Raman characterization of Mechanochromic materials

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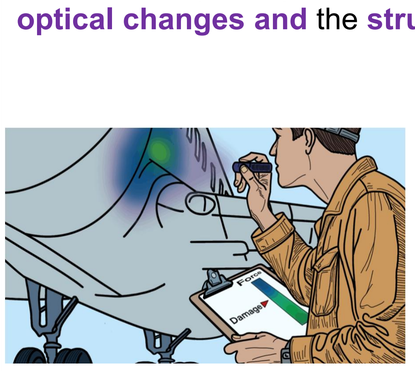
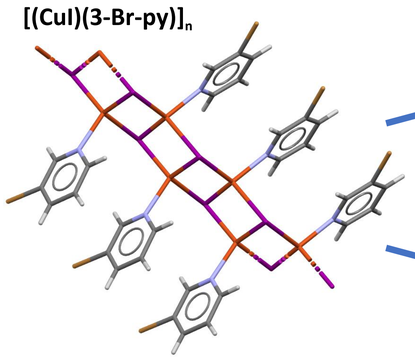
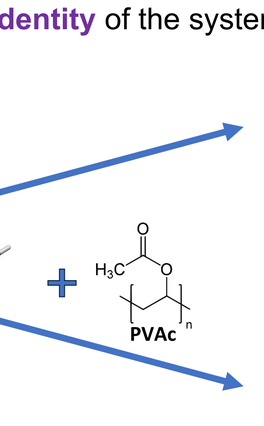
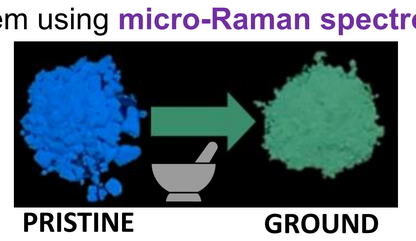
Introduction

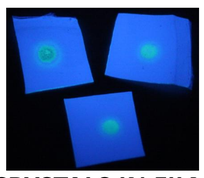
Mechanochromic polymer-based materials can detect structural failure. A **copper(I) halide-based hybrid coordination polymer**, involving **Cu-I bonds** as a backbone and **3Br-pyridine** as a ligand, is here investigated. When mechanical stress is applied to pristine material, whether through **grinding**, microscopic **indentation**, or macroscopic **impact**, its optical properties change dramatically. This work focuses on the study of the **correlation between** the **optical changes and** the **structural** as well as **chemical identity** of the system using **micro-Raman spectroscopy**.



