

Supplementary Information

for

Crystal form selectivity by humidity control: the case of the ionic co-crystals of nicotinamide and CaCl_2

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TGA measurements.

Despite all attempts to obtain pure compounds, the TGA curves suggests the presences of a small amount of $\text{CaCl}_2 \cdot \text{XH}_2\text{O}$. It is known that the dehydration process of $\text{CaCl}_2 \cdot \text{XH}_2\text{O}$ strongly depends on the heating rate and a recent study shows that at $\sim 142^\circ\text{C}$ there is a complete conversion of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to the anhydrous form.¹

In figure S.I. 1 the small step between $90\text{--}130^\circ\text{C}$ could be ascribed to the release of water due to the presence of small percentage of $\text{CaCl}_2 \cdot \text{XH}_2\text{O}$ not detectable by X-ray diffraction, while step between 130°C to 200°C the release of the crystallization water molecule of $\text{Nic} \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$ (calc 7.16% obs. 6.59%) and the formation of the anhydrous form. At 250°C the decomposition occurred.

The variable temperature XRD shows no changes in the pattern between 90°C – 130°C also after the sample was kept at 100°C for 1 hour (see figure S.I. 2)

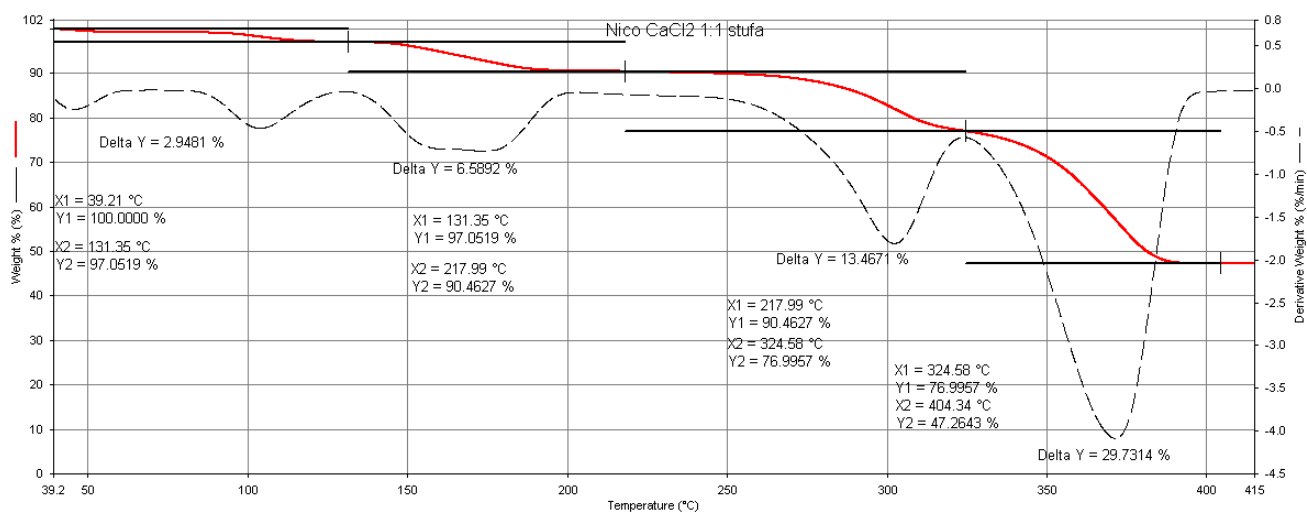


Figure SI 1. TGA curves of $\text{Nic} \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$. Sample obtained by kneading CaCl_2 anhydrous and Nicotinamide with 1 drop of ethanol. The sample was kept at 75°C for at least 1 hour to remove adsorbed water. The first step between 90°C – 140°C is ascribable to the release of water due to the presence of $\text{CaCl}_2 \cdot \text{xH}_2\text{O}$.

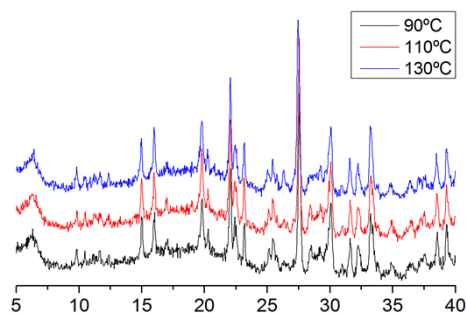


Figura SI 2. Variable temperature XRD patterns of $\text{Nic}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$ powder. No ICC phase transition is detected in the range 90-130C

$\text{Nic}\cdot\text{CaCl}_2\cdot 4\text{H}_2\text{O}$ loses three water molecules before 90°C. After this temperature the thermogram is comparable to that one observed for $\text{Nic}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$; also in this case there is a step between 90°-130°C is due to the presence of a small percentage of $\text{CaCl}_2\cdot\text{XH}_2\text{O}$ (Figure S.I. 3)

