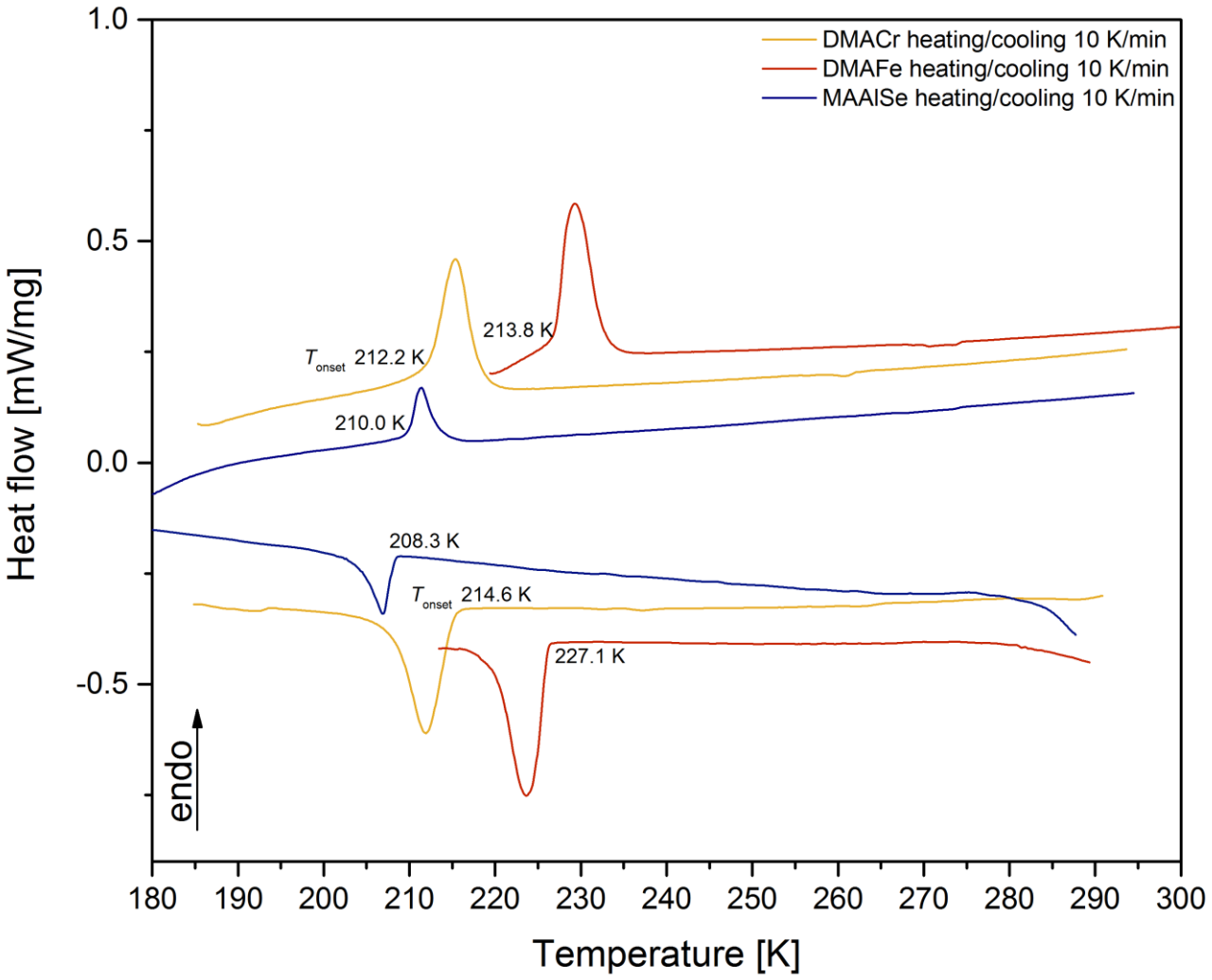
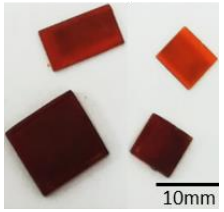
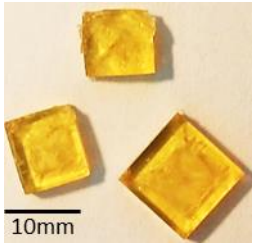
Thermal analysis DSC



DSC curves repistered in the temperature range from 180 to 300 during heating and cooling of the sample with scanning rate 10 K/min



DMAFe



DMACr

MAAlSe

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Thermodynamic parameters

$$\Delta H \rightarrow \Delta S = \frac{\Delta H}{T_{P.F.}} = R \ln N$$

Thermodynamic parameters	DMACr	MAAlSe
$T_{P.F.}$ [K]	212	210
ΔH [kJ/mol]	1.83	0.68
ΔS [J/K·mol]	8.6	3.3
N	3	1.2
	I – discontinuous order-disorder	II – continuous displacive