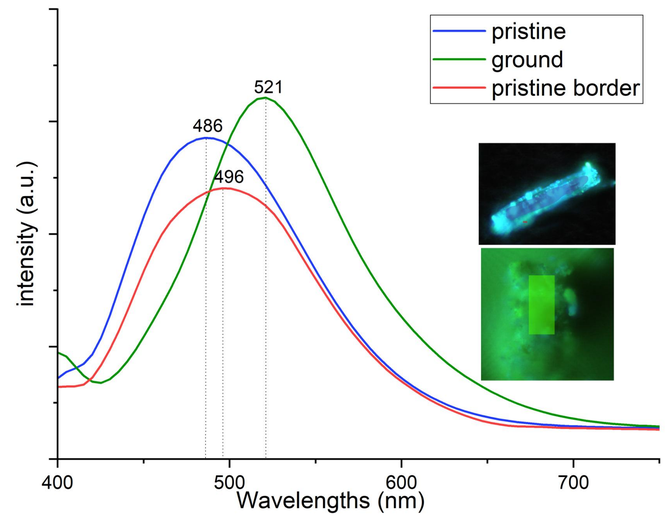






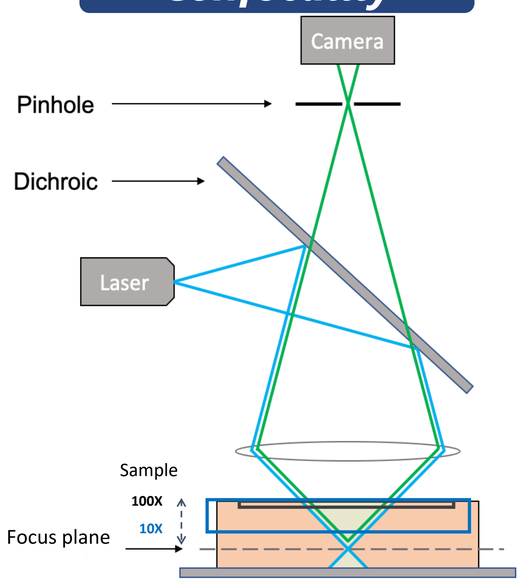


Emission Spectra



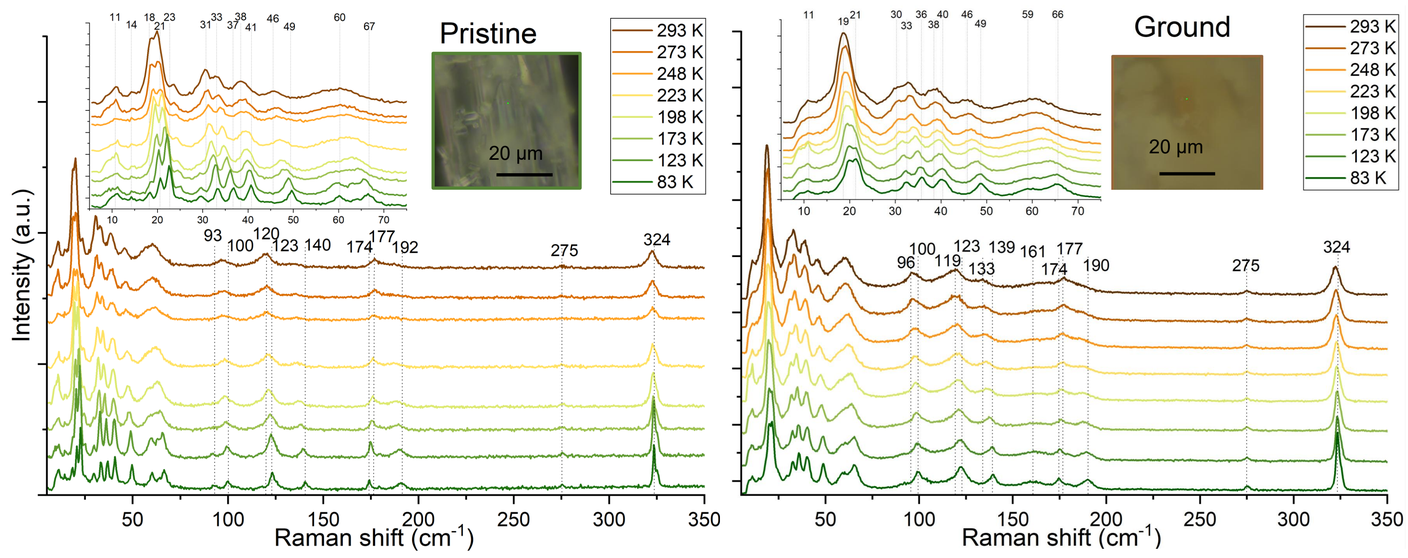
Emission spectra of the materials show that **defects** in the pristine crystals result in **differences in emission**.

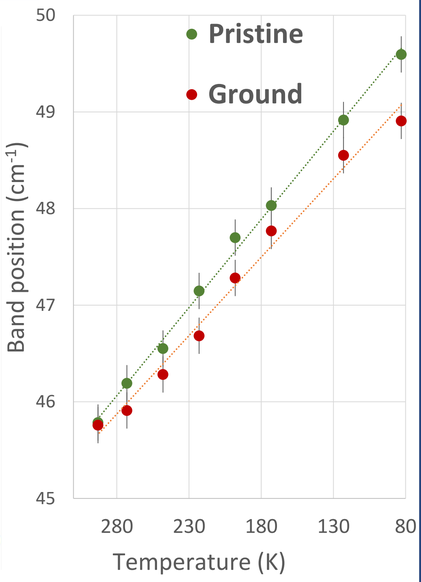
Confocality



The **greater** the magnification and **the N.A.** the **swallower** is the focus plane.