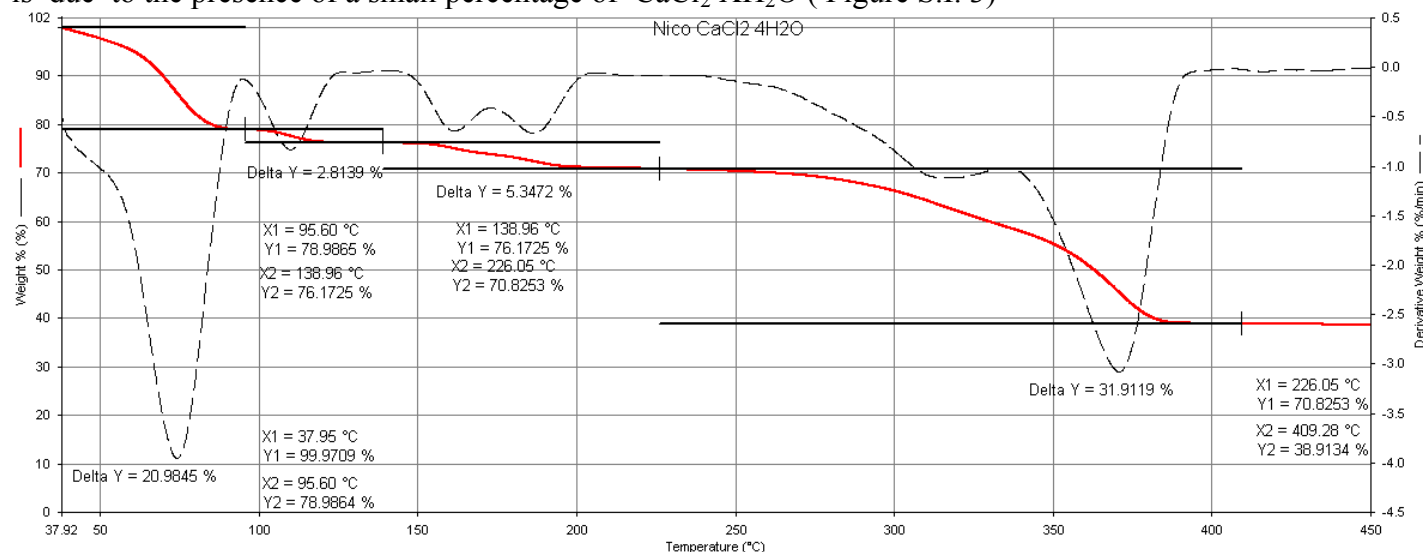


Figure SI 3. TGA curves of $\text{Nic}\cdot\text{CaCl}_2\cdot 4\text{H}_2\text{O}$. Sample obtained exposing $\text{Nic}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$ to HR 75%.

Rietveld refinements of patterns collected on powders exposed to different RH

Rietveld refinement of the diffractogram collected on the sample of $\text{Nic}\cdot\text{CaCl}_2$ after been exposed to HR 12% for two weeks (2θ range 5-40°, step size 0.02°, time/step 20 s, 0.04 rad soller, kVxmA 40x40). The pattern has been described by two crystalline phases: $\text{Nic}\cdot\text{CaCl}_2$ and $\text{Nic}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$. The refinement converged to $R_{wp} = 8.635\%$ and $\chi^2 = 1.734$ values

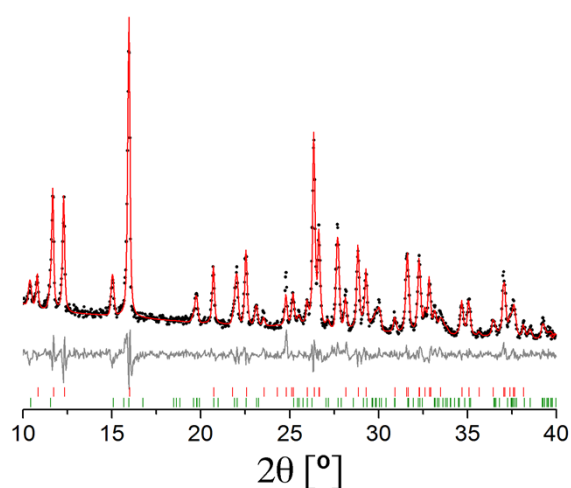


Figure S.I. 4 Experimental (black dots), calculated (red line) and difference (grey line) patterns for **Nic·CaCl₂·H₂O** (black line) after two weeks at 12% RH. Peak positions are marked in red and green for **Nic·CaCl₂** and **Nic·CaCl₂·H₂O** respectively

Rietveld refinement of the diffractogram collected on the sample of **Nic·CaCl₂** after been exposed to HR 53% for two weeks (2θ range 5-40°, step size 0.02°, time/step 20 s, 0.04 rad soller, kVxmA 40x40). The pattern has been modelled using three phases: **Nic·CaCl₂·H₂O**, triclinic **CaCl₂·4H₂O** and trigonal **CaCl₂·2H₂O**. The refinement converged to $R_{wp} = 8.777\%$ and $\chi^2 = 1.426$ values.

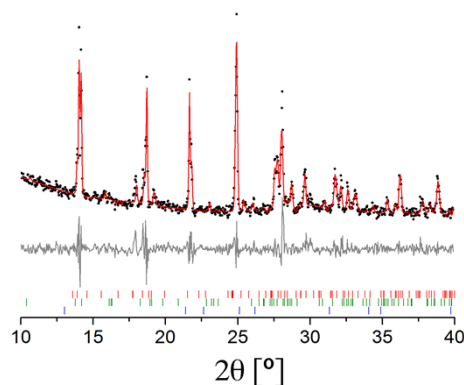


Figure S.I. 5 Experimental (black dots), calculated (red line) and difference (grey line) patterns for **Nic·CaCl₂·H₂O** (black line) after two weeks at 54% RH. Peak positions are marked in red, green and blue for **Nic₂·CaCl₂·2H₂O**, **CaCl₂·4H₂O** and **CaCl₂·2H₂O** respectively.