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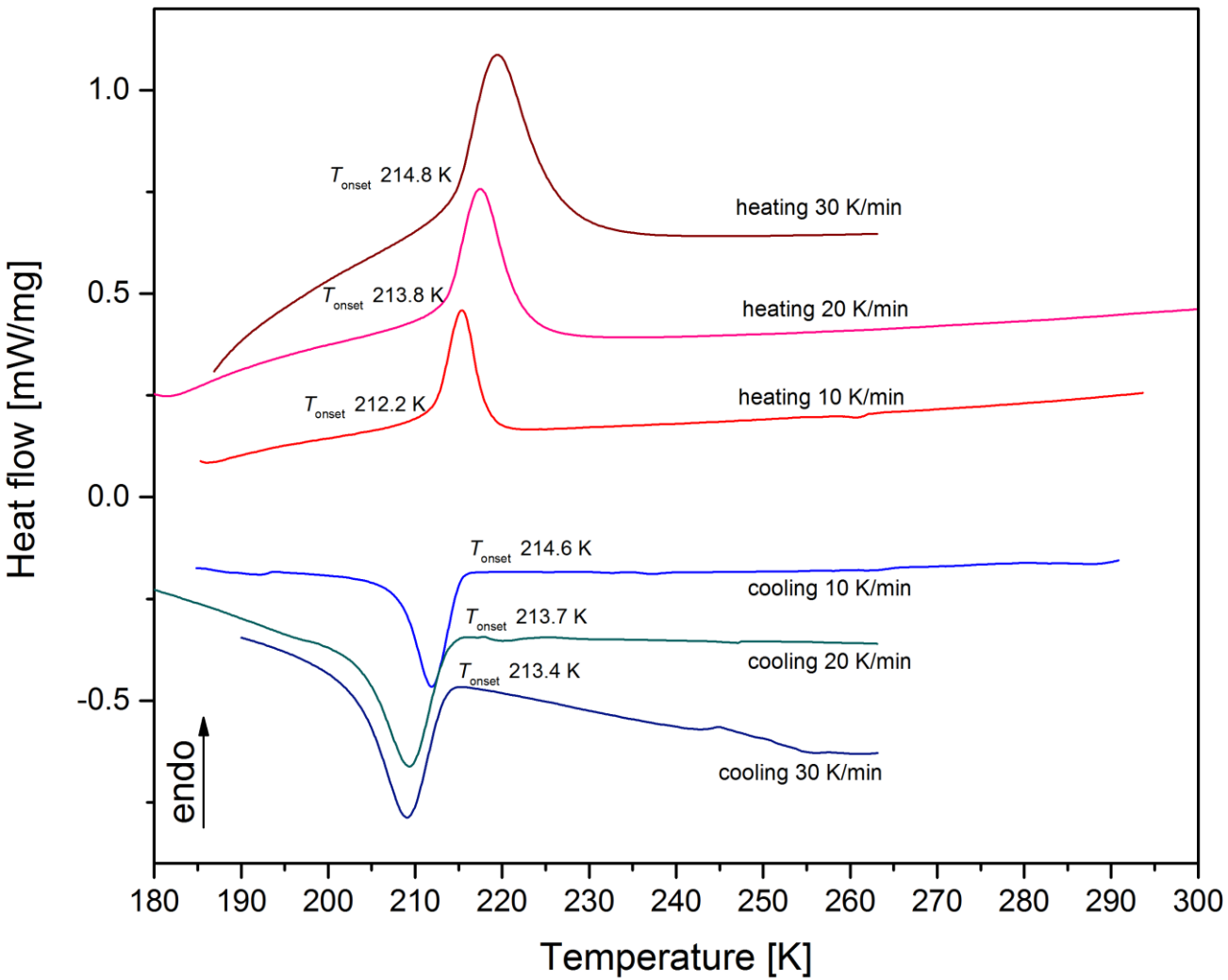
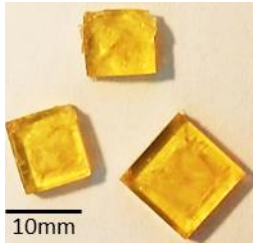
Thermal analysis DSC





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DSC curves repistered in the temperature range from 180 to 300 during heating and cooling of the sample with different scanning rate 10,20,30 K/min