Temperature-dependent Raman spectra on powders

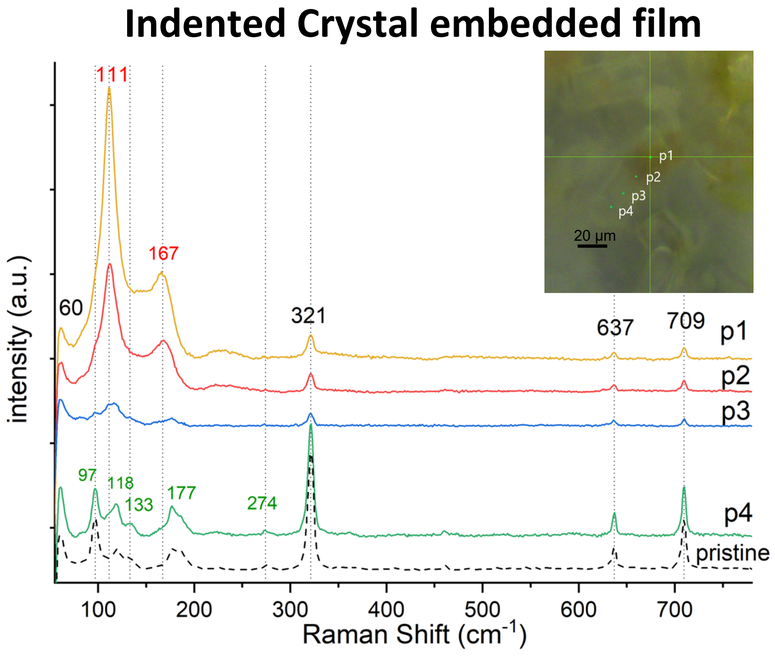




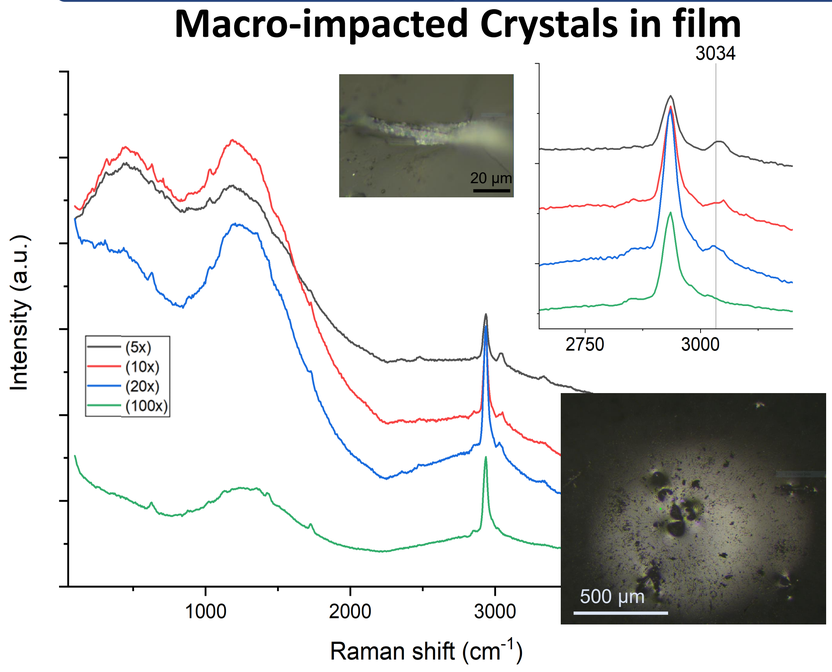
Band position **shifts linearly** at higher energies with temperature, showing that **no phase transition** occurs.

Stress effects in crystals in PVAc films

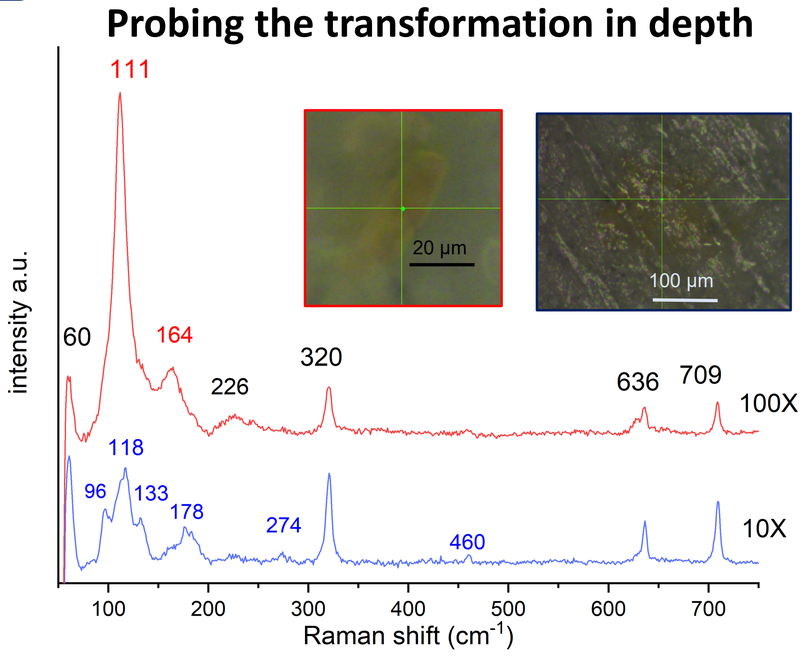
Indented Crystal embedded film



Macro-impacted Crystals in film



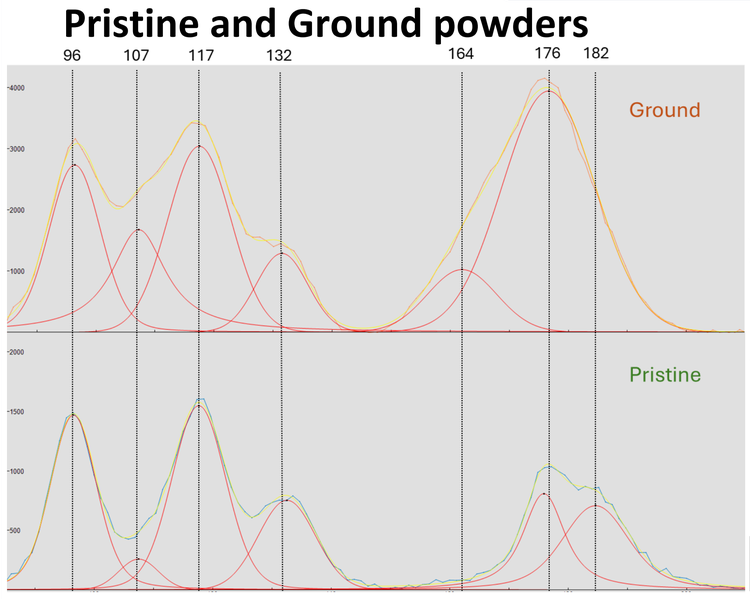
Probing the transformation in depth

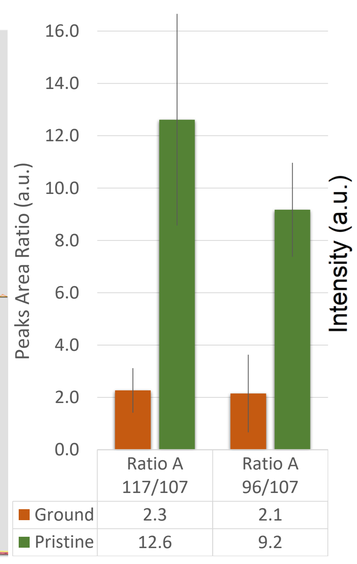


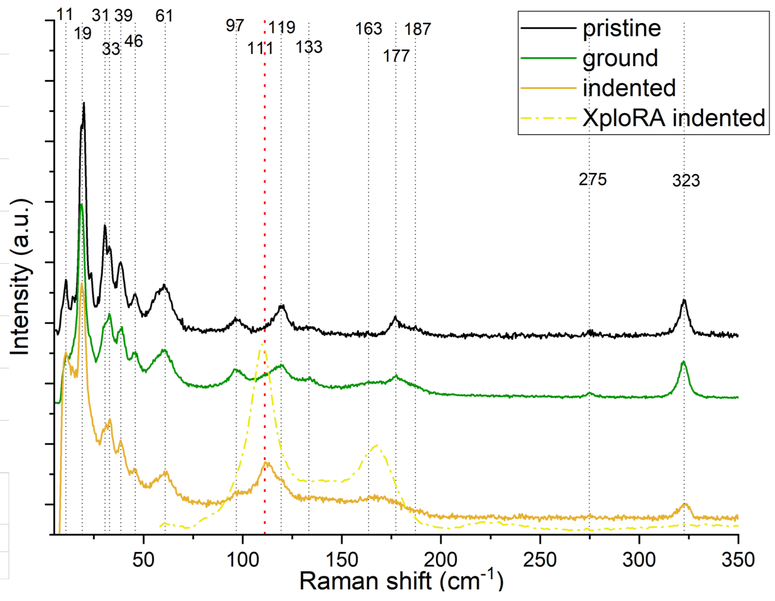
Moving from 5x to 100x, results in probing progressively **thinner volumes** of the sample, until the signal collected belongs on majority to the damaged crystal. Due to the indentation or the impact, the **characteristic bands of 3-Br-Pyridine become less intense**.

Mechanical stress effects in powders

Pristine and Ground powders



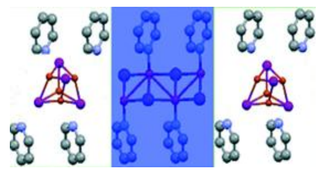




Minor **differences** between pristine and ground powder samples are observed, marked by the **appearance of the band** at 107 cm^{-1}.

Conclusions

Under stress, the overall crystal structure is preserved. However, in the ground material the appearance of **new bands** and changes in relative intensities suggest **slight structural modifications** in the **Cu-I**, **Cu-Cu** bonds. Furthermore, indentation reveals that some **pyridine** ligands break off from the Cu–I chain, showing **changes** in the intensity of its **vibrational bands**.



Modified from Han et al. 2021

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