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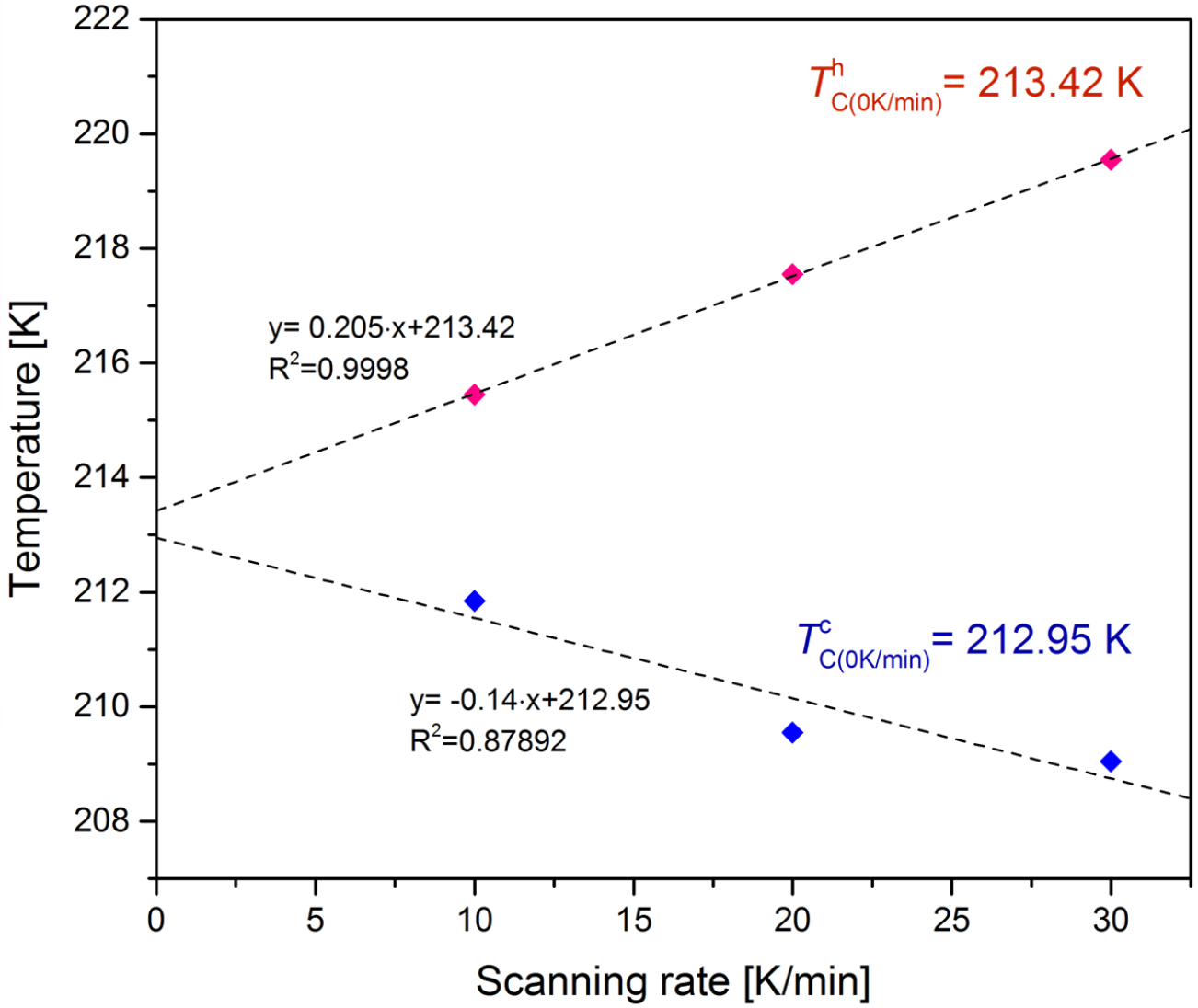
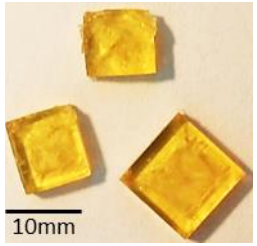
Thermal analysis DSC





DMACr

Extrapolation of the temperatures obtain different scanning rates to zero rate

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Conclusions

1. The main goal of the project was full thermal characteristic of two kinds organic-inorganic hybrids.

2. The DSC and TGA-DTA measurements were performed for chosen crystals.

3. The shape of the thermal anomaly and significant change of entropy suggests the first order PT for CPs. Whereas, in the case of alum, the phase transition is second order.

4. Based on Boltzmann relation, the order-disorder character and displacive nature were observed for CPs and alums hybrids, respectively.

5. The phase transition temperatures, at heating = 213.42 K and at cooling = 212.95 K, were calculated by extrapolating to zero scanning rate the end values obtained at different scanning rates

The end….